Radical Sequential Processes Promoted by 1,5-Radical Translocation Reaction: Formation and [3 + 2] Anulation of Alkenesulfanyl Radicals

Laura Capella, Pier Carlo Montevecchi,* and Maria Luisa Navacchia

Dipartimento di Chimica Organica "A. Mangini", Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy

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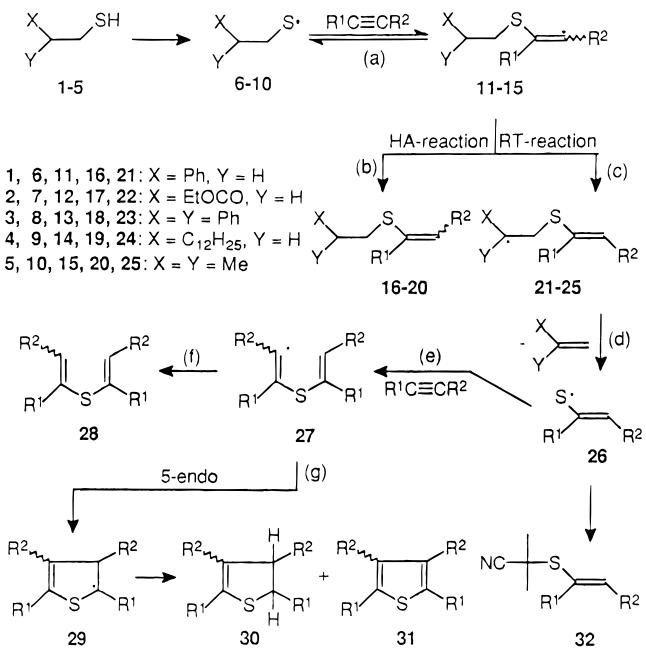
Radical addition of 2-substituted ethanethiols **1**−**5** to alkyl-, dialkyl-, and phenylacetylenes affords the corresponding *β*-sulfanylalkenyl radicals, which can undergo 1,5-radical translocation (RT reaction) in competition with intermolecular hydrogen abstraction (HA reaction). The RT reaction is the first step of a sequential radical process leading to alkenesulfanyl radicals through an "intermolecular sulfanyl radical transaddition" from an alkene to an alkyne molecule. Alkenesulfanyl radicals can undergo a regioselective [3 + 2] anulation reaction with a CC triple bond, eventually leading to thiophene products through 5-*endo* cyclization of vinyl radicals onto CC double bond. The effect of the nature of ethanethiol and alkyne substituents on the RT/HA ratio has been investigated, and results will be discussed.

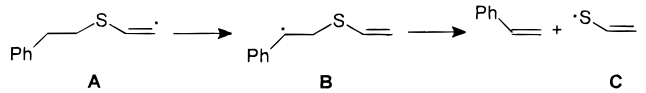
The 1,5-radical migration of a hydrogen atom is a well-known reaction, but its potentiality has not been fully explored yet. Its synthetic use is primarily confined to the Barton reaction, involving 1,5-hydrogen shift toward an alkoxy radical[1] and to the Hofmann−Loffler reaction,[2] which involves a similar 1,5-hydrogen shift toward an aminyl radical cation.

Nevertheless, the "1,5-radical translocation"[3] easily occurs also from alkenyl radicals, providing that a stabilized alkyl radical can be formed. Thus, a *δ*-methylene having substituents capable of stabilizing the incoming radical must be present. We will refer to this methylene as "activated methylene" and to the stabilizing substituents as "activating groups". The new "translocated" alkyl radicals can suitably cyclize on the alkene double bond to form CC bonds.[4,5] An extensive study on the nature of the X and Y activating groups in radical translocation reactions of alkenyl radicals has been recently reported by Curran.[4]

During our researches on the reactivity of *β*-sulfanyl-substituted alkenyl radicals,[6] we have evidenced that alkenesulfanyl radicals **C** can be produced from 2-(phenethylsulfanyl)alkenyl radicals **A** by 1,5-radical translocation and subsequent loss of styrene through *β*-scission of resulting benzyl radicals **B**.[6c] We recognized that this unprecedented process was worth further consideration, generation of the previously unknown alkenesulfanyl radicals representing a novel synthetic use of the 1,5-radical translocation reaction.

Scheme 1





On this basis, we have been prompted to investigate the sequential radical process, outlined in Scheme 1, involving formation of alkenesulfanyl radicals **26** and their [3 + 2] anulation reaction with an alkyne triple bond. During our study we have considered the radical reaction of ethanethiols **1**−**5**, carrying different activating groups, with a number of alkynes, including alkyl-, dialkyl, phenyl-, and phenylalkylacetylenes.

Recently, radical sequential reactions have been object of noticeable interest, representing a useful synthetic

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(2) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337−350.
(3) The term of "radical traslocation" has been introduced by Curran. Radicals are generated at favorable sites and then "traslocated" to new sites. See: Curran, D. P.; Kim, D.; Liu, H. T.; Shen, W. *J. Am. Chem. Soc.* **1988**, *110*, 5900.
(4) Curran, D. P.; Shen, W. *J. Am. Chem. Soc.* **1993**, *115*, 6051.
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(6) (a) Benati, L.; Montevecchi, P. C; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2103. (b) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1659. (c) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Org. Chem.* **1994**, *59*, 2818. (d) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc. Perkin Trans. 1* **1995**, 1035. (e) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Org. Chem.* **1995**, *60*, 7941.

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Table 1. Relative Yields (%) of RT Products (28, 30, 31, and 36) and HA Products from Radical Addition of Phenethyl Thiol 1 and 2-(Methoxycarbonyl)ethanethiol (2) to Alkynes

entry	thiol	alkyne	RT products	HA products	overall yield
1	**1**	hex-1-yne	**28a** (28) + **30a** (3)	**16a** (69)	72
2	**1**	*tert*-butylacetylene	**28b** (90)	**16b** (10)	72
3	**1**	(trimethylsilyl)acetylene	**28c** (90)	**16c** (10)	70
4	**1**	hex-3-yne	**28d** (8) + **31d** (6)	**16d** + **33** (86)	70
5	**1**	oct-4-yne	**28e** (6) + **31e** (4)	**16e** (90)	67
6	**1**	phenylacetylene	**28f** (6) + **30f** (27)	**16f** (67)	74
7	**1**	phenylpropyne	**30g** (75)	**16g** (25)	75
8	**2**	hex-1-yne	**28a** (18) + **30a** (2)	**17a** (80)	96
9	**2**	*tert*-butylacetylene	**28b** (60)	**17b** (40)	70
10	**2**	hex-3-yne	**28d** (5) + **31d** (3)	**17d** (92)	81
11	**2**	phenylacetylene	**28f** (3) + **30f** (15)	**17f** (82)	85

method for obtaining complex products from simple starting molecules in a one-pot process.[7]

Results and Discussion

Sulfanyl radical addition to carbon carbon triple bond readily occurs, giving the corresponding vinyl radicals in a reversible manner.[8] The addition is strictly regioselective, occurring to the terminal carbon atom with terminal alkynes and to the alkyl-substituted carbon atom with alkylarylacetylenes. Sulfanyl radicals can be produced in several ways, i.e., from thiols by hydrogen abstraction with AIBN or with the triethylborane/O_2 method[6e,9] or from the corresponding disulfides by thermal or photochemical homolysis of the S−S bond.

