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Stereo-recognizing transformation of (*E*)-alkenyl halides into sulfides catalyzed by nickel(0) triethyl phosphite complex

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Abstract—(*E*)-Alkenyl halides were transformed into (*E*)-alkenyl sulfides by the nickel(0) triethyl phosphite complex-catalyzed reaction with thiols, whereas (*Z*)-alkenyl halides gave alkynes under the same reaction conditions. Aryl halides were also transformed into aryl sulfides using the same reagent system.

1. Introduction

Alkenyl sulfides are useful synthetic intermediates and are employed as precursors for acyl anion equivalents,[1] equivalents of enolates,[2] Michael acceptors,[3] components of [2+2] cycloadditions,[4] and synthetic intermediates for certain cyclic compounds.[5] Among various methods for their preparations, the transition metal-catalyzed transformation of alkenyl halides or triflates into alkenyl sulfides has attracted much attention in recent years. A variety of palladium(0) complexes have been found to serve as effective catalysts.[6] Transformation of alkenyl halides into sulfides using a stoichiometric[7] or a catalytic[8] amount of copper(I) complexes has also been reported. Alkenyl sulfides are obtained by the σ-aryl-Ni[PPh_3]$_2$Cl-catalyzed reaction of alkenyl halides with thiols under phase transfer conditions.[6b] Bis(bipyridine)nickel(II) bromide also catalyzes the transformation though rather drastic conditions are indispensable.[9]

In connection with our study on the titanocene(II)-promoted reaction of alkenyl sulfones with unsaturated compounds,[10] we required a practical method for the stereoselective preparation of disubstituted alkenyl sulfides from alkenyl halides. Despite the above extensive studies, a little has been known about the stereochemistry of the transformation.[8] The foregoing reactions catalyzed by transition metals require rather high reaction temperature and long reaction time. The catalysts used in these reactions are either expensive or difficult to be handled in an uncontrolled environment. Then we explored an alternative practical method for the stereoselective transformation of alkenyl halides into sulfides using a less expensive and air-stable catalyst and found that nickel(0) triethyl phosphite complex **1**[11] was extremely effective for the conversion. The nickel catalyst **1** is easily prepared by the treatment of nickel(II) chloride with triethyl phosphite and is stable in air.

2. Results and discussion

The treatment of β-bromostyrene **2a** (*E*/*Z*=85:15–90:10) with benzenethiol **4a** (1.2 equiv) at 120 °C in the presence of **1** (5 mol %) and triethylamine (2 equiv) in DMF produced β-(phenylthio)styrene **3a** in 90% yield (Table 1, entry 1). The decrease in the yield of **3a** was observed when the reaction was carried out at lower temperature (50 °C) (entry 2). The quantitative formation of **3a** was achieved by the reaction using *N*,*N*-diethylaniline (2.0 equiv) as a base at 70 °C (entry 3). The alkenyl sulfide **3a** was obtained in satisfactory yield using 1.5 equiv of *N*,*N*-diethylaniline even at 50 °C (entry 4). On the contrary, the reaction of **2a** with cyclohexanethiol **4b** under the same reaction conditions gave no alkenyl sulfide. To increase the nucleophilicity of the alkanethiol **4b**, sodium hydride was used as a base, and the alkenyl sulfide **3b** was obtained in 44% yield along with 40% recovery of the starting material (entry 6). Lengthening of reaction time gave a similar result, but the starting material was completely consumed in a short period of time by the use of THF as a co-solvent to produce **3b** in good yield (entry 7) (Scheme 1).

