Synthesis of (*Z*)-1-Organylthiobut-1-en-3-ynes: Hydrothiolation of Symmetrical and Unsymmetrical Buta-1,3-diynes

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Abstract: Hydrothiolation of 1-organylbuta-1,3-diynes and 1,4-diorganylbuta-1,3-diynes with the sodium organylthiolate anions, which were generated in situ by reacting diphenyl and dibutyl disulfide with $NaBH_4$ in ethanol, results in the regio-, stereo-, and chemoselective formation of (*Z*)-1-organylthio-4-organylbut-1-en-3-ynes and (*Z*)-1-organylthio-1,4-diorganylbut-1-en-3-ynes, respectively.

Key words: hydrothiolation, organylthiolate anion, vinyl sulfides, 1,3-diacetylenes, (*Z*)-1-organylthiobut-1-en-3-ynes

Vinyl sulfides are present in naturally occurring compounds with important biological activity.[1] Griseoviridin, for example, is a type A streptogramin antibiotic, first isolated from *Streptomyces graminofaciens*,[1a,b] and benzylthiocrellidone is a yellow pigment isolated from the bright-red sponge *Crella spinulata*.[1c]

These compounds are versatile and useful intermediates in organic synthesis.[2–13] They can be converted into the corresponding aldehyde, ketone,[2] carboxylic acid, or ester[3] by acid hydrolysis or through the thio-Claisen rearrangement.[4] The carbon–sulfur bond can be reductively cleaved by reactions with lithium[5] or samarium reagents,[6] affording the corresponding vinyl lithium or vinyl samarium species, which are trapped with electrophiles.[5,6] Vinyl sulfides are acceptors in Michael addition, Peterson olefination,[7] and have shown good reactivity in Diels–Alder cycloadditions reactions.[9]

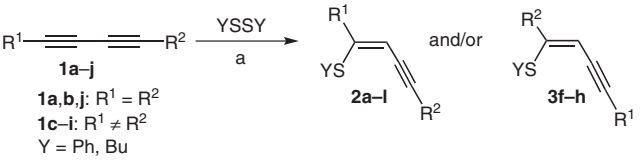
Another factor that increases the range of synthetic possibilities of vinyl sulfides is the stabilizing influence of a sulfur atom toward neighboring cations or anions,[10] as well as their use as synthetic equivalents of enolonium ions.[11] Indeed, vinyl sulfides can be desulfurized by Raney nickel[12] or stereospecifically reduced through a cross-coupling reaction with Grignard reagents using nickel(II) salts as catalysts.[13] This last reaction was used to perform the synthesis of several di-[13b] and polyfunctionalized olefins.[13a,c]

One of the more widely used methods for the synthesis of vinyl heteroatomic derivatives is the nucleophilic addition of heteroatomic anions to acetylenes. Except for some few charged acetylene derivatives, or in radical conditions, this type of reaction occurs in a *trans* addition process, and furnishes selectively the *Z*-vinylic isomer. Almost all of the methods described in the literature for the preparation of vinyl sulfides employ the addition of thiolate anions to terminal alkynes. The nucleophilic species are generated by the reaction of volatile, bad-smelling, highly toxic, and air-sensitive alkylthiols with an alkaline base (KOH, NaOH, NaOR, or KOR)[13] and in liquid ammonia.[14] Although the *Z*-isomer is the main product, formation of the *E*-isomer (4–5%) has also been described.[15]

Despite the large number of papers describing the synthesis of vinyl sulfides, the preparation of (*Z*)-1-organylthiobut-1-en-3-ynes by the hydrothiolation of mono- and disubstituted 1,3-diacetylenes has been little studied.[16]

We describe here a new, general, and highly stereoselective method for the preparation of (*Z*)-1-organylthiobut-1-en-3-ynes **2** and **3**, employing the addition of the organylthiolate anions, generated in situ by the reaction of commercially available PhSSPh and BuSSBu with $NaBH_4$, to buta-1,3-diynes[17,18] (Scheme 1, Table 1).

To the best of our knowledge, the method described herein is the first employment of the YSSY/$NaBH_4$ system (Scheme 1) for the selective reduction of conjugated triple bonds. Moreover, to furnish exclusively the ***Z***-isomer **2** and/or **3**, the in situ generation of the organylthiolate an-



Scheme 1 *Reagents and conditions*: (a) EtOH, $NaBH_4$, N_2, reflux.

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ions avoids the use of the bad-smelling, volatile, toxic PhSH or BuSH.