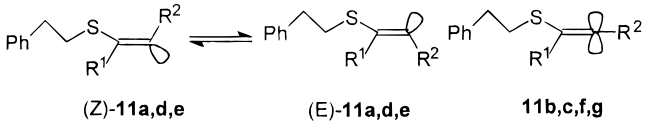
Under the above conditions phenethylsulfanyl radical **6** reacted with hex-1-yne to give products **28a** and **16a** in variable amounts, together with small amounts of thiophene **30a**. Vinyl sulfide **16a** was derived from the vinyl radical **11a** through intermolecular hydrogen abstraction, while the divinyl sulfide **28a** resulted from the following sequential process: 1,5-hydrogen migration from the activated δ-methylene affords the 1,5-translocated radical **21a**, which undergoes β-scission of the carbon−sulfur bond leading to the alkenesulfanyl radical **26a** with loss of stryrene. Regioselective addition of radical **26a** to an additional alkyne moleule gives the vinyl radical **27a**, from which the bis-vinyl sulfide **28a** arises by hydrogen abstraction. The small amounts of thiophene **30a** derive from radical **27a** through 5-*endo* cyclization onto the adiacent double bond (Scheme 1).

The best reaction conditions for obtaining the major amounts of **28a** (and **30a**) are those described under General Procedure (see Experimental Section).

According to this procedure, a benzene solution of thiol **1** was added within 4 h to a refluxing benzene solution containing a 5-fold excess of hex-1-yne and AIBN. Under these conditions products **28a** and **16a** were formed in a ca. 30:70 ratio (see Experimental Section) (Table 1, entry 1). Comparable results were obtained by carrying out the above reaction at 110 °C in a sealed tube (GC analysis). Further increase in the addition time (up to 8 h) did not lead to an appreciable improvement of the **28a**/**16a** ratio, while a decrease (0.5 h) led to a substantial decrease in the above ratio as result of the enhancement of the thiol concentration (with thiol being a good hydrogen donor). Thermolysis of bis(phenethyl) disulfide in chlorobenzene at 180 °C for 12h in the presence of hex-1-yne led to results strictly comparable to those obtained by generating thiyl radicals **6** from thiol **1**, although noticeable amounts of unreacted disulfide were detected (GC analysis). On the contrary, thiyl radicals **6**, when generated from the corresponding disulfide by photolysis with a high-pressure mercury lamp, reacted with hex-1-yne to give unsatisfactory results. GLC analysis of the reaction mixture showed a 5:95 RT/HA products ratio. Poor results were also obtained by generating thiyl radicals **6** from thiol **1** at room temperature with a 10-fold excess of triethylborane in the presence of oxygen.

Under the conditions of General Procedure, thiols **1** and **2** were reacted with a number of alkynes. In all cases we have examined, products deriving from the corresponding vinyl radicals **11a**−**g** and **12a,b,d,f** through both hydrogen abstraction (HA products **16a**−**g** and **17a,b,d,f**) and 1,5-radical translocation (RT products **28**, **30** and **31**) were observed. The relative yields of the RT products and the HA products were found to be strongly dependent on both the nature of R^1 and R^2 substituents and the nature of the activating groups (X = Ph or EtOCO, Y = H) (see Table 1).

The dependence of the RT product/HA product ratio on the R^1 and R^2 substituent nature is probably due to steric effects. For example, the linear α-phenylalkenyl radicals **11f** and **11g** (Table 1, entries 6 and 7) afforded RT products in a different extent. The effect of the β-methyl substituent in increasing the RT product/HA product ratio could be related to the increased steric hindrance to the approach of the radical scavenger by increasing the size of the β-substituent.[14]



(Z)-**11a,d,e** (E)-**11a,d,e** **11b,c,f,g**

(7) (a) Curran, D. P. Radical addition reactions. In *Comprehensive Organic Synthesis*; Pergamom Press: Oxford, U.K., 1991; Vol. 4, Chapter 4.2. (b) Molander, G. A.; Harris, C. R. *J. Am. Chem. Soc.* **1995**, *117*, 3705.

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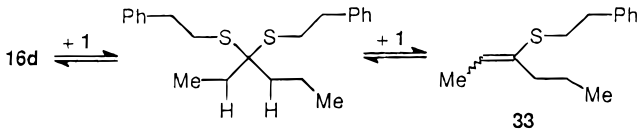
(13) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 969. Giese, B; Lachein, S., *Angew. Chem., Int. Ed. Engl.* **1982,** *21*, 768. Singer, L. A.; Chen, J., *Tetrahedron Lett.* **1969**, 4849.

(14) It is generally accepted that steric hindrance between radical scavenger and the substituent *cis* to the radical center is an important effect in determining the stereochemistry of radical addition of thiols to alkynes (refs 6a,d; see also: Chatgilialoglu, C.; Ferreri, C. Free Radical Addition involving C−C triple bonds. In The Chemistry of Triple-bonded Functional Groups; Patai, S., Ed.; J. Wiley: New York, 1994; Suppl. C2, Vol. 2, Chapter 16.

Table 2. Products (Relative Yields, %) from Reactions of Phenylacetylene with Ethanethiols 1−5 and Thiolacetic Acid (38)

		products, relative yields (%)					
entry	thiol	**28f**	**30f**	1:1 adduct	**34**	RT/HA ratio	overall yield
1	1	5	24	(**16f**) 59	12	33:67	82
2	2	2	13	(**17f**) 69	16	18:82	98
3	3	18	56	(**18f**) 0	19	100:0	67
4	4	traces	7	(**19f**) 79	14	8:92	65
5	5	8	45	(**20f**) 36	10	60:40	75
6	38	0	0	(**40**) 60	40	0:100	36

Scheme 2

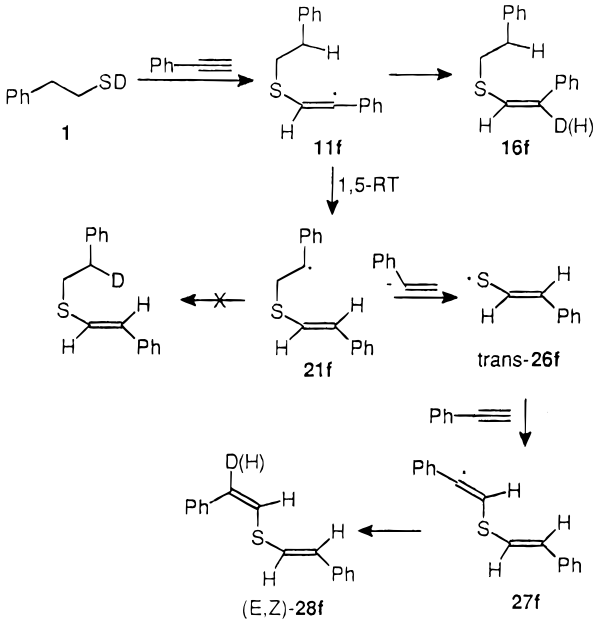


Similarly, radicals **11b** and **11c** (which are in turn believed to be sp-linear[6b,15]) gave a high RT product/HA product ratio, probably as a result of the steric hindrance between the bulky α-substituent and the radical scavenger (Table 1, entries 2 and 3).