The alkenyl sulfides **3** obtained by the reaction of β-bromostyrene **2a** were the mixtures of stereoisomers with predominance of *E*-configuration. We considered the possibility that

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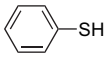
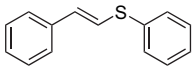
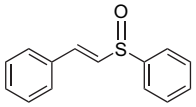
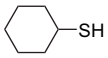
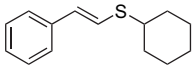
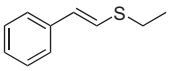
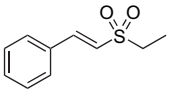
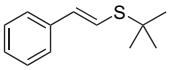
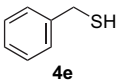
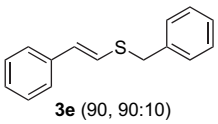
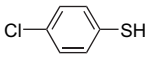
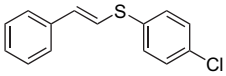
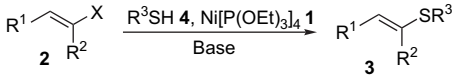
Table 1. Reaction of β-bromostyrene **2a**[a] with thiols **4**

Entry	Thiol **4**	Base (equiv)	Solvent	Temp (°C)	Time (h)	Product (yield/%,[b] ratio of stereoisomers)
1	 **4a**	Et_3N (2.0)	DMF	120	23	 **3a** (90, 93:7)
2	**4a**	Et_3N (2.0)	DMF	50	23	**3a** (53, 99:1)
3	**4a**	$PhNEt_2$ (2.0)	DMF	70	23	**3a** (98, 89:11)
4	**4a**	$PhNEt_2$ (1.5)	DMF	50	24	**3a** (88, 89:11)
5[c]	**4a**	$PhNEt_2$ (1.5)	DMF	50	24	 **5a** (93, 100:0)
6	 **4b**	NaH (1.5)	DMF	50	24	 **3b** (44, 88:12)
7	**4b**	NaH (1.5)	DMF/THF	50	2.5	**3b** (93, 88:12)
8	 **4c**	NaH (1.5)	DMF/THF	50	2.5	 **3c** (91, 91:9)
9[c]	**4c**	NaH (1.5)	DMF/THF	50	2.5	 **6** (78, 100:0)
10	 **4d**	NaH (1.5)	DMF/THF	50	2.5	 **3d** (95, 90:10)
11	 **4e**	NaH (1.5)	DMF/THF	50	8	 **3e** (90, 90:10)
12	 **4f**	NaH (1.5)	DMF/THF	50	4	 **3f** (85, 87:13)

[a] *E*/*Z*=85:15–90:10.
[b] Isolated yield.
[c] The alkenyl sulfide **3** was oxidized with MCPBA in the same vessel without any isolation or purification.

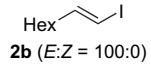
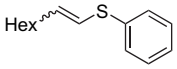
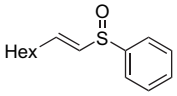
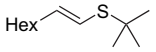
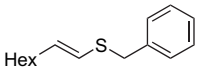
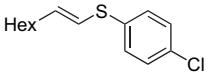
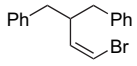
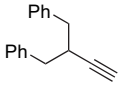
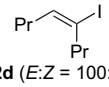
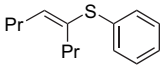
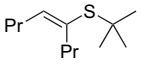
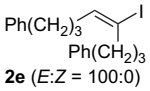
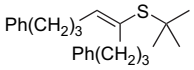
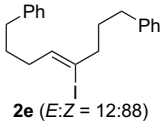
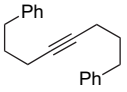
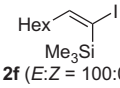
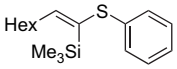
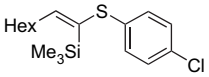


Scheme 1. Formation of alkenyl sulfides by the reaction of alkenyl halides with thiols.

the concomitant formation of *Z*-alkenyl sulfides was due to the photoisomerization of the *E*-isomers during and after isolation, since such isomerization has been known.[12] Then the reactions of **2a** with **4a** and **4c** were performed in the dark, and a dichloromethane solution of *m*-chloroperbenzoic acid (MCPBA) (10 equiv) was added to the mixtures to oxidize the resulting alkenyl sulfides **3a** and **3c**. The sulfoxide **5a** formed from the reaction with **4a** and the sulfone **5b** formed from that with **4c** were single isomers with *E*-configuration (entries 5 and 9).[13] These facts indicate that the reaction is stereoselective. If the reaction is stereospecific, it is undeniable that (*Z*)-β-bromostyrene **2a** isomerizes to the *E*-isomer under the reaction conditions; such isomerization explains the excess formation of *E*-isomers over theoretical amount estimated by the ratio of stereoisomers of the starting material **2a**.