The reaction described in Scheme 1 was studied with several 1,3-diacetylenes. In all cases, only the *Z*-isomer was obtained, with no formation of the *E*-isomer. Thus, symmetrical 1,4-diphenylbuta-1,3-diyne (**1a**, $R^1 = R^2 = Ph$) gives exclusively (*Z*)-1-phenylthio-1,4-diphenylbut-1-en-3-yne (**2a**)[19] and (*Z*)-butylthio-1,4-diphenylbut-1-en-3-yne (**2i**) with 72% and 76% yields, respectively (entries 1 and 9, Table 1).

Table 1 (*Z*)-1-Organylthiobut-1-en-3-ynes Obtained

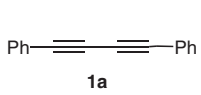
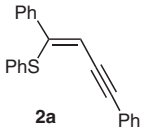
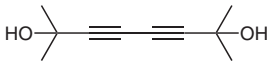
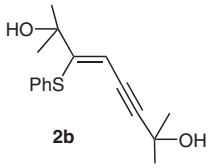
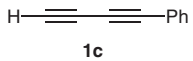
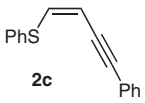
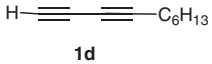
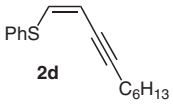
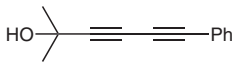
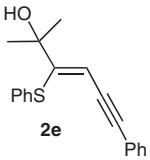
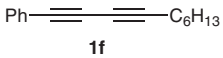
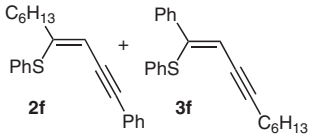
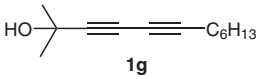
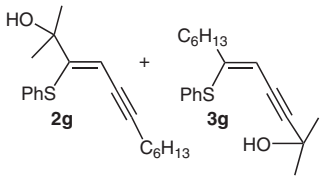
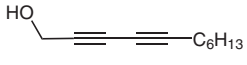
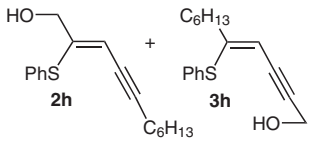
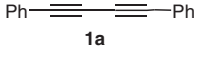
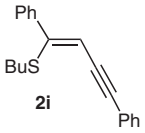
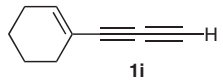
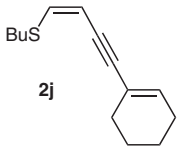
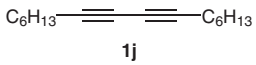
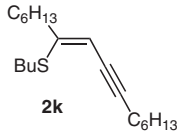
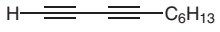
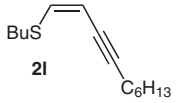
Entry	Buta-1,3-diyne **1**[a]	Products **2** and **3**	Ratio **2**/**3**[b]	Time (h)	Yield (%)[c,d]
1	 **1a**	 **2a**	–	3	72
2	 **1b**	 **2b**	–	2.5	93
3	 **1c**	 **2c**	100:0	2	75[e]
4	 **1d**	 **2d**	100:0	2.5	78[f]
5	 **1e**	 **2e**	100:0	3	54
6	 **1f**	 **2f** **3f**	97:3	6	35
7	 **1g**	 **2g** **3g**	69:31	3	62
8	 **1h**	 **2h** **3h**	91:9	3	68
9	 **1a**	 **2i**	–	8	71

Table 1 (*Z*)-1-Organylthiobut-1-en-3-ynes Obtained (continued)

Entry	Buta-1,3-diyne **1**[a]	Products **2** and **3**	Ratio **2/3**[b]	Time (h)	Yield (%)[c,d]
10	 **1i**	 **2j**	100:0	5	50[g]
11	 **1j**	 **2k**	–	9	65
12	 **1d**	 **2l**	100:0	4	70[e]

[a] Terminal butadiynes **1c** and **1d** were prepared and used in situ.
[b] Determined by GC and ^{1}H NMR.
[c] Isolated yields.
[d] Products purified by column chromatography.
[e] Overall yield (two steps from the alcohol **1e**).
[f] Overall yield (two steps from the alcohol **1g**).
[g] Overall yield (two steps from the 6-cyclohexenyl-2-methylhexa-3,5-diyn-2-ol **1k**).

The 2,7-dimethyl-3,5-octadiyne-2,7-diol **1b**, $R^1 = R^2$ = *i*-PrOH) gives the (*Z*)-2,7-dimethyl-3-phenylthiooct-3-en-5-yne-2,7-diol (**2b**) with 93% yield after refluxing for 2.5 hours (entry 2, Table 1).