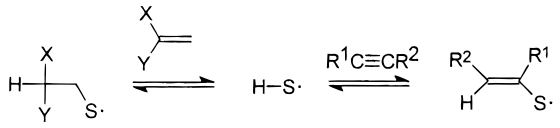
α,β-Dialkyl-substituted radicals **11d** and **11e** (Table 1, entries 4 and 5) gave instead predominant formation of HA products over RT products. It can likely be inferred that steric hindrance between the alkyl substituents R^1 and R^2 shifts the equilibrium between *E*- and *Z*-interconverting isomers toward the *Z*-configuration, which is not suitable for the RT reaction.[16] Reaction of thiol **1** with hex-3-yne gave a regioisomeric mixture of (*E*)- and (*Z*)-**16d** and (*E*)- and (*Z*)-**33**. We found that the **16d**/**33** ratio considerably changed when the isomeric mixture was allowed to stand at room temperature for several days in the presence of small amounts of thiol **1**. In this light, adduct **33** can be considered as deriving from **16d** through a postisomerization process, possibly involving reversible addition of thiol to the carbon−carbon double bond (Scheme 2).[17]

In principle, the effect of the X-activating groups (X = Ph or EtOCO) in determining the RT product/HA product ratio should be related to the different stability of the resulting translocated radicals **21** and **22**. The effect the activating groups is more evident by comparison of results collected in Table 2, showing the RT products/HA products ratios from reactions of ethanethiols **1**−**5** with phenylacetylene carried out under the conditions of General Procedure. An increase in the stability of the translocated radical generally favors the 1,5-radical translocation over the hydrogen abstraction reaction. In particular, no hydrogen abstraction product **18f** was formed from 2,2-diphenylethanethiol (**3**), having two phenyl substituents as activating groups. However, it would appear that the stability of the new translocated radicals cannot be the only determining factor. In fact, thiol **5** gave a RT products/HA products ratio higher than that of thiol **2**, in spite of the fact that a *tert*-alkyl radical is less stable than a benzylic radical.

Scheme 3



The entire process, leading to alkenesulfanyl radicals **26** from alkanesulfanyl radicals **6**−**10**, can be envisaged as a formal "intermolecular sulfanyl radical transaddition" from an alkene toward an alkyne molecule. The driving force should be the higher stability of radicals **21**−**25** with respect to **11**−**15**.



It is noteworthy that β-scission is the exclusive reaction exhibited by radical intermediates **21**−**25**. Indeed, β-cleavage of the carbon−sulfur bond of β-sulfanyl-substituted alkyl radicals is a fast reaction.[10] In agreement, no products deriving from radicals **21**−**25** through 5-*endo* cyclization on the adjacent double bond were formed in all the examined cases. Moreover, we ruled out the possibility that radicals **21**−**25** undergo a competing hydrogen abstraction reaction leading to adducts **16**−**20** by reacting S-deuterated thiol **1** with phenylacetylene. The resulting adduct **16f** was found to be deuterated at the α-vinylic position (ca. 70:30 D/H ratio) (Scheme 3), whereas no deuterium was incorporated at the benzylic position (^{1}H NMR analysis).

As outlined above, alkenesulfanyl radicals **26** undergo regioselective addition to the alkyne triple bond leading to vinyl radicals **27**. However, competing side reactions can occur under the reaction conditions employed For example, products **32a,b,d**, deriving from trapping of **26a,b,d** by 2-cyanopropyl radicals, have been evidenced (Scheme 1).

Radicals **27** undergo 5-*endo* cyclization onto the adjacent double bond, eventually leading to thiophene derivatives **30** and **31**, in competition with the hydrogen abstraction reaction leading to bis-vinyl sulfides **28**. Products **28** are generally obtained as (*E*,*E*)- and (*E*,*Z*)-isomeric mixtures. Reaction of thiol **1** with phenylacetylene led to alkenyl sulfides **28f** in a ca. 90:10 (*E*,*Z*)/(*Z*,*Z*) ratio. ^{1}H NMR analysis of sulfides **28f** obtained from the

(15) Griller, D.; Cooper, J. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 4269.

(16) Dialkylacetylenes undergo radical addition of benzenethiol leading to (*Z*) and (*E*)-adducts in a Z/*E* ratio increasing with the size of alkyl substituents (refs 6a,e). The predominant formation of *trans*-addition (*Z*)-products with hex-3-yne and oct-4-yne would result from predominant occurrence of (*Z*)-radicals in the mixture of equilibrating (*Z*)- and (*E*)-radicals, owing to steric hindrance between the alkyl substituents.

(17) Reversible radical addition of thiols to alkenyl sulfides leading to dithioacetals has been reported (Oswald, A. S.; Griesbaum, K.; Hudson, B. E.; Bregman, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 2877).

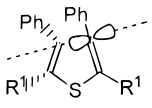
reaction of S-deuterated thiol **1** showed that the (*E*,*Z*)-isomer had incorporated deuterium in the position *trans* to the sulfur atom (D/H ca. 65:35). According to reaction mechanism (Scheme 3), it can be inferred that *trans*-alkenylthio radicals **26f** are formed from **21f**. Moreover, according to the general evidence for radical addition of thiols to phenylacetylenes,[6a,d] α-phenyl-substituted radical **27f** mainly undergoes hydrogen abstraction from the side *trans* to the sulfur atom (Scheme 3).