The reactions of (*E*)-1-alkenyl halides **2** and thiols **4** also gave (*E*)-alkenyl sulfides **3** in high yields (Table 2). Although the reaction of **2a** with **4a** gave the alkenyl sulfide **3g** as a mixture of stereoisomers, the corresponding sulfoxide **5b** was obtained as a single stereoisomer by the reaction in the dark and subsequent oxidation. What is striking is that the reaction of (*Z*)-**2c** with 2-methyl-2-propanethiol **4d** gave no alkenyl sulfide but the alkyne **7a** was selectively produced (entry 6). The elimination also took place in the absence of the thiol **4d**. The result marks a sharp contrast with the conventional transition metal-catalyzed transformations.[6a,8]

Table 2. Reaction of 1-alkenyl halides **2** with thiols **4**[a]

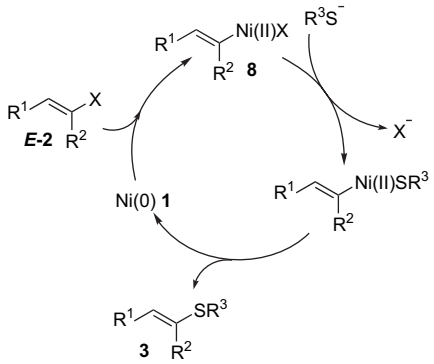
Entry	Alkenyl halide **2**	Thiol **4**	Base (equiv)	Solvent	Time (h)	Product (yield/%,[b] ratio of stereoisomers)
1	 **2b** (*E*:*Z* = 100:0)	**4a**	$PhNEt_2$ (1.5)	DMF	24	 **3g** (90, 52:48)
2[c]	**2b**	**4a**	$PhNEt_2$ (1.5)	DMF	24	 **5b** (86, 100:0)
3	**2b**	**4d**	NaH (1.5)	DMF/THF	3	 **3h** (91, 100:0)
4	**2b**	**4e**	NaH (1.5)	DMF/THF	1	 **3i** (93, 100:0)
5	**2b**	**4f**	NaH (1.5)	DMF/THF	4	 **3j** (89, 82:18)
6	 **2c** (*E*:*Z* = 0:100)	**4d**	NaH (1.5)	DMF/THF	4	 **7a** (70, 81[d])
7	 **2d** (*E*:*Z* = 100:0)	**4a**	$PhNEt_2$ (1.5)	DMF	26	 **3k** (85, 87:13)
8	**2d**	**4d**	NaH (1.5)	DMF/THF	3	 **3l** (98, 100:0)
9	 **2e** (*E*:*Z* = 100:0)	**4d**	NaH (1.5)	DMF/THF	2.5	 **3m** (91, 100:0)
10	 **2e** (*E*:*Z* = 12:88)	**4d**	NaH (1.5)	DMF/THF	1	 **7b** (51)[e]
11	 **2f** (*E*:*Z* = 100:0)	**4a**	$PhNEt_2$ (1.5)	DMF	24	 **3n** (87, 100:0)
12	**2f**	**4f**	$PhNEt_2$ (1.5)	DMF	26	 **3o** (86, 100:0)

[a] All reactions were carried out at 50 °C.
[b] Isolated yield.
[c] The alkenyl sulfide **3** was oxidized with MCPBA in the same vessel without any isolation or purification.
[d] In the absence of **4d**.
[e] The corresponding alkenyl sulfide **3m** was formed in 7% yield as a single isomer. 1,8-Diphenyl-4-octene was also obtained (9%) and (*Z*)-**2e** was recovered (11%).

