Free-Radical Addition of Alkanethiols to Alkynes. Rearrangements of the Intermediate β-Thiovinyl Radicals†

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A variety of 2-mercapto-substituted vinyl radicals have been produced through the free-radical reaction of alkanethiols (including phenethyl, allyl, and benzyl mercaptans) with monosubstituted acetylenes in benzene at 90 °C. The 2-(benzylthio)vinyl radicals **6** readily rearranged to (vinylthio)methyl radicals **7** *via* a novel 1,4-migration of the phenyl group from thiomethyl to vinyl carbon; 2-(phenethylthio)vinyl radicals **12** underwent internal 1,5-hydrogen transfer to form β-thio-substituted benzyl radicals **13** which in turn suffered fast β-elimination of vinylthio radicals **18**; and 2-(allylthio)-vinyl radical **20** underwent kinetically preferred 5-exo cyclization to give the primary radical **26** which could easily rearrange to the more stable ring-expanded radical **25**.

In a previous paper[1] we reported a study of the free-radical reactions of benzenethiol and diphenyl disulfide with phenyl- and alkylacetylenes. These reactions smoothly proceed by regioselective addition of benzenethio radicals to carbon–carbon triple bonds to give 1-alkyl- and 1-phenyl-2-(phenylthio)vinyl radicals, whose chemical reactivity was found to be strongly determined by structural features and the bulkiness of adjacent vinylic substituents. Linear sp-hybridized 1-phenyl (and 1-*tert*-butyl) radicals showed a definite preference for undergoing hydrogen transfer from benzenethiol and S_H2 reaction with the disulfide on the side *trans* to PhS, whereas the bent (and rapidly inverting) sp^2-hybridized 1-alkyl analogues could suffer attack of thiol or disulfide to an extent largely dependent upon both the size of either of the radical scavengers and that of the substituent *cis* to either of the radical centers. Moreover, these 2-(phenylthio)vinyl radicals, particularly the sp-hybridized ones, also showed a tendency to exhibit homolytic intramolecular cyclization reactions leading to benzothiophene products. From this evidence we were subsequently led to devise a novel synthetic route to 3-(and 2,3-di)substituted benzothiophenes employing the thermal reaction of diphenyl disulfide with alkynes promoted by di-*tert*-butyl peroxide.[2]

Here we report our results for a study of the free-radical additions of a number of alkanethiols, including the benzyl mercaptans **1**, X = H, OMe, CN, as well as phenethyl and allyl mercaptan, to phenylacetylene (**2a**), hex-1-yne (**2b**), and *tert*-butylacetylene (**2c**). The primary aim of this study was to explore the chemical reactivity of corresponding 2-mercapto-substituted vinyl radical intermediates, which were of interest to us since in principle they might exhibit, besides hydrogen abstraction reaction from the mercaptan present, further attractive decomposition modes such as, *inter alia*, intramolecular 1,5- and/or 1,6-cyclizations to the phenyl or vinyl moiety of the 2-mercapto sustituent.

Results and Discussion

Reaction of benzyl mercaptan **1**, X = H (0.1 M), with 2.5 molar equiv of the alkynes **2a–c** in benzene at 90 °C, in the presence of azobisisobutyronitrile (AIBN) (0.1 equiv) (procedure A), was virtually complete within 2 h and led to the formation of isomeric *E*/*Z* mixtures of the benzyl vinyl sulfide adducts **3a–c**, X = H, together with minor amounts (15–23%) of the rearranged methyl vinyl sulfides **4a–c**, X = H, which were configurationally pure (Table 1, entries 1–3). Very slow addition (ca. 3 h) of the thiol **1**, X = H, to the alkyne **2a** in benzene (procedure B) brought about a significant increase in the amount of the rearranged product **4a** (35%) at the expense of the sulfide adduct **3a** (Table 1, entry 1). The occurrence of both the vinyl sulfide products **3a–c**, X = H, and **4a–c**, X = H, is ascribable to the intervention of the thiovinyl radicals **6a–c**, X = H, which were expected to result from addition of initially formed benzylthio radicals to the terminal carbon of the alkynes **2a–c**.[1,2] Hydrogen transfer from the thiol **1**, X = H, would afford the sulfides **3a–c**, X = H, as mixtures of the (*E*)- and (*Z*)-isomers,[1,2] whereas competing rearrangement to the more stable (vinylthio)methyl radicals **7a–c**, X = H, would lead to the isomeric sulfides **4a–c**, X = H, through eventual thiol scavenging (Scheme 1).

The rearranged radicals **7a–c**, X = H, most likely form through cyclization of their precursors **6a–c**, X = H, to the *ipso* position of the aromatic ring of the 2-mercapto substituent, followed by ring opening of the resulting spirocyclohexadienyl radicals **8a–c**, X = H, with preferred cleavage of the CH_2–C bond (Scheme 1). The intervention of related spirocyclohexadienyl radicals in intramolecular aromatic *ipso* substitution by carbon- and nitrogen-centered radicals has previously been invoked in numerous instances,[3] but *to our knowledge no definite examples of ipso* substitutions of carbon-centered radicals have been

† Dedicated to Prof. Antonio Tundo on the occasion of his 70th birthday.

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(1) Benati, L; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2103.

(2) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1992**, 1659.

(3) Crimshaw, J.; Haslett, R. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 657. Togo, H.; Kikuchi, O. *Heterocycles* **1989**, *28*, 373. Benati, L.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Chem. Commun.* **1979**, 141. McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1984**, 371, 377. McNab, H.; Smith, G. S. *J. Chem. Soc., Perkin Trans. 1* **1984**, 381. Hickson, C. H.; McNab, H. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1569. Hey, D. H. *Q. Rev. Chem. Soc.* **1971**, *25*, 483 and references cited therein. Chottard, J. C.; Julia, M. *Tetrahedron* **1972**, *28*, 5615 and references cited therein.