The 5-*endo* cyclization of alkenyl radicals onto the CC double bond is considered a stereoelectronically disfavored process. Actually, these reactions are quite rare, although examples have been reported.[11]

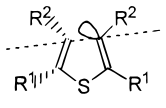
Competition between the 5-*endo* cyclization and the hydrogen abstraction reaction is strongly affected by the nature of R^1 and R^2 substituents, as evidenced from results obtained by reacting thiols **1** and **2** with a number of different alkynes (Table 1). With hex-1-yne (Table 1, entry 1, 8) sulfide **28a** was the main RT product, in addition to very small amounts of the thiophene derivative **30a**. The poor tendency of **27a** to undergo 5-*endo* cyclization on the alkene double bond parallels the behavior encountered with related *β*-(phenylsulfanyl)-α-alkyl-substituted vinyl radicals **34**, R^1 = H, R^2 = alkyl, which were found not to undergo *ortho* cyclization onto the phenyl ring (similar to a 5-*endo* cyclization) even at very high reaction temperature.[6b] However, when a further alkyl substituent is present in the *β*-position (Table 1, entries 4, 5, and 10), alkenyl radicals **27d,e** showed a greater propensity to undergo 5-*endo* cyclization. The effect of the *β*-alkyl substituent (previously observed[6b] in related cyclizations on the phenyl ring of radicals **34**, R^1 = R^2 = alkyl) is unclear.

34

The marked α-phenyl effect in promoting 5-*endo* cyclization can be explained according to Baldwin−Beckwith's rules for radical cyclizations.[12] The transition state for a 5-*endo*-*trig* cyclization is achieved when the unpaired electron containing orbital and the CC double bond form an angle of 109°. This situation is better achieved for α-phenyl linear sp-hybridized vinyl radicals **27f,g**,[9a,13] having the unpaired electron in the p-orbital, rather than for α-alkyl bent vinyl radicals **27a,d,e**, having the unpaired electron in the sp^2-orbital.



27f,g

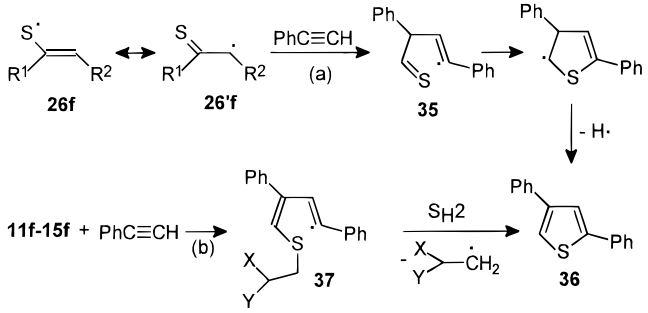


27a,d,e

A remarkable effect in promoting 5-*ortho* cyclization onto the phenyl ring had been also provided by radicals **34** having bulky α-substituents, such as *tert*-butyl and trimethylsilyl groups.[6b] In contrast with this early evidence, no 5-*endo* cyclization products were obtained from radicals **27b,c** (Table 1, entries 2, 3, and 9). We suggest that steric hindrance between the bulky substituents inhibits radicals **27b,c** from reaching the *cisoid* conformation suitable for cyclization.

In all cases we have examined, reaction of thiols **1**−**5** with phenylacetylene gave, besides the HA products **16**−**20f** and the RT products **28f, 30f,** and **31f**, 2,4-diphenylthiophene **36** (Table 2). In principle, thiophene **36** might have been derived from the alkenesulfanyl radical **26f**, which can exist in the mesomeric form **26′f** and be considered an ambident radical. Thus, thiophene **36** could arise by addition of the carbon-centered radical **26′f** to phenylacetylene and subsequent ring closure of the resulting vinyl radical **35** by intramolecular addition to the carbon−sulfur double bond (Scheme 4, path a). However, another route is opened for thiophene **36**, which could result from radicals **11f**−**15f** through initial addition to a further molecule of phenylacetylene (Scheme 4, path b). Resulting vinyl radicals **37** could give thiophene **36** by S_H2 reaction at sulfur, with displacement of a 2-substituted ethyl radical. A similar behavior has been previously encountered in radical addition of thiophenethiol to phenylacetylene.[6e]

Scheme 4

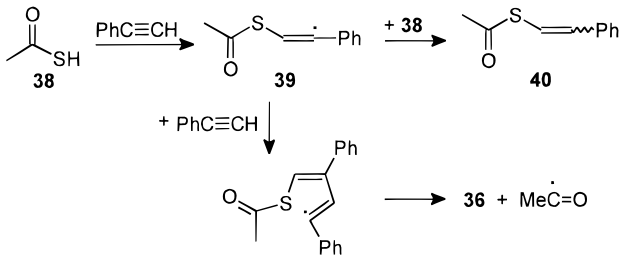


Both proposed mechanisms involve initial carbon-centered radical addition to phenylacetylene. However, the route involving radical **26′f** does not appears to be conceivable in our opinion. In fact, the ratio of addition products to phenylacetylene by the sulfur-centered radical **26** (RT products **28f** and **30f**) and by the carbon-centered radical **26′f** (thiophene **36**) cannot depend on the reaction conditions, including the nature of the thiol **1**−**5**. Vice versa, we can observe from Table 2 that the (**28f** + **30f**)/**36** ratio strongly depends on the nature of the thiol **1**−**5** employed. This finding is instead in agreement with the route involving radical **11f**−**15f** addition to phenylacetylene. This reaction should compete with both hydrogen abstraction and radical translocation, and it is expected to be strongly influenced by the nature of the thiol employed. Compelling evidence came from reaction of thiolacetic acid (**38**) with phenylacetylene. Reaction of thiol **38** with hex-1-yne has been previously reported to give only the thiol/alkyne adduct.[18] In contrast, we found that thiol **38** reacted with phenylacetylene to give comparable amounts of 1:1 adduct **40** and thiophene **36**, although in somewhat low overall yields (Scheme 5 and Table 2, entry 6). No thiophene derivative **30f**, or bis-vinyl sulfide **28f**, or other products possibly deriving from 1,5-radical translocation could be detected.

Finally, attempts to trap radicals **26** by addition on alkene double bonds failed. Reaction of thiol **2** with phenylacetylene carried out in the presence of a 10-fold excess of cyclohexene or methyl acrylate did not lead to any product deriving from radical addition of **26f** to the carbon−carbon double bond. The product patterns of the above reactions were identical to those obtained from the same reaction carried out in the absence of any alkene (GC, GC-MS, and TLC analyses). Indeed, the failure to

(18) Kampmeier, J. A.; Chen, G. *J. Am. Chem. Soc.* **1975**, *87*, 2608.

Scheme 5



give addition products would not result from the incapability of radical **26f** of adding to alkenes. In this respect, radical **26f** would show a behavior similar to that generally exhibited by other sulfanyl radicals, which are known to undergo rapid and reversible addition on the carbon−carbon double bond.[10]

Conclusions

The overall findings show that alkenesulfanyl radicals **26** can be smoothly generated by radical addition of ethanethiols carrying 2-activating groups to alkynes through transaddition of a sulfanyl radical moiety from an alkene to an alkyne molecule. This process is promoted by an initial 1,5-radical translocation from an alkenyl to an alkyl position. Alkenesulfanyl radicals **26** add to CC triple bond in a regioselective fashion; however, the subsequent 5-*endo* cyclization of resulting alkenyl radicals **27** on the adjacent double bond occurs in a satisfactory manner only with linear sp-hybridized α-phenyl radicals.