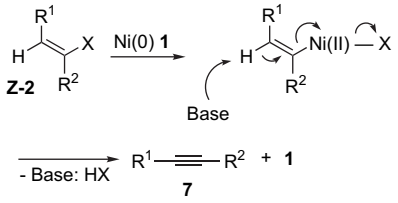
Similar to the reactions of 1-alkenyl halides, the reaction mode of highly substituted alkenyl halides was also dependent on its configuration; the treatment of *E*-**2e** with **4d** in the presence of **1** produced the *E*-alkenyl sulfide **3m** selectively whereas a similar treatment of *Z*-**2e** gave the internal alkyne **7b** (see entries 9 and 10). The loss of stereoselectivity observed in the reaction of **2d** with **4a** (entry 7) would be due to the photoisomerization since the alkenyl sulfide **3k** (*E*/*Z*=83:17) was readily transformed into a one-to-one mixture of the stereoisomers on standing under fluorescent light.

A plausible pathway for the nickel(II) **1**-promoted reaction of (*E*)-alkenyl halides **2** with thiols is illustrated in Scheme 2. Ligand exchange of the vinylnickel species **8**, generated by the oxidative addition of the halide **2** to **1**, with the thiolate anion and subsequent reductive elimination afford alkenyl sulfides **3**. It is suggested that the β-hydride elimination of organonickel species is more difficult than that of organopalladium compounds.[14] Therefore, the observed preferential formation of alkynes **7** in the reaction of (*Z*)-alkenyl halides **2** with thiols would be attributable to the 'E2 elimination' shown in Scheme 3 rather than the β-hydride elimination.

Since the elimination proceeds in an anti-fashion, the substitution is more favorable to the (*E*)-alkenyl halides than the E2 elimination.

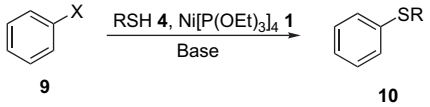


Scheme 2. A plausible mechanism for the formation of alkenyl sulfides from (*E*)-alkenyl halides.



Scheme 3. A plausible mechanism for the formation of alkynes from (*Z*)-alkenyl halides.

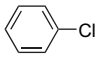
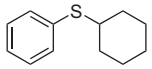
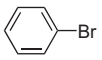
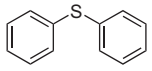
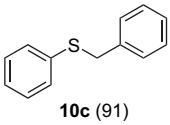
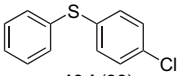
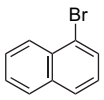
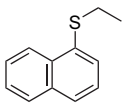
The formation of *p*-chlorophenyl sulfides **3f**, **3j**, and **3o** indicates that aryl chlorides are inactive toward the nickel(0)–thiol system. In fact, the reaction of chlorobenzene **9a** with cyclohexanethiol **4b** gave no sulfide and the starting material was recovered quantitatively. On the contrary, bromobenzene **9b** and iodobenzene **9c** do react with thiols **4** to produce aryl sulfides **10** under similar conditions (Scheme 3, Table 3). The synthetic utility of the present method was demonstrated by the gram-scale reaction of **9c** with **4b** (entry 4). The yield of the sulfide **10a** was comparable to the other reactions, which were performed on a 0.3 mmol scale (Scheme 4).



Scheme 4. Formation of aryl sulfides by the reaction of aryl halides with thiols.

Since aryl sulfides and sulfones are important compounds in pharmaceutical industry, transition metal-catalyzed coupling reactions of aryl halides and triflates with thiols have been extensively studied and a variety of palladium complexes are employed as a catalyst for the transformation.[6b,d,e,g,15] Both stoichiometric[16] and catalytic[17] amounts of copper(I) species are also employed. Recently cesium hydroxide monohydrate-promoted coupling of aryl halides with thiols was reported.[18] Nickel compounds, such as σ-aryl-Ni[PPh_3]$_2$Cl,[6b] *o*-phenylene-bis[diphenylphosphino]nickel(II) bromide complex,[19] and the nickel(0) species generated from a nickel(II) bromide-1,1′-bis(diphenylphosphino)ferrocene–zinc powder system,[20] have also been investigated as catalysts for this transformation. The reactions catalyzed by these nickel complexes, however, suffer from high reaction temperature or long reaction time. The results described here indicate that nickel(0) triethyl phosphite complex **1** is a good alternative to the above catalysts.