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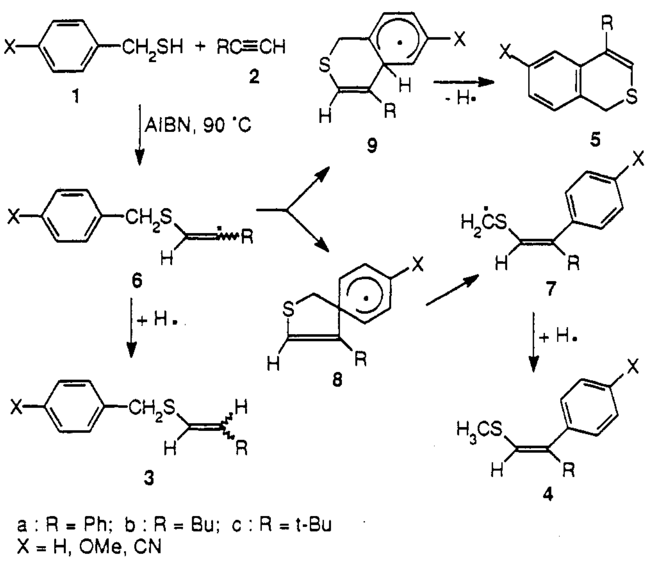
Table 1. Product Yields[a] for Free-Radical Additions of Benzyl Mercaptans 1 to Alkynes 2 at 90 °C[b]

entry	benzyl mercaptan	alkyne	benzyl vinyl sulfide[c]	methyl vinyl sulfide	thiopyran
1	1, X = H	**2a**	**3a** (65) [55]	**4a** (23) [35]	
2	1, X = H	**2b**	**3b** (70)	**4b** (20)	
3	1, X = H	**2c**	**3c** (80)	**4c** (15)	
4	1, X = OMe	**2a**	**3a** (48)	**4a** (35)	**5a** (<2)
5	1, X = OMe	**2b**	**3b** (60) [27]	**4b**(30) [63]	**5b**(2) [4]
6	1, X = OMe	**2c**	**3c** (75)	**4c** (15)	
7	1, X = CN	**2a**	**3a** (25)	**4a** (60)	
8	1, X = CN	**2b**	**3b** (25)	**4b** (65)	
9	1, X = CN	**2c**	**3c** (75)	**4c** (20)	

[a] Yields isolated by column chromatography. [b] Reactions were run in benzene in the presence of 2.5 equiv of alkyne 2 (procedure A). Yields in square brackets refer to reactions carried out according to procedure B (see Experimental Section). [c] Mixture of (*E*)- and (*Z*)-isomers.

Scheme 1



encountered. Very recently, concrete evidence has been provided that similar spirocyclohexadienyl radical intermediates are also produced in intramolecular cyclizations of vinyl radicals, which bear an ArN=C(Ph)– group in the 2-position, to make quinoline derivatives.[4]

The findings obtained from analogous reactions of the 4-substituted benzyl mercaptans 1, X = OMe, CN, with the alkynes **2a–c** were fully consistent with this mechanism.

As can be seen from Table 1 (entries 4–9), similarly to the parent thiol, both 4-substituted derivatives 1, X = OMe, CN, were found to react smoothly with the alkynes **2a–c** to give *E*/*Z* mixtures of the adducts **3a–c**, X = OMe, CN, accompanied by the rearranged compounds **4a–c**, X = OMe, CN, which were generally formed configurationally pure. However, the 4-methoxy-substituted 1, X = OMe and, especially, the 4-cyano-substituted thiol 1, X = CN, reacted with the alkynes **2a,b** to furnish the rearrangement products **4a,b**, X = OMe, CN, to a proportion considerably higher than that encountered in the corresponding reactions with the parent thiol (Table 1, entries 1, 2, 4, 5, 7, 8). This trend is consistent with resonance stabilization by the OMe and CN substituents to the presumed intermediates **8a,b** which would thence favor intramolecular aromatic attack of their radical precursors **6a,b**.

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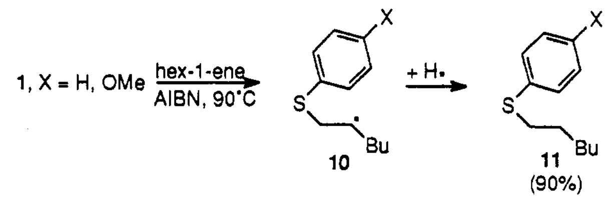
Scheme 2



On the other hand, the radical reactions of the above 4-substituted thiols 1, X = OMe, CN, with *tert*-butylacetylene **2c** essentially led to no parallel increase in the formation of the rearranged products **4c**, X = OMe, CN, which only occurred to a limited extent, analogous to that which was observed in the corresponding reaction of the thiol 1, X = H (Table 1, entries 3, 6, 9). It is possible that rearrangement of the 1-*tert*-butyl-substituted radicals **6b**, X = H, OMe, CN, was generally discouraged by steric hindrance caused by the bulky 1-*tert*-butyl substituent.

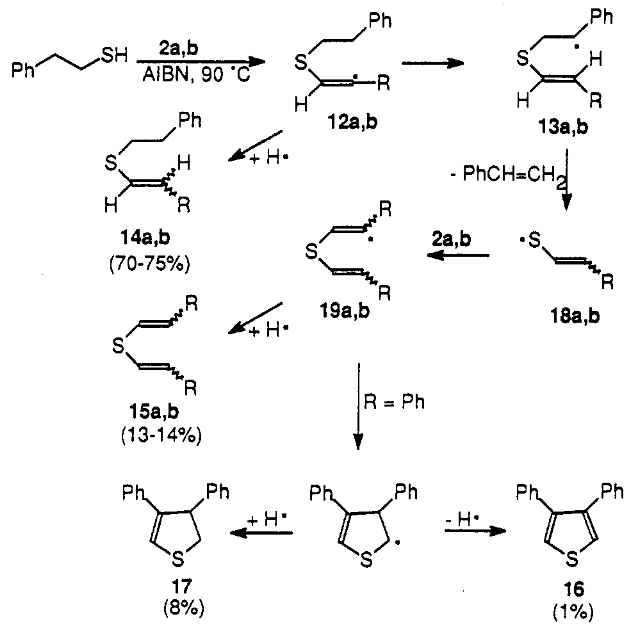
As mentioned above, the rearranged vinyl sulfides **4a–c** were generally shown to form in a single configuration, which was assumed to be *Z* on the basis of the presumed mechanism.