Experimental Section

Thiols **1, 2, 4, 5**, and **38** and all the alkynes employed were commercially available. Thiol **3** was prepared according to Volante's method[19] in 30% yield and was reacted without further purification. [^{1}H NMR δ (200 MHz) 1.35 (1H, t, J = 7.5 Hz; collapsing to singlet upon irradiation at δ 3.20), 3.20 (2H, t, J = 7.5 Hz), 4.15 (1H, t, J = 7.5 Hz; collapsing to singlet upon irradiation at δ 3.20), 7.15−7.35 (10H, m); MS *m*/*z* (rel intensity) 214 (M^+, 10), 167 (100), 165 (50), 152 (30); HRMS calcd for $C_{14}H_{14}S$ 214.08162, found 214.08153.]

Adducts **16a**[6c] and **16f**,[6c] dialkenyl sulfides **28a**[6c] and **28f**,[6c] and thiophene derivatives **30f**,[20] **31f**,[21] and **36**,[21,22] were identified by GC-MS spectral comparison with authentic specimens. Structural assignment to the new reaction products generally arose from ^{1}H NMR and MS spectral data in addition to elemental analysis. Adducts **16a**−**g**, **17a,b,d,f**, **19f**, **20f**, and dialkenyl sulfides **28a**−**f** were separated as E/Z mixtures. Compounds **16g**, **28d**, and **28e** were not isolated as pure products. Mixtures with the corresponding thiophene derivatives **30g**, **31d**,[22] and **31e**,[23] respectively, were obtained. Their identification arose by careful GC-MS and ^{1}H NMR spectral analysis in addition to HRMS. Column chromatography was performed on Merck silica gel (0.040−0.063 particle size) by gradual elution with light petroleum ether (bp 40−70 °C)−diethyl ether.

Reactions of Thiols 1−5 and 38 with Alkynes. General Procedure. A benzene solution (10 mL) of the appropriate thiol **1**−**5** and **38** (2 mmol) in boiling benzene (40 mL) was added within 4 h with a syringe pump to a solution of the appropriate alkyne (10 mmol) and AIBN (55 mg, 0.33 mmol). Further portions of AIBN (55 mg) were added after 1.5 and 3 h. The reaction mixture was refluxed for a further 1 h; afterward the solvent was removed and the residue was analyzed by GC/MS and then chromatographed.

Reactions of Thiols 1−5 with Phenylacetylene. Elution with light petroleum ether gave, besides the products described below, 1,3,5-triphenylbenzene[24] (ca. 20−30 mg); elution with light petroleum ether/diethyl ether 95:5 gave a mixture of products probably deriving from addition of 2-cyanopropyl radicals to phenylacetylene (ca. 50−60 mg).[24] Further elution with light petroleum ether/diethyl ether 90:10 gave noticeable amounts (yield not determined) of complex mixtures of unidentifiable products.

From Phenethyl Thiol 1. Chromatography gave 2,4-diphenylthiophene (**36**) (47 mg, 10%), 3,4-diphenyl-2,3-dihydrothiophene (**30f**) (95 mg, 20%), dialkenyl sulfide **28f** (20 mg, 4%) [ca. 15:85 (*E*,*E*)/(*E*,*Z*) mixture], and a ca. 80:20 (*Z*)/(*E*) mixture of (*Z*)- and (*E*)-adduct **16f** (230 mg, 48%). A benzene solution of **30f** was refluxed for 30 min in the presence of 1.5 molar equiv of DDQ; the reaction was filtered on a silica gel column (h = 10 cm) and the solvent distilled off to yield 3,4-diphenylthiophene (**31f**) (ca. 100%).

The reaction was repeated by using S-deuterated phenethyl thiol (90:10 D/H ratio), which was prepared by shaking a benzene solution (5 mL) of **1** (2 mmol) with D_2O (0.5 mL). Chromatography allowed for separation of a fraction containing a 30:70 mixture of (*Z*)-**16f** and (*Z*)-α-deuterio-*β*-styrylphenethyl sulfide [1-deuterio-(*Z*)-**16f**] [^{1}H NMR δ (200 MHz) 3.0 (4H, m), 6.26 (0.7 H, br s, line width ca. 3.5 Hz), 6.26 (0.3 H, A part of an AB system, J = 10.8 Hz), 6.48 (0.3 H, B part of an AB system, J = 10.8 Hz), 7.2−7.5 (10H, m)] and an ca. 15:85 mixture of (*E*,*E*)-**28f** and (*Z*)-α-deuterio-*β*-styryl (*E*)-*β*-styryl sulfide (1-deuterio-(*E*,*Z*)-**28f**) (D/H ratio ca. 65:35) [^{1}H NMR δ (200 MHz) 6.49 (0.65 H, br s, line width ca. 3,5 Hz), 6.49 (0.35 H, A part of an AB system, J = 11 Hz), 6.62 (0.35 H, B part of an AB system, J = 11 Hz), 6.7 (1H, A′ part of an A′B′ system, J = 15 Hz), 6.85 (1H, B′ part of an A′B′ system, J = 15 Hz), 7.2−7.6 (aromatic protons)].

From 2-(Ethoxycarbonyl)ethanethiol 2. Chromatography gave thiophene **36** (75 mg, 16%), dihydrothiophene **30f** (60 mg, 13%), dialkenyl sulfide **28f** (10 mg, 2%), and a 90:10 (*Z*)/(*E*) mixture of 2-(ethoxycarbonyl)ethyl *β*-styryl sulfide (**17f**) (320 mg, 69%) [^{1}H NMR δ (200 MHz) 1.27 (3H, t, J = 7.5 Hz), 2.7 (2H, t, J = 7.0 Hz), 3.07 (2H, t, J = 7.0 Hz), 4.15 (2H, q, J = 7.5 Hz), 6.24 (0.9H, A part on AB system, J = 10.6 Hz), 6.4 (0.1H, A′ part of an A′B′ system, J = 15 Hz,), 6.48 (0.9H, B part of an AB system, J = 10.6 Hz), 6.62 (0.1H, B′ part of an A′B′system, J = 15 Hz), 7.2−7.5 (5H, m); MS *m*/*z* (rel intensity) 236 (M^+, 100), 135 (70), 134 (20), 91 (60). Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; O, 13.54, S, 13.57. Found: C, 66.40; H, 6.80; S, 13.65]

From 2,2-Diphenylethanethiol (3). Chromatography gave diphenylethylene (yield not determined), thiophene **36** (60 mg, 13%), dihydrothiophene **30f** (175 mg, 38%), and dialkenyl sulfide **28f** (55 mg, 12%).