Table 3. Formation of aryl sulfides **10**[a]

Entry	Aryl halide **9**	Thiol **4**	Time (h)	Aryl sulfide **10** (yield/%)
1	 **9a**	**4b**	4	 **10a** (-)
2	 **9b**	**4b**	4	**10a** (78)
3[b]	 **9c**	**4a**	24	 **10b** (90)
4[c]	**9c**	**4b**	4	**10a** (90)
5	**9c**	**4e**	8	 **10c** (91)
6	**9c**	**4f**	4	 **10d** (88)
7	 **9d**	**4c**	4	 **10e** (81)

[a] All reactions were carried out in DMF/THF at reflux and 1.5 equiv of NaH was used as a base, unless otherwise noted.
[b] Carried out in DMF at 70 °C using 1.5 equiv of $PhNEt_2$ as a base.
[c] Performed on a 10 mmol scale.

3. Conclusion

We have developed a practical method for the transformation of (*E*)-alkenyl halides into the corresponding (*E*)-alkenyl sulfides using the inexpensive and air-stable nickel(0) catalyst. In addition, aryl halides are transformed into aryl sulfides by the same procedure. These reactions proceed under mild conditions and afford the sulfides in good to high yields. Further study on the nickel(0) triethyl phosphite complex-catalyzed C−X bond scission is currently in progress.

4. Experimental

4.1. General

DMF was distilled from calcium hydride under reduced pressure. THF was distilled from sodium and benzophenone. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. Tetrakis(triethyl phosphite)-nickel(0) was prepared according to the literature procedure.[11] ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra

were recorded in $CDCl_3$ on a JEOL AL300. Chemical shifts (δ) were quoted in parts per million from tetramethylsilane for ^1H and $CDCl_3$ for ^{13}C NMR spectroscopies. IR spectra were measured on a JASCO FTIR 460 plus and absorptions were reported in cm^{-1}. Elemental analyses were performed on a Perkin–Elmer 2400II analyzer.

4.2. Transformation of alkenyl and aryl halides into sulfides

Typical procedure using benzenethiol: tetrakis(triethyl phosphite)nickel(0) (11 mg, 0.015 mmol) was placed in a flask with DMF (0.3 mL) under argon. A DMF (0.6 mL) solution of β-bromostyrene (**2a**) (55 mg, 0.3 mmol), a DMF (0.6 mL) solution of *N*,*N*-diethylaniline (67 mg, 0.45 mmol), and benzenethiol (**4a**) (0.94 M in DMF, 0.34 mL, 0.36 mmol) were successively added to the flask at room temperature. The mixture was heated to 50 °C and stirred for 24 h. The reaction was quenched by the addition of 1 M NaOH and the organic materials were extracted with ether. The organic layer was washed with 1 M NaOH and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by PTLC (hexane) to give **3a** (56 mg, 88%; *E*/*Z*=89:11).

Typical procedure using p-chlorobenezenethiol or alkanethiols: cyclohexanethiol (**4b**) (0.97 M in DMF, 0.35 mL, 0.36 mmol) was added to sodium hydride (55 wt % in mineral oil, 20 mg, 0.45 mmol) under argon and the mixture was stirred for 10 min at room temperature. Tetrakis(triethyl phosphite)nickel(0) (11 mg, 0.015 mmol), DMF (0.3 mL), and a THF (1.2 mL) solution of β-bromostyrene (**2a**) (55 mg, 0.3 mmol) were successively added to the mixture, which was stirred for 2.5 h at 50 °C. The reaction was quenched by the addition of 1 M KOH and the organic materials were extracted with ether. The organic layer was washed with 1 M KOH and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by PTLC (hexane) to afford **3b** (61 mg, 93%; *E*/*Z*=88:12).