Our findings are noteworthy since they appear to reveal that 2-(benzylthio)-substituted vinyl radicals **6**, irrespective of the nature of the 1-substituent, generally exhibit a marked tendency to suffer 5-membered rather than 6-membered ring cyclization to the aromatic ring of the adjacent mercapto substituent. In fact, no evidence for any intramolecular 1,6-cyclization could be obtained in all cases examined, except for the methoxy-substituted radicals **6a,b**, X = OMe, which possibly also led to the corresponding benzothiopyrans **5a,b**, X = OMe. However, these products occurred to a very slight extent (Table 1, entries 4 and 5, and Scheme 1) and could not be fully characterized.

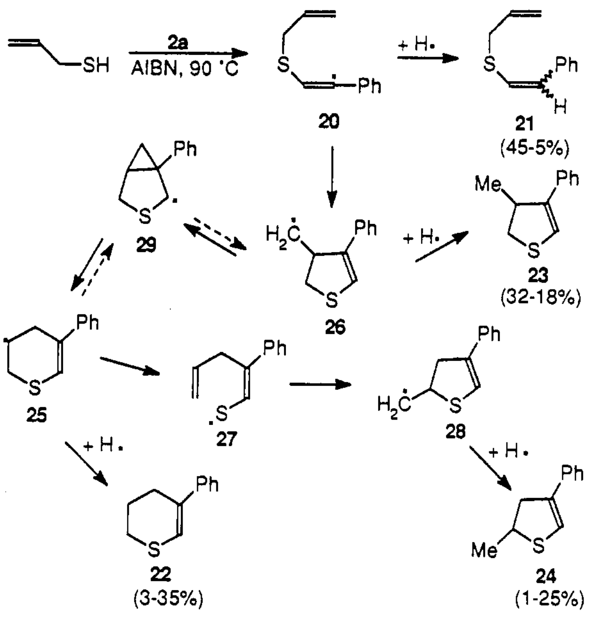
Nevertheless, the possibility that the radicals **6** might be capable of undergoing competing cyclization in a 6-endo, but reversible, fashion cannot be excluded *a priori*. Indeed, rearomatization of the possible cyclohexadienyl intermediates **9** might be discouraged under our reductive conditions. This possibility was not substantiated by our reaction of 4-methoxytoluenethiol 1, X = OMe, with hex-1-yne **2b**, when repeated at very low thiol concentration (procedure B). In this case, the yield of the methyl sulfide **4b**, X = OMe, strongly increased, as expected, at the expense of the adduct **3b**, X = OMe, but the concomitant increase in the yield of the thiopyran **5b**, X = OMe, was not significant (Table 1, entry 5). The apparent preference of the β-thiovinyl radicals **6** for intramolecular addition to the adjacent aromatic ring in a 5-exo fashion would parallel that normally exhibited by alkenyl-substituted vinyl radicals in related cyclizations to alkenes (*vide infra*), but to date no precedent is available in corresponding vinyl radical cyclizations to arenes.

In this work, we also briefly investigated the related 2-(benzylthio)-substituted alkyl radicals **10** in order to ascertain whether these intermediates might exhibit analogous cyclization processes. However, the free-radical addition of toluenethiol 1, X = H, and its 4-methoxy-substituted derivative 1, X = OMe, to hex-1-ene, carried out with different thiol concentrations (procedures A and B), exclusively led to the adducts 11, X = H, OMe. Apparently, under our reaction conditions the only route opened to the radicals **10**, X = H, OMe, would be hydrogen transfer from the thiol scavenger (Scheme 2).

Scheme 3



Scheme 4



Under our usual conditions phenethyl mercaptan was treated with phenylacetylene (**2a**) and hex-1-yne (**2b**) to give *E*/*Z* mixtures of the corresponding adducts **14a,b** which were accompanied by minor amounts of the sulfides **15a,b** and, in the case of the alkyne **2a**, the thiophene derivatives **16** and **17** (Scheme 3). In these cases the resulting thiovinyl radicals **12a,b**, besides undergoing hydrogen transfer from the mercaptan, cleanly suffered intramolecular 1,5-hydrogen atom transfer to give the corresponding benzyl radicals **13a,b** rather than possible 6-exo cyclization to the adjacent phenyl ring which, in principle, might have led to displacement of a more stable β-thioethyl radical. The observed bis-vinyl sulfides **15a,b**, as well as thiophenes **16** and **17**, can be envisaged to arise from initially-formed benzyl radicals **13a,b** through the following reaction pathways: β-elimination to afford styrene (which was detected by GC–MS analysis, but not isolated) and the corresponding vinylthio radical **18a,b**, which would furnish the vinyl radical **19a,b** by subsequent addition to the alkyne **2a,b**. Eventual hydrogen abstraction reaction of **19a,b** would lead to the bis-vinyl sulfide **15a,b**, whereas competing 5-endo cyclization of the radical **19a** would result in the formation of both thiophene derivatives **16** and **17** (Scheme 3). These findings provide two unprecedented examples of vinylthio radical additions to alkynes, which are certainly worthy of further attention.

The reaction of allyl mercaptan (0.1 M) with phenylacetylene (**2a**), performed under standard conditions, furnished a rather complex mixture. Column chromatography separated the thiopyran **22** and an inseparable mixture of the isomeric thiophenes **23** and **24** in a 50:38:12 ratio, respectively, and in 65% overall yield, besides a small amount (5%) of an isomeric *E*/*Z* mixture of the allyl vinyl sulfide **21** (Scheme 4).

The product distribution pattern indicated that, for the intermediate 2-(allylthio)vinyl radical **20**, cyclization on the adjacent double bond was largely favored over the hydrogen abstraction reaction leading to the adducts **21**. In fact, the thiophene **23** and the thiopyran **22** were the hydrogen abstraction products of the exo- and endo-cyclic radical intermediates **26** and **25**, respectively, whereas the isomeric thiophene **24** presumably arose from **25** by competing ring opening leading to the thio radical **27**, subsequent 5-exo cyclization of the latter to give the radical **28**, and eventual hydrogen abstraction reaction of **28** (Scheme 4).