When the unsymmetrical buta-1,3-diynes **1c–i** ($R^1 \neq R^2$, entries 3–8, 10, 12) were used, the (*Z*)-1-phenylthiobut-1-en-3-ynes[20] and (*Z*)-1-butylthiobut-1-en-3-yne[21] type **2** were obtained with high chemoselectivity. Thus, (*Z*)-1-phenylthio-4-phenylbut-1-en-3-yne (**2c**, 75%) and (*Z*)-1-butylthiodec-1-en-3-yne (**2l**, 70%) obtained exclusively by reacting the terminal 4-phenylbuta-1,3-diyne **1c** and deca-1,3-diyne **1d** with the phenyl and butylthiolate anions, respectively, as described in Scheme 1 (entries 3 and 12, Table 1).

We observed that the terminal triple bond is more reactive than the substituted triple bond, because of the steric hindrance caused by the phenyl **1c** or *n*-hexyl group **1d**. Replacing the terminal hydrogen in **1c** with the larger *n*-hexyl group results in a slower reaction rate and loss of selectivity in **1f**, showing that steric factors are acting. Thus, a mixture of **2f** and **3f** was obtained in a 97:3 ratio and modest yield (35%) after refluxing **1f** and phenylthiolate anion for six hours (entry 5, Table 1). This last result shows that electronic factors are also important. During the attack of the phenylthiolate anion on the diacetylene **1f**, a negative charge is developed at the adjacent carbon (C-2), and two possible transition states **4f** and **5f** could be proposed (Figure 1). Transition state **4f** is more stable than **5f**, because of stabilization of the incipient carbanion by the phenyl acetylenic moiety, which removes electrons more effectively than the octynyl group in **5f** (electronic factor). However, 3% of **3f** was obtained, because the bulky group *n*-hexyl impedes the PhS^- attack (steric factor).

In the cases of compounds **1e**,**g**,**h**, the propargylic triple bonds underwent addition of the phenylthiolate anion more easily than did triple bonds bearing a phenyl (entry 5, Table 1) or alkyl substituent (entries 7 and 8, Table 1). This occurred because of the formation of cyclic five-membered transition states **4g–i** (Figure 1), which is responsible for the intramolecular protonation of the incipient carbanion formed in C-2. For the reaction of **1c**,**d**,**f**, ethanol acts as the proton donor, as depicted in **4f** and **5f** (Figure 1). With the propargylic derivatives **1e**,**g**,**h** the role of the steric and electronic factors is more easily seen. Thus, the (*Z*)-2-methyl-3-phenylthio-6-phenylhex-3-en-5-yn-2-ol (**2e**) was the only product obtained when 2-methyl-6-phenylhexa-3,5-diyn-2-ol **1e** was submitted to the hydrothiolation reaction for three hours (54% yield, entry 5, Table 1). This result indicates a preference for addition at the propargylic triple bond. Formation of the intermediate **4g** (Figure 1) is favored by both the cyclic intermediate and the phenyl acetylenic moiety. However, the hydrothiolation of compound **1g** (entry 7, Table 1) occurs with lower chemoselectivity, due the weak stabilization of the transition state **4h** (Figure 1).

The difference in yields and chemoselectivities between the hydrothiolation of **1h** (68%, **2h/3h** = 91:9) and **1g** (62%, **2g/3g** = 69:31) is due to steric factors, when the carbinolic hydrogens in **1h** are replaced by two methyl groups in **1g** (compare structures **4i** and **4h**, Figure 1). However, the intramolecular protonation via the formation of the cyclic structure **4h** or **4i** is more important. Thus, **2g** remains the main product formed.

Consequently, it is noteworthy that the hydrothiolation of buta-1,3-diynes **1a–e** and **1i**,**j** was regio-, stereo-, and chemoselective, affording only one of the possible iso-

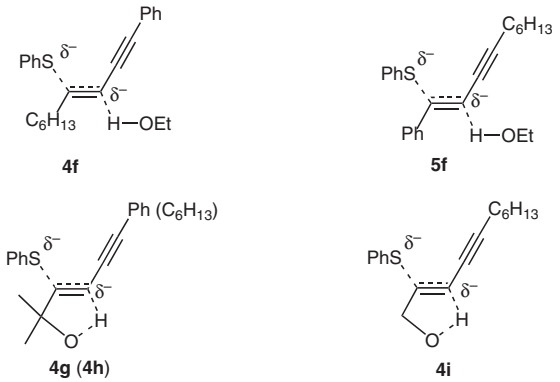


Figure 1 Possible transition states in the hydrothiolation reaction

mers, whereas in the other cases only two isomers were observed.