4.2.1. 1-Phenyl-2-(phenylthio)ethene (3a)[8] (*E*/*Z*=89:11). IR (neat): 3058, 3023, 1598, 1582, 1494, 1476, 1088, 1025, 945, 737, 691; ^1H NMR: 6.50 (d, *J*=10.8 Hz, 0.11H), 6.59 (d, *J*=10.6 Hz, 0.11H), 6.73 (d, *J*=15.4 Hz, 0.89H), 6.88 (d, *J*=15.4 Hz, 0.89H), 7.20–7.55 (m, 10H); ^{13}C NMR: 123.3, 126.0, 126.9, 127.1, 127.16, 127.20, 127.6, 128.3, 128.65, 128.72, 129.0, 129.1, 129.8, 130.0, 131.8, 135.2, 136.5.

4.2.2. 1-(Cyclohexylthio)-2-phenylethene (3b)[8] (*E*/*Z*=88:12). IR (neat): 3022, 2928, 2852, 1597, 1570, 1446, 1266, 998, 939, 737, 691; ^1H NMR: 1.19–1.53 (m, 5H), 1.57–1.69 (m, 1H), 1.71–1.89 (m, 2H), 1.94–2.12 (m, 2H), 2.82–3.05 (m, 1H), 6.33 (d, *J*=11.0 Hz, 0.12H), 6.43 (d, *J*=11.0 Hz, 0.12H), 6.56 (d, *J*=15.6 Hz, 0.88H), 6.76 (d, *J*=15.6 Hz, 0.88H), 7.14–7.52 (m, 5H); ^{13}C NMR (*E*-isomer): 25.6, 26.0, 33.6, 45.3, 124.0, 125.5, 126.9, 128.6, 137.1.

4.2.3. 1-(Ethylthio)-2-phenylethene (3c)[21] (*E*/*Z*=91:9). IR (neat): 3021, 2971, 2925, 1597, 1570, 1495, 1446, 1265, 937, 738, 691; ^1H NMR: 1.36 (t, *J*=7.4 Hz, 3H), 2.83 (q, *J*=7.4 Hz, 2H), 6.26 (d, *J*=11.0 Hz, 0.09H), 6.46 (d, *J*=15.6 Hz, 1.00H), 6.73 (d, *J*=15.6 Hz, 0.91H), 7.14–7.50 (m, 5H); ^{13}C NMR: 14.5, 15.4, 26.5, 124.8, 125.4, 126.5, 126.7, 126.8, 127.1, 128.2, 128.5, 128.6, 137.1.

4.2.4. 1-Phenyl-2-(*tert*-butylthio)ethene (3d)[8] (*E*/*Z*=90:10). IR (neat): 3023, 2961, 2924, 2898, 1597, 1457, 1445, 1365, 1162, 944, 740, 691; ^1H NMR: 1.41 (s, 8.1H), 1.43 (s, 0.9H), 5.43 (d, *J*=11.2 Hz, 0.10H), 5.49 (d, *J*=11.5 Hz, 0.10H), 6.71 (d, *J*=15.3 Hz, 0.90H), 6.88 (d, *J*=15.3 Hz, 0.90H), 7.17–7.52 (m, 5H); ^{13}C NMR (*E*-isomer): 31.0, 44.3, 122.0, 125.8, 127.2, 128.6, 132.0, 137.0.

4.2.5. 1-(Benzylthio)-2-phenylethene (3e)[8] (*E*/*Z*=90:10). IR (neat): 3027, 1590, 1494, 1451, 935, 739, 712, 690; ^1H NMR: 3.99 (s, 1.80H), 4.01 (s, 0.20H), 6.25 (d, *J*=11.0 Hz, 0.10H), 6.42 (d, *J*=10.8 Hz, 0.10H), 6.52 (d, *J*=15.6 Hz, 0.90H), 6.71 (d, *J*=15.6 Hz, 0.90H), 7.15–7.46 (m, 10H); ^{13}C NMR: 37.3, 124.3, 125.6, 127.0, 127.3, 127.4, 127.9, 128.5, 128.6, 128.7, 128.8, 129.4, 136.9, 137.2.