In principle, the cyclized radicals **26** and **25** might result from the β-thiovinyl radical **20** through competing 5-exo and 6-endo cyclizations. Alternatively, cyclization of the radical **20** might initially lead to the radical **26**, which might then rapidly rearrange to the more stable ring-expanded radical **25** through the strained intermediate **29** (Scheme 4). Such ring expansions are well precedented for simple multiply bonded alkyl radicals.[5-7] This latter possibility was supported by our observation that the ratio of **23** to **22** and **24** gradually increased with increasing thiol concentration, thereby indicating that 5-exo cyclization was kinetically preferred. The proportion of the thiophene **23** was in fact significantly diminished in favor of **22** and **24** when the alkyne **2a** was treated very slowly (over 3 h) with the thiol reactant (the observed **22**:**23**:**24** ratio was 40:20:40). On the other hand, the ratio of **23** to **22** and **24** was strongly enhanced when the alkyne **2a** was treated in the presence of a much higher thiol concentration (ca. 2 M) (the resulting **22**:**23**:**24** ratio in such case was 9:87:4, respectively).

On this basis, the cyclization of the (allylthio)vinyl radical **20** would be consistent with our present evidence obtained with 2-(benzylthio)vinyl radicals **6** as well as with several recent observations that vinyl radicals undergo ring closure to alkenes exclusively or predominantly in the exo mode.[6,7b-d,8]

(5) Jasperse, C. P.; Curran, D. P.; Fevig, T. L. *Chem. Rev.* **1991**, *91*, 1287.
(6) Stork, G.; Mook, R., Jr. *Tetrahedron Lett.* **1986**, *27*, 4529. Stork, G.; Mook, R., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2829.
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(8) For related aryl radical cyclizations forming five-membered rings, see: Inanaga, J.; Ujikawa, O.; Yamaguchi, M. *Tetrahedron Lett.* **1991**, *32*, 1737. Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050. Beckwith, A. L. J.; Shankaran, K.; Sloan, C. P.; Snieckus, V. *Tetrahedron Lett.* **1985**, *26*, 6001.

In conclusion, our present work has enlarged our knowledge of the chemistry of β-thiovinyl radicals by showing that (i) 2-(benzylthio)vinyl radicals **6** can easily rearrange to thiomethyl radicals **7** through a novel 1,4-migration of phenyl group from thiomethyl to vinyl carbon, probably as a result of their marked tendency to effect 5-exo cyclization to the phenyl ring of their 2-mercapto substituent; (ii) 2-(phenethylthio)vinyl radicals **12** readily undergo internal 1,5-hydrogen transfer to form corresponding β-thio-substituted benzyl radicals **13**, which are in turn efficient precursors of vinylthio radicals; and (iii) the 2-(allylthio)vinyl radical **20** would undergo kinetically preferred 5-exo cyclization, but the primary product **26** would suffer ring expansion to give the more stable cyclized product **25**.

Experimental Section

Structural assignment of reaction products was generally made on the basis of ^{1}H NMR and MS spectral data, in addition to elemental analysis. Compounds **21**, **23**, and **24** were obtained as inseparable mixtures; their identification arose from careful GC–MS and ^{1}H NMR spectral analysis of mixtures containing these products in variable amounts.

^{1}H NMR spectra were recorded on a Varian Gemini 200 (200-MHz) instrument and are for $CDCl_3$ solutions with Me_4Si as internal standard. Mass spectra were determined by the electron impact method on a VG 7070 instrument. GC–MS analyses were performed on a C. Erba QMD 1000 instrument. Column chromatography was carried out on Merck silica gel (0.040–0.063 particle size) by gradual elution with light petroleum (bp 40–70 °C)/diethyl ether.

Materials. The unknown 4-cyanobenzyl mercaptan (**1**, X = CN) was obtained in 80% yield from 4-cyanobenzyl bromide and thiourea, according to a known procedure: [mp 35–36 °C; ^{1}H NMR δ 1.30 (1H, t, J = 8 Hz), 3.80 (2H, d, J = 8 Hz), 6.70 (A part of an AB system, J = 9 Hz) 6.9 (B part of an AB system, J = 9Hz); MS m/e (rel inten) 149 (M^+, 10), 147 (70), 146 (100), 130 (40), 116 (55), 103 (30), 102 (30). All the other starting materials were commercially available and were used as received, except AIBN, which was recrystallized from $CHCl_3$.

Reactions of Alkanethiols with Alkynes 2a–c and Hex-1-ene. Procedure A. A solution of the benzyl mercaptan **1**, X = H, OMe, CN, phenethyl mercaptan, or allyl mercaptan (2 mmol), alkyne **2a–c** (or hex-1-ene) (5 mmol), and AIBN (0.2 mmol) in benzene (20 mL) was heated in a sealed tube at 90 °C for 2 h. After this time the reaction mixture was directly analyzed by GC–MS and/or chromatographed. All the reactions, except those carried out with hex-1-ene and with 4-cyanobenzyl mercaptan (**1**, X = CN), led to complete consumption of the starting thiol.

Results described below refer to reactions performed by this procedure, unless otherwise stated. Product yields for reactions of benzyl mercaptans **1** with alkynes **2** are reported in Table 1.

Procedure B. A solution of the appropriate thiol (2 mmol) and AIBN (1 mmol) in benzene (10 mL) was added during 3 h to a boiling solution of the appropriate alkyne **2** (or hex-1-ene) (5 mmol) and AIBN (0.2 mmol) in benzene (20 mL). The resulting solution was refluxed for further 30–40 min and then analyzed by GC–MS and/or chromatographed.

Reaction of Benzyl Mercaptan (1, X = H) with Phenylacetylene (2a). Chromatography gave an inseparable mixture of (*E*)- and (*Z*)-2-(benzylthio)-1-phenylethylene [(*E*)[9] - and (*Z*)-**3a**, X = H] in 40:60 ratio, as determined by ^{1}H NMR [^{1}H NMR $\delta_{(Z)\text{-isomer}}$ 4.08 (2H, s), 6.38 (1H, A part of an AB system, J = 10.5 Hz), 6.57 (1H, B part of an AB system, J = 10.5 Hz), 7.3–7.7 (10H, m); MS m/e (rel inten) 226 (M^+, 40), 135 (30), 134 (25), 91 (100). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17. Found: C, 80.0; H, 6.30; S, 14.0] and 1,1-diphenyl-2-(methylthio)-ethylene (**4a**, X = H) as an oil [^{1}H NMR δ 2.45 (3H, s), 6.70 (1H, s), 7.3–7.7 (10H, m); MS m/e (rel inten) 226 (M^+, 100), 211 (50), 178 (60), 165 (15). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.24; S, 14.16. Found: C, 80.1; H, 6.30; S, 14.0]; this compound **4a**, X = H, gave 1,1-diphenylethane as the exclusive product upon treatment with Ni-Raney in boiling ethanol (GC–MS analysis).