On the basis of the results obtained, we believe that the mechanism of the hydrothiolation of alkynes is similar to the hydroselenation and hydrotelluration.[22,23]

In conclusion, we developed a new method for the regio-, stereo-, and chemoselective hydrothiolation of buta-1,3-diynes employing the sodium phenyl and butylthiolate generated in situ by reaction of PhSSPh and BuSSBu with $NaBH_4$ in ethanol, respectively. The method is general and can be used for preparation of conjugated (*Z*)-thioenynes in good yields, avoiding the use of highly toxic and bad-smelling thiols as starting material. Studies regarding the use of these thioenynes in the preparation of enediynes and iodo thiophenes are now in progress in our laboratory.

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(19) **Typical Procedure for the Synthesis of (*Z*)-1-Phenylthio-1,4-diorganylbut-1-en-3-ynes**
To a solution of 1,4-diphenylbuta-1,3-diyne **1a**[17] (1.797 g, 5 mmol) and PhSSPh (1.845 g, 2.5 mmol) in 95% EtOH (20 mL) under a nitrogen atmosphere, $NaBH_4$ (0.57 g, 15 mmol) was added at r.t. and under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 3 h, allowed to reach r.t., diluted with EtOAc (3 × 20 mL), and washed with brine (3 × 30 mL) and

H_2O (3 × 30 mL). After drying the organic phase over anhyd $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on SiO_2 using hexane as mobile phase, to give pure (*Z*)-1-phenylthio-1,4-diphenylbut-1-en-3-yne (**2a**) as a white solid; mp 92–95 °C; yield 72%. GC-MS: *m/z* (%) = 312 [M^+], 202, 149, 105, 77, 28 (100). IR (KBr): 3072 (m), 2195 (m), 1680 (m), 1580 (s), 1481 (vs), 1440 (vs), 1071 (m), 1024 (m), 750 (vs), 740 (s), 687 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.32 (s, 1 H), 7.03–7.7 (m, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 87.60, 98.36, 112.27, 123.34, 126.39, 127.49, 127.88, 127.93, 128.27, 128.35, 128.64, 128.75, 129.25, 129.51, 131.60, 138.38, 147.20.

(20) **Typical Procedure for the Synthesis of (*Z*)-1-Phenylthio-4-organylbut-1-en-3-ynes**

A solution of 1-phenylbuta-1,3-diyne (**1c**, 10 mmol) was obtained in situ by reaction of 2-hydroxy-2-methyl-6-phenylhexa-3,5-diyne (**1e**, 1.84 g, 10 mmol) with powered NaOH (25 mg) in dry xylene (11 mL) under reflux for 15 min.[22] The temperature was then allowed to reach r.t., and 95% EtOH (70 mL) and PhSSPh (1.845 g, 5.0 mmol) were added. The reaction was run under an atmosphere of N_2 and $NaBH_4$ (0.57 g, 15 mmol) was added. The resulting reaction mixture was refluxed for 3 h, diluted with EtOAc (70 mL), and washed with brine (4 × 30 mL). After drying the organic phase over anhyd $MgSO_4$, the solvent was removed under reduced pressure, and the residue purified by flash chromatography on SiO_2 using hexane as mobile phase, to give the pure phenylthio enyne **2c** as a yellow oil; yield 75%. GC-MS: *m/z* = 236 [M^+], 202, 149, 126, 115, 77, 51, 28 (100). IR (neat): 689 (vs), 742 (s), 756 (s), 816 (m), 1480 (m), 1488 (m), 1553 (w), 1585 (w), 2205 (w), 3055 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.83 (d, *J* = 10 Hz, 1 H), 6.75 (d, *J* = 10 Hz, 1 H), 7.22–7.54 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 85.62, 97.95, 106.36, 123.26, 127.45, 128.30, 129.18, 129.19, 129.23, 130.31, 130,33, 130.36, 130.39, 130.41, 131.45, 131.49, 134.73, 138.91.

(21) **1-Butylthio-4-cyclohexenylbut-1-en-3-yne (2j)**

The same procedure for obtaining **2c** was performed,[20] however, 6-cyclohexenyl-2-methylhexa-3,5-diyn-2-ol (**1k**) and BuSSBu were used as starting materials, affording the pure compound **2j** as a yellow oil; yield 50%. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.74–1.72 (m, 11 H), 2.07 (m, 2 H), 2.15 (m, 2 H), 2.74 (t, *J* = 7.2 Hz, 2 H)), 5.56 (d, *J* = 9.6 Hz, 1 H), 6.11 (s, 1 H), 6.39 (d, *J* = 9.6 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 21.4, 21.5, 22.2, 25.6, 29.1, 32.4, 33.3, 83.4, 99.1, 104.8, 120.8, 134.2, 138.7.

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