4.2.6. 1-(4-Chlorophenylthio)-2-phenylethene (3f) (*E*/*Z*=87:13). IR (neat): 3080, 1474, 1445, 1393, 1096, 959, 953, 817, 741, 690; ^1H NMR: 6.41 (d, *J*=10.6 Hz, 0.13H), 6.62 (d, *J*=10.6 Hz, 0.13H), 5.74 (d, *J*=15.4 Hz, 0.87H), 5.82 (d, *J*=15.4 Hz, 0.87H), 7.17–7.54 (m, 9H); ^{13}C NMR: 122.4, 125.1, 126.1, 127.3, 127.8, 128.0, 128.3, 128.7, 129.3, 130.9, 131.2, 137.7, 132.9, 133.8, 136.2. Anal. Calcd for $C_{14}H_{11}ClS$: C, 68.14; H, 4.49. Found: C, 68.11; H, 4.56.

4.2.7. 1-(Phenylthio)-1-octene (3g)[8] (*E*/*Z*=52:48). IR (neat): 3006, 2925, 2855, 1584, 1478, 1465, 1440, 1090, 1025, 949, 738, 689; ^1H NMR: 0.89 (t, *J*=6.1 Hz, 3H), 1.20–1.50 (m, 8H), 2.17 (dt, *J*=7.1, 7.0 Hz, 0.52H), 2.25 (dt, *J*=7.1, 5.8 Hz, 0.48H), 5.83 (dt, *J*=9.2, 7.2 Hz, 0.48H), 6.00 (dt, *J*=15.0, 7.1 Hz, 0.52H), 6.13 (d, *J*=14.8 Hz, 0.52H), 6.19 (d, *J*=9.2 Hz, 0.48H), 7.14–7.37 (m, 5H); ^{13}C NMR: 14.1, 22.6, 28.8, 28.9, 29.0, 29.1, 31.6, 31.7, 33.1, 120.5, 122.5, 126.0, 126.1, 128.3, 128.7, 128.90, 128.92, 133.8, 137.9.

4.2.8. (*E*)-1-(*tert*-Butylthio)-1-octene (3h). IR (neat): 2925, 2856, 1457, 1364, 1161, 950; ^1H NMR: 0.88 (t, *J*=6.8 Hz, 3H), 1.21–1.43 (m, 17H), 2.11 (dt, *J*=6.7, 6.7 Hz, 2H), 5.89 (dt, *J*=15.0, 6.8 Hz, 1H), 6.06 (dt, *J*=14.7, 1.1 Hz, 1H); ^{13}C NMR: 14.1, 22.6, 28.7, 29.1, 30.8, 31.6, 33.3, 43.5, 119.6, 138.2. Anal. Calcd for $C_{12}H_{24}S$: C, 71.93; H, 12.07. Found: C, 71.72; H, 12.24.

4.2.9. (*E*)-1-(Benzylthio)-1-octene (3i).[8] IR (neat): 3064, 3029, 3005, 2925, 2854, 1495, 1454, 1236, 943, 698; ^1H NMR: 0.87 (t, *J*=6.9 Hz, 3H), 1.15–1.38 (m, 8H), 2.03 (dt, *J*=6.7, 6.7 Hz, 2H), 3.83 (s, 2H), 5.67 (dt, *J*=15.0, 7.2 Hz, 1H), 5.89 (d, *J*=14.8 Hz, 1H), 7.18–7.36 (m, 5H); ^{13}C NMR: 14.1, 22.6, 28.6, 29.1, 31.6, 33.1, 37.6, 121.8, 127.0, 128.4, 128.8, 132.7, 137.9.

4.2.10. 1-(4-Chlorophenylthio)-1-octene (3j) (*E*/*Z*=82:18). IR (neat): 2955, 2926, 2855, 1475, 1094, 1012, 815; ^1H NMR: 0.87–0.91 (m, 3H), 1.18–1.49 (m, 8H), 2.13–2.27 (m, 2H), 5.86 (dt, *J*=9.2, 7.3 Hz, 0.18H), 5.98–6.13 (m, 1.82H), 7.19–7.17 (m, 4H); ^{13}C NMR: 14.1, 22.6, 28.8, 28.88, 28.93, 29.1, 31.59, 31.63, 33.1, 120.0, 121.8, 128.97, 129.0, 129.4, 129.8, 131.8, 132.0, 134.7, 135.1, 135.3, 138.9. Anal. Calcd for $C_{14}H_{19}ClS$: C, 65.99; H, 7.52. Found: C, 66.09; H, 7.56.