The reaction, repeated according to procedure B, led to a mixture of the sulfides (*Z*)- and (*E*)-**3a**, X = H, and **4a**, X = H, in 35:25:40 ratio, as shown by ^{1}H NMR spectroscopy. Flash chromatography gave these products as an unresolved mixture in 90% overall yield.

Reaction of Benzyl Mercaptan (1, X = H) with Hex-1-yne (2b). Chromatography gave 1-(methylthio)-2-phenylhex-1-ene (**4b**, X = H) as an oil [^{1}H NMR δ 0.85 (3H, t), 1.2–1.4 (4H, m), 2.22 (3H, s), 2.45 (2H, br t, J = 7.5 Hz), 5.95 (1H, br s), 7.2–7.4 (5H, m); MS m/e (rel inten) 206 (M^+, 80), 163 (50), 135 (20), 129 (35), 117 (25), 115 (100), 91 (35). Anal. Calcd for $C_{13}H_{18}S$: C,-75.67; H, 8.79; S, 15.54. Found: C, 76.0; H, 8.85; S, 15.4] and an inseparable 1:1 mixture of (*E*)- and (*Z*)-1-(benzylthio)hex-1-ene [(*E*)- and (*Z*)-**3b**, X = H]: ^{1}H NMR δ 0.9 (6H, m), 1.2–1.4 (8H, m), 2.0–2.2 (4H, m), 3.88 (2H, s), 3.90 (2H, s) 5.59 (1H, A part of an ABX_2 system, J_{AB} = 9.5 Hz, J_{AX} = 7.2 Hz), 5.73 (1H, A' part of an $A'B'X'_2$ system, $J_{A'B'}$ = 15 Hz, $J_{A'X'}$ = 6.8 Hz), 5.9–6.0 (2H, m), 7.2–7.4 (10H, m); MS m/e (rel inten) 206 (M^+, 15), 91 (100). Anal. Calcd for $C_{13}H_{18}S$: C,75.67; H, 8.79; S, 15.54. Found: C,75.95; H, 8.85; S, 15.45.

Reaction of Benzyl Mercaptan (1, X = H) and 3,3-Dimethylbut-1-yne (2c). Chromatography gave a 75:25 mixture of (*E*)- and (*Z*)-1-(benzylthio)-3,3-dimethylbut-1-ene [(*E*)- and (*Z*)-**3c**, X = H] [^{1}H NMR $\delta_{(E)\text{-isomer}}$ 0.97 (9H, s), 3.85 (2H, s), 5.72 (1H, A part of an AB system, J = 15.5 Hz), 5.85 (1H, B part of an AB system, J = 15.5 Hz), 7.25–7.35 (5H, m); $\delta_{(Z)\text{-isomer}}$ 1.12 (9H, s), 3.85 (2H, s), 5.45 (1H, A part of an AB system, J = 10.5 Hz), 5.76 (1H, B part of an AB system, J = 10.5 Hz), 7.25–7.35 (5H, m); MS m/e (rel inten) 206 (M^+, 80), 191 (80), 115 (40), 91 (100), 65 (50). Anal. Calcd for $C_{13}H_{18}S$: C,75.67; H, 8.79; S, 15.54. Found: C, 75.95; H, 8.90; S, 15.45] and 3,3-dimethyl-1-(methylthio)-2-phenylbut-1-ene (**4c**, X = H) as an oil: ^{1}H NMR δ 1.13 (9H, s), 2.18 (3H, s), 6.33 (1H, s), 7.0–7.4 (5H, m); MS m/e (rel inten) 206 (M^+, 50), 191 (100), 143 (40), 128 (50). Anal. Calcd for $C_{13}H_{18}S$: C,75.67; H, 8.79; S, 15.54. Found: C, 76.0; H, 8.90; S, 15.45.

Reaction of 4-Methoxybenzyl Mercaptan (1, X = OMe) with Phenylacetylene (2a). Chromatography separated a fraction (25 mg, 5%) containing a mixture of (*E*)- and (*Z*)-**3a**, X = OMe, as determined by ^{1}H NMR. GC–MS analysis of this fraction detected the presence of a product which possibly was the thiopyran **5a**, X = OMe: MS m/e (rel inten) 254 (M^+, 90), 253 (100), 221 (20). Further elution gave an inseparable 1:2 mixture of (*E*)- and (*Z*)-1-[(4-methoxybenzyl)thio]-2-phenylethylene [(*E*)-and (*Z*)-**3a**, X = OMe] (220 mg, 43%): ^{1}H NMR $\delta_{(E)\text{-isomer}}$ 3.78 (3H, s), 3.98 (2H, s), 6.55 (1H, A part of an AB system, J = 16 Hz), 6.75 (1H, B part of an AB system, J = 16 Hz), 6.8–7.4 (9H, m); $\delta_{(Z)\text{-isomer}}$ 3.78 (3H, s), 3.95 (2H, s), 6.25 (1H, A part of an AB system, J = 11 Hz), 6.45 (1H, B part of an AB system, J = 11 Hz), 6.8–7.4 (9H, m); MS m/e (rel inten) 256 (M^+, 15), 121 (100), 91 (10). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.95; H,6.30; O, 6.25; S,12.50. Found: C, 75.10; H, 6.35; S, 12.4] and 1-(4-methoxybenzyl)-2-(methylthio)-1-phenylethylene **4a**, X = OMe, as an oil: ^{1}H NMR δ 2.30 (3H, s), 3.82 (3H, s), 6.46 (1H, s), 6.8–7.4 9H, m); MS m/e (rel inten) 256 (M^+, 100), 241 (50), 226 (65), 210 (30), 197 (25), 165 (50). Anal. Calcd for $C_{16}H_{16}OS$: C, 74.95; H, 6.30; O, 6.25; S, 12.50. Found: C, 75.15; H, 6.35; S, 12.4.