From *n*-Dodecyl Thiol 4. Chromatography gave 2,4-diphenylthiophene (**36**) (42 mg, 9%), dihydrothiophene **30f** (20 mg, 4.5%), and a 80:20 (*Z*)/(*E*) mixture of *n*-dodecyl *β*-styryl sulfide (**19f**) (300 mg, 50%) [^{1}H NMR δ (200MHz) 0.8−0.9 (3H, m), 1.1−1.4 (18H, m), 1.55−1.75 (2H, m), 2.65−2.8 (2H, m), 6.24 (0.8H, A part of an AB system, J = 11 Hz), 6.43 (0.8H, B part of an AB system, J = 11 Hz), 6.45 (0.2H, A′ part of an A′B′ system, J = 15 Hz), 6.72 (0.2H, B′ part of an A′B′ system, J = 15 Hz), 7.15−7.5 (5H, m); MS *m*/*z* (rel intensity) 304 (M^+, 90), 136 (100), 135 (95). Anal. Calcd for $C_{20}H_{32}S$: C, 78.88; H, 10.59; S, 10.53. Found: C, 79.20; H, 10.65; S, 10.48]. Traces amounts of dialkenyl sulfide **28f** were detected by GC/MS.

From 2-Methylpropanethiol (5). Chromatography gave 2,4-diphenylthiophene (**36**) (35 mg, 7.5%), dihydrothiophene **30f** (160 mg, 34%), a ca. 80:20 (*Z*)/(*E*) mixture of 2-methylpropyl *β*-styryl sulfide (**20f**) (100 mg, 27%) [^{1}H NMR δ (200 MHz) 1.02 (4.8H, d, J = 7.5 Hz), 1.03 (1.2H, d, J = 7.5 Hz), 1.8−2.0

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(1H, m), 2.70 (2H, d, J = 7.5 Hz), 6.24 (0.8H, A part of an AB system, J = 11 Hz), 6.41 (0.8H, B part of an AB system, J = 11 Hz), 6.47 (0.2H, A′ part of an A′B′ system, J = 15 Hz), 6.73 (0.2H, B′ part of an A′B′ system, J = 15 Hz), 7.2−7.5 (5H, m); MS *m*/*z* (rel intensity) 192 (M^+, 60), 136 (80), 135 (100). Anal. Calcd for $C_{12}H_{16}S$: C, 74.94, H, 8.39, S, 16.67. Found: C, 74.65; H, 8.43; S, 16.60], and dialkenyl sulfide **28f** (35 mg, 6%).

Reaction of Thiolacetic Acid (38) with Phenylacetylene. Elution with light petroleum ether gave 2,4-diphenylthiophene (**36**) (68 mg, 14%) and a (*Z*)-adduct, (*Z*)-**40** (75 mg, 21%) [^{1}H NMR δ (200 MHz) 2.45 (3H, s), 6.72 (1H, d, J = 10.7 Hz), 6.93 (1H, d, J = 10.7 Hz), 7.2−7.4 (5H, m); MS *m*/*z* (rel intensity) 178 (M^+, 30), 136 (100), 135 (90), 91 (30). Anal. Calcd for $C_{10}H_{10}OS$: C, 67.38, H, 5.65, O, 8.98; S, 17.99. Found: C, 67.70; H, 5.68; S, 17.90]. Further elution with light petroleum-diethyl ether 90:10 gave complex mixtures of unidentifiable products.

Reactions of Thiols 1−2 with Hex-1-yne. From Phenethyl Thiol 1. Chromatography gave a mixture of (*E*,*E*)- and (*E*,*Z*)-bis(hex-1-en-1-yl) sulfide **28a** (80 mg, 20%), 3,4-dibutyl-2,3-dihydrothiophene (**30a**) (10 mg, 2%) [^{1}H NMR δ (200 MHz) 0.9 (6H, m), 1.2−1.5 (10H, m), 2.0−2.2 (2H, m; allylic methylene), 2.7−2.85 (1H, m), 2.92 (1H, ABX system, J_{AX} = 10.5 Hz; J_{AB} = 6.0 Hz), 3.35 (1H, dd, J_1 10.5 Hz, J_2 = 8.5 Hz), 5.65 (1H, br s); MS *m*/*z* (rel intensity) 198 (M^+, 50), 141 (100); HRMS calcd for $C_{12}H_{22}S$ 198.14422, found 198.14445], and a ca. 1:1 (*E*)/(*Z*) mixture of phenethyl hex-1-en-1-yl sulfide (**16a**) (220 mg, 50%). GC/MS analysis of the reaction mixture showed the presence of possible adduct **32a** [MS *m*/*z* (rel intensity) 183 (M^+, 30), 140 (40), 126 (50), 115 (20), 73 (100)].

From 2-(Ethoxycarbonyl)ethanethiol (2). Chromatography gave bis(hexenyl) sulfide **28a** (65 mg, 17%), dihydrothiophene **30a** (10 mg, 2%), and a 50:50 (*Z*)/(*E*) mixture of 2-(ethoxycarbonyl)ethyl hex-1-en-1-yl sulfide (**17a**) (335 mg, 78%) [^{1}H NMR δ (200 MHz) 0.8−0.95 (3H, m), 1.25−1.45 (4H, m), 1.27 (3H, t, J = 7.5 Hz), 2.0−2.2 (2H, m), 2.62 (2H, t, J = 7.0 Hz), 2.85−2.95 (2H, m), 4.15 (2H, q, J = 7.5 Hz), 5.62 (0.5H, A part of an ABX_2 system, J_{AB} = 9 Hz, J_{AX} = 6.8 Hz), 5.72 (0.5H, A′ part of an A′B′X′$_2$ system, $J_{A'B'}$ = 15 Hz, $J_{A'X'}$ = 6.8 Hz), 5.88 (0.5H, B part of an ABX_2 system, J_{AB} = 9 Hz, J_{AX} = 1.4 Hz), 5.88 (0.5H, B′ part of an A′B′X′$_2$ system, $J_{A'B'}$ = 15 Hz, $J_{B'X'}$ = 1.0 Hz); MS *m*/*z* (rel intensity) 216 (M^+, 50), 173 (30), 115 (70), 85 (100), 82 (70), 73 (90). Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32; O, 14.79, S, 14.82. Found: C, 60.90; H, 9.37; S, 14.75].