Reaction of 4-Methoxybenzyl Mercaptan (1, X = OMe) with Hex-1-yne (2b). Chromatography gave 2-(4-methoxyphenyl)-1-(methylthio)hex-1-ene (**4b**, X = OMe) as an oil [^{1}H NMR δ 0.9 (3H, t), 1.2–1.5 (4H, m), 2.25 (3H, s), 2.45 (2H, br t, J = 7.0 Hz), 3.82 (3H, s), 5.88 (1H, br s), 6.85 (2H, d, J = 9 Hz), 7.25 (2H, d, J = 9 Hz); MS m/e (rel inten) 236 (M^+, 100), 193 (30), 160 (30), 148 (75), 145 (45), 121 (40). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; O, 6.77; S, 13.56. Found: C, 71,40; H, 8.60; S, 13.45], a fraction (60 mg, 12%) containing **4b**, X = OMe, a 1:1 mixture of (*E*)- and (*Z*)-**3b**, X = O Me, and a product which probably was the thiopyran **5b**, X = OMe, in a 5:5:2 ratio: **5b**: ^{1}H NMR δ 2.55 (t, J = 7.5 Hz, $C{=}CCH_2$), 3.68 (s, $ArCH_2S$), 6.27 (s, $C{=}CH$); GC–MS m/e (rel inten) 234 (M^+, 100), 233 (90), 191 (90), 158 (40)], and an inseparable 1:1 mixture of (*E*)- and (*Z*)-**3b**, (X =

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OMe): ^{1}H NMR = 0.9 (6H, m), 1.2–1.4 (8H, m), 2.0–2.2 (4H, m), 3.80 (10H, s), 5.55 (1H, A part of an ABX_2 system, J_{AB} = 9 Hz, J_{AX} = 6.7 Hz), 5.66 (1H, A′ part of an $A'B'X'_2$ system, $J_{A'B'}$ = 15 Hz, $J_{A'X'}$ = 6.7 Hz), 5.85–5.96 (2H, m), 6.85 (2H, d, J = 9 Hz), 7.25 (2H, d, J = 9 Hz); MS m/e (rel inten) 236 (M^+, 70), 122 (50), 121 (100), 91 (35), 78 (60), 77 (60). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; O, 6.77; S, 13.56. Found: C, 71.35; H, 8.50; S, 13.50.

The reaction, repeated according to Procedure B, led to a mixture of the sulfides (Z)- and (E)-**3b**, X = OMe, and **4b**, X = OMe, in a 30:70 ratio, besides the thiopyran **5b**, X = OMe, (ca. 3–4%), as shown by ^{1}H NMR spectroscopy. Flash chromatography gave these products in an 90% overall yield.

Reaction of 4-Methoxybenzyl Mercaptan (1, X = OMe) with 3,3-Dimethylbut-1-yne (2c). Chromatography gave 3,3-dimethyl-2-(4-methoxyphenyl)-1-(methylthio)but-1-ene (**4c**, X = OMe) as an oil [^{1}H NMR δ 1.12 (9H, s), 2.23 (3H, s), 3.80 (3H, s), 6.0 (1H, s), 6.9 (2H, d, J = 9 Hz), 7.30 (2H, d, J = 9 Hz); MS m/e (rel inten) 236 (M^+, 85), 221 (100), 189 (35), 173 (50), 158 (35). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; O, 6.77; S, 13.56. Found: C, 71.0; H, 8.45; S, 13.65] and an inseparable 80:20 mixture of (E)- and (Z)-3,3-dimethyl-1-[(4-methoxybenzyl)-thio]but-1-ene [(E)- and (Z)-**3c**, H = OMe]: ^{1}H NMR $\delta_{(E)\text{-isomer}}$ 1.02 (9H, s), 3.80 (5H, s), 5.73 (1H, A part of an AB system, J = 16 Hz), 5.88 (1H, B part of an AB system, J = 16 Hz), 6.9 (2H, d, J = 9 Hz), 7.30 (2H, d, J = 9 Hz); $\delta_{(Z)\text{-isomer}}$ 1.17 (9H, s), 3.80 (5H, s), 5.45 (1H, A part of an AB system, J = 11 Hz), 5.78 (1H, B part of an AB system, J = 11 Hz), 6.9 (2H, d, J = 9 Hz), 7.3 (2H, d, J = 9 Hz); MS m/e (rel inten) 236 (M^+, 80), 122 (55), 121 (100), 91 (40), 78 (60), 77 (100). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; O, 6.77; S, 13.56. Found: C, 71.25; H, 8.60; S, 13.50.

Reaction of 4-Cyanobenzyl Mercaptan (1, X = CN) with Phenylacetylene (2a). Chromatography gave an inseparable 65:35 mixture of (Z)- and (E)-1-[(4-cyanobenzyl)thio]-2-phenylethylene [(Z)- and (E)-**3a**, X = CN] [^{1}H NMR $\delta_{(Z)\text{-isomer}}$ 4.0 (2H, s), 6.17 (1H, A part of an AB system, J = 11 Hz), 6.85 (1H, B part of an AB system, J = 11 Hz), 7.2–7.9 (9H, m); $\delta_{(E)\text{-isomer}}$ 4.0 (2H, s), 6.60 (2H, br s), 7.2–7.9 (9H, m); MS m/e (rel inten) 251 (M^+, 35), 135 (100), 134 (30), 117 (35), 116 (40), 91 (65). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.75. Found: C, 76.60; H, 5.25; N, 5.50; S, 12.70], 1-(4-cyanophenyl)-1-phenyl-2-(methylthio)ethylene (**4a**, X = CN): [mp 122–124 °C; ^{1}H NMR δ 2.37 (3H, s), 6.7 (1H, s), 7.1–7.8 (9H, m); MS m/e (rel inten) 251 (M^+, 100), 236 (100), 203 (20). Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.75. Found: C, 76.70; H, 5.15; N, 5.60; S, 12.70], and unreacted **1**, X = CN (30%).