Reaction of Thiols 1 and 2 with 3,3-Dimethylbut-1-yne. From Phenethyl Thiol 1. Elution with light petroleum ether gave a 97:3 (*E*,*E*)/(*E*,*Z*) mixture of bis(3,3-dimethylbut-1-en-1-yl) sulfide (**28b**) (260 mg, 65%) [^{1}H NMR δ (200 MHz) 1.05 (9H, s), 5.75 (1H, A part of an AB system, J = 15 Hz), 5.90 (1H, B part of an AB system); low-intensity doublets are present at δ 5.52 (J = 11Hz) and 5.87 (J = 15 Hz); MS *m*/*z* (rel intensity) 198 (M^+, 20), 183 (20), 57 (100). Anal. Calcd for $C_{12}H_{22}S$: C, 72.66; H, 11.18; S, 16.16. Found: C, 72.37; H, 11.24; S, 16.23] and a ca. 95:5 (*E*)/(*Z*) mixture of 3,3-dimethylbut-1-en-1-yl phenethyl sulfide (**16b**) (30 mg, 7%) [^{1}H NMR δ (*E*)-isomer [200 MHz] 1.05 (9H, s), 2.95 (4H, br s), 5.7 (1H, A part of an AB system, J = 15 Hz), 5.85 (1H, B part of an AB system, J = 15 Hz), 7.2−7.4 (5H, m); (*Z*)-isomer showed vinylic protons at δ 5.52 (d, J = 11 Hz) and 5.78 (d, J = 11 Hz); MS *m*/*z* (rel intensity) 220 (M^+, 30), 205 (30), 105 (100); HRMS calcd for $C_{14}H_{20}S$ 220.12857; found 220.12881]. Elution with light petroleum ether/diethyl ether 90:10 gave (*E*)-3,3-dimethylbut-1-en-1-yl 2-cyanopropyl sulfide (**32b**) as an oil (35 mg, 10%) [^{1}H NMR δ 1.05 (9H, s), 1.6 (6H, s), 6.05 (A part of an AB system, J = 15.2 Hz), 6.25 (B part, J = 15.2 Hz); MS *m*/*z* (rel intensity) 183 (M^+, 15), 168 (20), 115 (60), 101 (50), 99 (50), 83 (60), 59 (100); HRMS calcd for $C_{10}H_{17}NS$ 183.10817, found 183.10805].

From 2-(Ethoxycarbonyl)ethanethiol (2). Elution with light petroleum ether gave a 97:3 (*E*,*E*)/(*E*,*Z*) mixture of bis-(3,3-dimethylbut-1-en-1-yl) sulfide (**28b**) (165 mg, 42%) and an ca. 85:15 (*E*)/(*Z*) mixture of 3,3-dimethylbut-1-en-1-yl 2-(ethoxycarbonyl)ethyl sulfide (**17b**) (120 mg, 28%) [^{1}H NMR δ (200 MHz) 1.0 (7.65H, s), 1.11 (1.35H, s), 1.27 (3H, t, J = 7.5 Hz), 2.6 (2H, t, J = 7.0 Hz), 2.88 (2H, t, J = 7.0 Hz), 4.15 (2H, q, J = 7.5 Hz), 5.7 (0.15H, A part of an AB system, J = 10.2 Hz), 5.71 (0.15H, B part of an AB system, J = 10.2 Hz), 5.73 (0.85H, A′ part of an A′B′ system, J = 15.3 Hz), 5.82 (0.85H, B′ part of an A′B′ system, J = 15.3 Hz); MS *m*/*z* (rel intensity) 216 (M^+, 50), 201 (90), 115 (50), 113 (50), 101 (40), 99 (90), 83 (100). Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32, O, 14.79, S, 14.82. Found: C, 61.30; H, 9.37; S, 14.75]. Further elution with light petroleum ether/diethyl ether 90:10 gave complex mixtures of unidentifiable products.

Reaction of Thiols 1 and 2 with Hex-3-yne. From Phenethyl Thiol 1. Chromatography gave a 3:2 mixture of bis(hex-3-en-1-yl) sulfide (**28d**) [(*E*,*E*), (Z,Z), and (*E*,*Z*) isomeric mixture] and tetraethylthiophene **31d** (40 mg, 10% overall yield) [**28d**: ^{1}H NMR δ (200 MHz) 1.0 (6H, m), 2.0−2.2 (2H, m, allylic methylenes), 2.2−2.35 (2H, m, allylic methylenes), 5.4−5.8 (2H, vinylic protons). Triplets at δ 5.48 (J = 7.5 Hz, collapsing to singlet upon irradiation at δ 2.1), 5.59 (J = 7.5 Hz, collapsing to singlet upon irradiation at δ 2.1), 5.68 (J = 6.0 Hz, collapsing to singlet upon irradiation at δ 2.3), and 5.75 (J = 6.0 Hz, collapsing to singlet at δ 2.3); GC/MS *m*/*z* (rel intensity) 198 (M^+, 50), 169 (100), 155 (40); HRMS calcd for $C_{12}H_{22}S$ 198.14422; found 198.14447. **31d**: ^{1}H NMR δ (200 MHz) 1.08 (3H, t, J = 7.5 Hz), 1.28 (3h, t, J = 7.5 Hz), 2.47 (2H, q, J = 7.5 Hz, collapsing to singlet upon irradiation at δ 1.08), and 2.72 (2H, q, J = 7.5 Hz, collpasing to singlet upon irradiation at δ 1.28); GC/MS *m*/*z* (rel intensity) 196 (M^+, 30), 181 (100)] and a mixture of (*E*)- and (*Z*)-hex-3-en-1-yl phenethyl sulfide (**16d**) and (*E*)- and (*Z*)-hex-2-en-3-yl phenethyl sulfide (**33**) (260 mg, 60%). Repeated column chromatography allowed for separation of fractions containing almost pure (*E*)-**16d** and (*Z*)-**16d** [^{1}H NMR δ (300 MHz) [(*E*)-**16d**] 0.98 (3H, t, J = 7 Hz), 1.1 (3H, t, J = 7 Hz), 2.25 (4H, m), 2.80 (4H, m), 5.65 (1H, t, J = 6.7 Hz, collapsing to singlet upon irradiation at δ 2.25), 7.15−7.35 (5H, m); δ (300 MHz) [(*Z*)-**16d**] 1.0 (3H, t, J = 7.0 Hz), 1.1 (3H, t, J = 7.0 Hz), 2.10 (2H, quintuplet, J = 7.0 Hz, collapsing to quartet upon irradiation at δ 5.38), 2.22 (2H, q, J = 7.0 Hz), 2.85 (4H, m), 5.38 (1H, t, J = 7.0 Hz), 7.15−7.35 (5H, m); MS *m*/*z* (rel intensity) 220 (M^+, 60), 116 (80), 115 (80), 105 (100). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55. Found: C, 76.60; H, 9.20; S, 14.48]. A benzene solution of the (*E*)- and (*Z*)-**16d** mixture was allowed to stand at room temperature for 3 days in the presence of thiol **1** (ca. 0.2 molar equiv). ^{1}H NMR analysis showed formation of a ca. 1:1:1:1 mixture of (*E*)- and (*Z*)-**16d** and (*E*)- and (*Z*)-**33** [(*E*)- and (*Z*)-**33**: ^{1}H NMR δ (300 MHz) 0.9−1.0 (6H, m), 1.5−1.65 (4H, m), 1.72 (3H, d, J = 7.0 Hz), 1.82 (3H, dt, J_d = 6.7 Hz, J_t = 1.0 Hz), 2.15−2.30 (4H, m), 2.8−2.9 (4H, m), 5.54 (1H, q, J = 7.0 Hz, collapsing to singlet upon irradiation at δ 1.72), 5.74 (1H, qt, J_q = 6.7 Hz, J_t = 1.0 Hz, collapsing to triplet, J = 1.0 Hz, upon irradiation at δ 1.82, collapsing to quartet upon irradiation at δ 2.2), 7.15−7.4 (10H, m)]. GC/MS of the reaction mixture showed the presence of possible adduct **32d** [MS *m*/*z* (rel intensity) 183 (M^+, 10), 154 (40), 115 (15), 73 (100)].

From 2-(Ethoxycarbonyl)ethanethiol (2). Chromatography gave a 3:2 miture of bis(hex-3-en-1-yl) sulfide (**28d**) and tetraethylthiophene **31d** (25 mg, 6%) and a 55:45 (*Z*)/(*E*) mixture of 2-(ethoxycarbonyl)ethyl hex-3-en-1-yl sulfide (**17d**) (320 mg, 73%) [^{1}H NMR δ (200 MHz) 0.9−1.15 (6H, m), 1.27 (3H, t, J = 7.5 Hz), 2.0−2.3 (4H, m), 2.45−2.65 (2H, m), 2.8−2.95 (2H, m), 4.15 (2H, q, J = 7.5 Hz), 5.40 (0.55H, t, J = 7.0 Hz), 5.67 (0.45H, br t, J = 7.0 Hz); MS *m*/*z* (rel intensity) 216 (M^+, 30), 115(100). Anal. Calcd for $C_{11}H_{20}O_2S$: C, 61.07; H, 9.32; O, 14.79; S, 14.82. Found: C, 60.90; H, 9.35; S, 14.90].

Reaction of Phenethyl Thiol 1 with (Trimethylsilyl)-acetylene. Elution with light petroleum ether gave a ca. 90:10 (*E*,*E*) and (*E*,*Z*) mixture of bis(trimethylsilyl)vinyl sulfide (**28c**) (275 mg, 60%) [^{1}H NMR δ (200 MHz) [(*E*,*E*)-**28c**] 0.10 (9H, s), 6.0 (1H, d, J = 17.8 Hz) and 6.65 (1H, d, J = 17.8 Hz); (*E*,*Z*)-**28c** showed vinylic protons at δ 5.8 (d, J = 13 Hz), 7.05 (J = 13 Hz), 5.89 (d, J = 17.8 Hz), and 6.57 (17.8 Hz); MS *m*/*z* (rel intensity) 230 (M^+, 20), 127 (50), 73 (100). Anal. Calcd for $C_{10}H_{22}SSi_2$: C, 52.10; H, 9.62; S, 13.91; Si, 24.37. Found: C, 52.26; H, 9.65; S, 13.85] and (*E*)-trimethylsilyl phenethyl sulfide (**16c**) (45 mg, 10%) [^{1}H NMR δ (200 MHz) 0.10 (9H, s), 2.9−3.0 (4H, m), 5.85 (1H, d, J = 18 Hz), 6.50 (1H,d, J = 18

Hz), 7.2−7.6 (5H, m); MS *m*/*z* (rel intensity) 236 (M^+, 20), 195 (30), 132 (50), 105 (100), 73 (80). Anal. Calcd for $C_{13}H_{20}SSi$: C, 66.04; H, 8.53; S, 13.56, Si, 11.88. Found: C, 66.24; H, 8.57; S, 13.50].

Reaction of Phenethyl Thiol 1 with Oct-4-yne. Chromatography gave a 3:2 mixture of bis(oct-4-en-1-yl) sulfide (**28e**) [isomeric mixture] and tetrapropylthiophene **31e** (35 mg, 7% overall yield) [^{1}H NMR δ (200 MHz) 0.8−1.0 (12H, m), 1.3−1.7 (8H, m), 2.0−2.2 and 2.2−2.3 (4.8H, m, **28e** allylic methylenes), 2.38 (0.8H, t, J = 7.5 Hz, collapsing to singlet upon irradiation at δ 1.5; **31e** thienylic methylene), 2.62 (0.8H, t, J = 7.5 Hz, collapsing to singlet upon irradiation at δ 2.07; **31e** thienylic methylene), 5.5−5.8 [0.6H, ninylic protons; triplets of comparable intensity with J = 7.0 Hz are present at δ 5.54 (collapsing to singlet upon irradiation at δ 2.07), 5.65 (collapsing to singlet upon irradiation at δ 2.07), 5.68 (collapsing to singlet upon irradiation at δ 2.3), and 5.75 (collapsing to singlet upon irradiation at δ 2.3)]; GC/MS *m*/*z* (rel intensity) **28e** 254 (M^+, 30), 225 (70), 211 (100); **31e** 252 (M^+, 15) and 223 (100)] and a 70:30 (*Z*)/(*E*) mixture of oct-4-en-1-yl phenethyl sulfide (**16e**) (300 mg, 60%) [^{1}H NMR δ (200 MHz) 0.85−0.95 (6H, m), 1.3−1.55 (4H, m), 2−2.25 (4H, m), 2.8 (2.8H, br s), 2.85 (1.2H, br s), 5.42 (0.3H, t, J = 7 Hz), 5.64 (0.7H, J = 7 Hz), 7.15−7.35 (5H, m); MS *m*/*z* (rel intensity) 248 (M^+, 15), 144 (30), 143 (30), 105 (100). Anal. Calcd for $C_{16}H_{24}S$: C, 77.36; H, 9.74; S, 12.91. Found: C, 77.60; H, 9.80; S, 12.85]

Reaction of Phenethyl Thiol 1 with 1-Phenylpropyne. Chromatography gave 2,5-dimethyl-3,4-diphenyl-2,3-dihydrothiophene (**30g**) (100 mg, 19%), mp 84−85 °C [^{1}H NMR δ (200 MHz) 1.0 (3H, d, J = 7 Hz), 2.15 (3H, s), 4.25 (1H, A part of an AB system, J = 7 Hz), 4.40 (1H, B part of an ABX_3 system, five lines, $J_{AB} = J_{BX}$ = 7 Hz), 7.0−7.4 (10H, m); MS *m*/*z* (rel intensity) 266 (M^+, 100), 251 (100), 189 (55). Anal. Calcd for $C_{18}H_{18}S$: C, 81.15; H, 6.81; S, 12.04. Found: C, 81.40; H, 6.84; S, 11.98] and a 2:1 inseparable mixture of **30g** and phenethyl 1-phenylpropen-1-yl sulfide (**16g**) (*E*/Z mixture) (290 mg, 56% overall yield) [**16g**: ^{1}H NMR δ (200 MHz) 2.25 (3H, s), 2.80−3.10 (4H, m), 6.40 (0.25H, s), 6.50 (0.75H, s), and aromatic protons; GC/MS *m*/*z* (rel intensity) 254 (M^+, 30), 150 (100), 135 (30), 129 (50), 115 (40), 105 (50)].

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