Reaction of 4-Cyanobenzyl Mercaptan (1, X = CN) with Hex-1-yne (2b). Chromatography gave 2-(4-cyanophenyl)-1-(methylthio)hex-1-ene (**4b**, X = CN) as an oil [^{1}H NMR δ 0.9 (3H), 1.2–1.4 (4H, m), 2.27 (3H, s), 2.4–2.5 (2H, m), 6.10 (1H, br s), 7.40 (2H, d, J = 9 Hz), 7.65 (2H, d, J = 9 Hz); MS m/e (rel inten) 231 (M^+, 100), 188 (100), 154 (35), 140 (90). Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05; S, 13.86. Found: C, 72.95; H, 7.45; N, 6.0; S, 13.75], an inseparable 1:1 mixture of (E)- and (Z)-1-[(4-cyanobenzyl)thio]hex-1-ene [(E)- and (Z)-**3b**, X = CN) as an oil [^{1}H NMR δ 0.9 (6H, m), 1.2–1.4 (8H, m), 2.0–2.2 (4H, m) 3.87 (2H, s), 3.89 (2H, s), 5.55–5.90 (4H, m, collapsing to signals at δ 5.65 (1H, A part of an AB system, J = 9 Hz), 5.69 (1H, A′ part of an A′B′ system, J = 15 Hz), 5.83 (1H, B part of an AB system, J = 9 Hz), 5.84 (B′ part of an A′B′ system, J = 15 Hz) upon irradiation at δ 2.1), 7.40 (2H, d, J = 9 Hz), 7.65 (2H, d, J = 9 Hz); MS m/e (rel inten) 231 (M^+, 15), 188 (10), 130 (15), 116 (100). Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05; S, 13.86. Found: C, 72.85; H, 7.50; N, 6.0; S, 13.80], and unreacted **1**, X = CN (35%).

Reaction of 4-Cyanobenzyl Mercaptan (1, X = CN) with 3,3-Dimethylbut-1-yne (2c). Chromatography gave an inseparable 65:35 mixture of (E)- and (Z)-1-[(4-cyanobenzyl)thio]-3,3-dimethylbut-1-ene [(E)- and (Z)-**3c**, X = CN] [^{1}H NMR $\delta_{(E)\text{-isomer}}$ 0.98 (9H, s), 3.88 (2H, s), 5.77 (1H, A part of an AB system, J = 14 Hz), 5.80 (1H, B part of an AB system, J = 14 Hz), 7.45 (2H, d, J = 9 Hz), 7.65 (2H, d, J = 9 Hz); $\delta_{(Z)\text{-isomer}}$ 1.13 (9H, s), 3.88 (2H, s), 5.52 (1H, A part of an AB system, J = 11 Hz), 5.68 (1H, B part of an AB system, J = 11 Hz), 7.45 (2H, d J = 9 Hz), 7.65 (2H, d, J = 9 Hz); MS m/e (rel inten) 231 (M+, 39), 216 (60), 116 (100), 115 (40). Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05; S, 13.86. Found: C, 72.90; H, 7.45; N, 7.0; S, 13.75], 2-(4-cyanophenyl)-3,3-dimethyl-1-(methylthio)but-1-ene (**4c**, X = CN) as an oil [^{1}H NMR δ 1.10 (9H, s), 2.23 (3H, s), 6.08 (1H, s), 7.20 (2H, d, J = 9 Hz), 7.65 (2H, d, J = 9 Hz); MS m/e (rel inten) 231 (M^+, 45), 216 (100), 168 (30), 153 (25), 142 (30). Anal. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05; S, 13.86. Found: C, 73.05; H, 7.50; N, 6.0; S, 13.75], and unreacted **1**, X = CN (35%).

Reaction of Phenethyl Mercaptan with Phenylacetylene (2a). Chromatography gave 3,4-diphenylthiophene (**16**)[10] (5 mg, 1%), 2,3-dihydro-3,4-diphenylthiophene (**17**)[11] (40 mg, 8%), (E,E)-bis(β-styryl) sulfide [(E,E)-**15a**], contaminated with little amounts of its (E,Z)-isomer, (10 mg, 2%) [^{1}H NMR δ 6.71 (2H, A part of an AB system, J = 15.5 Hz), 6.87 (2H, B part of an AB system, J = 15.5 Hz), 7.2–7.6 (10H, m); GC–MS m/e (rel inten) 238 (M^+, 100), 237 (30), 205 (35), 134 (25), 128 (35), 121 (70), 120 (45), 115 (70), 91 (50), 77 (50)], (E,Z)-bis(β-styryl) sulfide [(E,Z)-**15a**], contaminated with little amounts of its (E,E)-isomer (55 mg, 12%) [^{1}H NMR δ 6.49 (1H, A part of an AB system, J = 11Hz), 6.62 (1H, B part of an AB system, J = 11 Hz), 6.68 (1H, A′ part of an A′B′ system, J = 15.5 Hz), 6.84 (1H, B′ part of an A′B′ system, J = 15.5 Hz), 7.2–7.6 (10 H, m); MS m/e (rel inten) 238 (M^+, 100), 237 (25), 205 (40), 134 (35), 128 (45), 121 (85), 116 (60), 115 (90), 91 (70), 77 (70)], and a 1:2 inseparable mixture of (E)- and (Z)-1-(phenethylthio)-2-phenylethylene [(E)- and (Z)-**14a**] (330 mg, 70%): ^{1}H NMR δ 3.0–3.1 (6H, m), 6.30 (1H, A part of an AB system, J = 10.5 Hz), 6.52 (1H, B part of an AB system, J = 10.5 Hz), 6.54 (0.5 H, A′ part of an A′B′ system, J = 15.5 Hz), 6.75 (0.75H, B′ part of an A′B′ system, J = 15.5 Hz), 7.2–7.6 (15H, m); MS, m/e (rel inten) 240 (M^+, 100), 149 (70), 115 (65), 105 (100), 91 (40), 77 (40). Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71; S, 13.34. Found: C, 80.3; H, 6.75; S, 13.2.

Reaction of Phenethyl Mercaptan with Hex-1-yne (2b). Chromatography gave a ca. 1:2 inseparable mixture of (E,E)- and (E,Z)-bis(hex-1-en-1-yl) sulfide [(E,E)-and (E,Z)-**15b**] (50 mg, 13%) [^{1}H NMR δ 0.85–0.95 (9H, m), 1.2–1.5 (12H, m), 2.0–2.2 (6H, m), 5.5–5.8 (3H, m, collapsing to three doublets at δ 5.70 (1H, d, J = 10 Hz), 5.68 (1H, d, J = 15 Hz), 5.71 (1H, d, J = 15 Hz) upon irradiation at δ 2.1), 5.93 (1H, d, J = 15 Hz), 5.97 (1H, d, J = 15 Hz), 5.99 (1H, d, J = 10 Hz); GC–MS m/e (rel inten) 198 (M^+, 70), 155 (30), 141 (25), 113 (25), 99 (45), 85 (100), 83 (50), 73 (40), 67 (40), 65 (35), 55 (60). Anal. Calcd for $C_{12}H_{22}S$: C, 72.66; H, 11.18; S, 16.16. Found: C, 73.0; H, 11.25; S, 16.0] and an 1:1 inseparable mixture of (E)- and (Z)-1-(phenethylthio)-hex-1-ene [(E)- and (Z)-**14b**] (330 mg, 75%): ^{1}H NMR δ 0.9 (6H, m), 1.2–1.4 (8H, m), 2.0–2.2 (4H, m), 2.88 (8H, s), 5.58 (1H, A part of an ABX_2 system, J_{AB} = 9.5 Hz, J_{AX} = 7 Hz, collapsing to a doublet, J = 9.5 Hz upon irradiation at δ 2.1), 5.66 (1H, A′ part of an $A'B'X'_2$ system, $J_{A'B'}$ = 15.5 Hz, $J_{A'X'}$ = 7 Hz, collapsing to a doublet, J = 15.5 Hz upon irradiation at δ 2.1), 5.95–5.96 (2H, m, collapsing to the B part of an AB system, J = 9.5 Hz, and the B′ part of an A′B′ system, J = 15.5 Hz, upon irradiation at δ 2.1), 7.15–7.35 (10H, m); MS m/e (rel inten) 220 (M^+, 20), 143 (20), 105 (100), 104 (80). Anal. Calcd for $C_{14}H_{20}S$: C, 76.30; H, 9.15; S, 14.55. Found: C, 76.65; H, 9.20; S, 14.45.

Reaction of Allyl Mercaptan with Phenylacetylene (2a). Chromatography gave a fraction containing 2,3-dihydro-5-phenyl-4H-thiopyran (**22**), 2,3-dihydro-3-methyl-4-phenylthiophene (**23**),[12] 2,3-dihydro-2-methyl-4-phenylthiophene (**24**), and a 70:30 mixture of (Z)- and (E)-1-(allylthio)-2-phenylethylene (**21**) (265 mg, 75% overall yield) in 50:35:10:10 ratio, as determined by ^{1}H NMR. Repeated column chromatography isolated pure thiopyran **22** as an oil: ^{1}H NMR δ 2.15 (2H, m), 2.55 (2H, m, collapsing to br s upon irradiation at δ 2.15), 2.90 (2H, m, collapsing to a singlet upon irradiation at δ 2.15), 6.40 (1H, br s), 7.1–7.4 (5H, m); MS m/e (rel inten) 176 (M^+, 100), 147 (90), 129 (50), 128 (20), 115 (30). Anal. Calcd for $C_{11}H_{12}S$: C, 74.95, H, 6.86, S, 18.19. Found: C, 75.4; H, 6.90; S, 18.0. The reaction was repeated according to procedure B. Flash chromatography gave a fraction containing products **22**, **23**, **24**, and **21** (250 mg, 70% overall yield)

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in 35:25:35:5 ratio, as determined by ^{1}H NMR analysis. The reaction was further repeated in neat alkyne **2a** (0.63 mL) as solvent (ca. 3.2 M). Flash chromatography gave the products **22**, **23**, **24**, and **21** (280 mg, 80% overall yield) in 3.5:40:1.5:55 ratio, as determined by ^{1}H NMR analysis. **24**: ^{1}H NMR δ 1.45 (3H, d, J = 7 Hz), 2.8 (1H, ddd, J_1 = 15 Hz, J_2 = 5.2 Hz, J_3 = 1.5 Hz), 3.30 (1H, ddd, J_1 = 15 Hz, J_2 = 8.5 Hz, J_3 = 1.5 Hz), 3.95 (1H, m), 6.55 (1H, t, J = 1.5 Hz), 7.1–7.5 (5H, m); GC–MS *m/e* (rel inten) 176 (M$^+$, 100), 161 (100), 128 (50). **21**: ^{1}H NMR $\delta_{(Z)\text{-isomer}}$ 3.40 (2H, dt, J_d = 5.3 Hz, J_t = 1 Hz), 5.16 (1H, br d, J = 10 Hz), 5.24 (1H, br d, J = 14 Hz), 5.8–6.0 (1H, m), 6.20 (1H, A part of an AB system, J = 11 Hz), 6.43 (1H, B part of an AB system, J = 11 Hz), 7.1–7.5 (5H, m); $\delta_{(E)\text{-isomer}}$ 3.45 (2H, d, J = 7 Hz), 5.16 (1H, br d, J = 10 Hz), 5.24 (1H, br d, J = 18 Hz), 6.54 (1H, A part of an AB system, J = 15 Hz), 6.68 (1H, B part of an AB system, J = 15 Hz), 7.1–7.5 (5H, m); GC–MS *m/e* (rel inten) 176 (M$^+$, 50), 135 (100), 134 (40), 91 (90).

results were obtained by performing the reaction according to procedure B (GC–MS analysis).

Reaction of 4-Methoxybenzyl Mercaptan (1, X = OMe) with Hex-1-ene. Chromatography gave 1-[(4-methoxybenzyl)-thio]hexane (**11**, X = OMe) (260 mg, 90%) as an oil [^{1}H NMR δ 0.90 (3H, t, J = 7 Hz), 1.2–1.7 (8H, m), 2.40 (2H, t, J = 7 Hz), 3.65 (2H, s), 3.80 (3H, s), 6.85 (2H, d, J = 9 Hz), 7.75 (2H, d, J = 9 Hz); MS *m/e* (rel inten) 238 (M$^+$, 10), 121 (100). Anal. Calcd for $C_{14}H_{22}OS$: C, 70.54; H, 9.30; O, 6.71; S, 13,45. Found: C, 70.95; H, 9.35; S, 13.35] and unreacted **1**, X = OMe (ca. 40%). The same results were obtained by performing the reaction according to procedure B (GC–MS analysis).

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