4.2.11. (*E*)-4-(Phenylthio)-4-octene (*E*-3k).[22] IR (neat): 3072, 2958, 2930, 2871, 1583, 1476, 1463, 1439, 740, 690; ^{1}H NMR: 0.86 (t, *J*=7.3 Hz, 3H), 0.94 (t, *J*=7.4 Hz, 3H), 1.38–1.57 (m, 4H), 2.09–2.19 (m, 4H), 5.88 (t, *J*=7.4 Hz, 1H), 7.14–7.33 (m, 5H); ^{13}C NMR: 13.7, 13.8, 21.7, 22.7, 31.2, 33.0, 126.1, 128.8, 129.8, 133.5, 136.0, 137.4.

4.2.12. (*Z*)-4-(Phenylthio)-4-octene (*Z*-3k). IR (neat): 2958, 2924, 2871, 1583, 1476, 1463, 740, 691; ^{1}H NMR: 0.82 (t, *J*=7.4 Hz, 3H), 0.93 (t, *J*=7.3 Hz, 3H), 1.37–1.53 (m, 4H), 2.13 (t, *J*=7.3 Hz, 2H), 2.32 (dt, *J*=7.3, 7.3 Hz, 2H), 5.91 (t, *J*=7.1 Hz, 1H), 7.12–7.26 (m, 5H); ^{13}C NMR: 13.3, 13.8, 21.5, 22.7, 31.9, 39.6, 125.6, 128.7, 129.1, 132.9, 136.8.

4.2.13. (*E*)-4-(*tert*-Butylthio)-4-octene (3l). IR (neat): 2959, 2871, 1457, 1378, 1362, 1164, 1148, 900; ^{1}H NMR: 0.89 (t, *J*=7.2 Hz, 3H), 0.93 (t, *J*=7.1 Hz, 3H), 1.31 (s, 9H), 1.33–1.58 (m, 4H), 2.10 (dt, *J*=7.2, 7.5 Hz, 2H), 2.26 (t, *J*=7.5 Hz, 2H), 5.93 (t, *J*=7.5 Hz, 1H); ^{13}C NMR: 13.7, 13.8, 21.8, 22.7, 31.38, 31.44, 36.8, 45.4, 133.1, 142.9. Anal. Calcd for $C_{12}H_{26}S$: C, 71.21; H, 12.95. Found: C, 71.64; H, 12.63.

4.2.14. 4-(*tert*-Butylthio)-1,8-diphenyl-4-octene (3m). IR (neat): 3026, 2936, 2857, 1496, 1454, 1362, 1162, 746, 698; ^{1}H NMR: 1.29 (s, 9H), 1.70 (tt, *J*=7.5, 7.5 Hz, 2H), 1.83 (tt, *J*=7.7, 7.7 Hz, 2H), 2.09 (dt, *J*=4.4, 7.4 Hz, 2H), 2.28 (t, *J*=7.5 Hz, 2H), 2.58 (t, *J*=8.0 Hz, 2H), 2.60 (t, *J*=7.8 Hz, 2H), 5.96 (t, *J*=7.4 Hz, 1H), 7.10–7.32 (m, 10H); ^{13}C NMR: 28.9, 30.1, 31.2, 31.4, 34.2, 35.4, 35.5, 45.5, 125.6, 125.8, 128.2, 128.3, 128.4, 128.4, 133.5, 142.1, 142.3, 142.4. Anal. Calcd for $C_{24}H_{32}S$: C, 81.76; H, 9.15. Found: C, 82.12; H, 9.49.

4.2.15. (*E*)-1-(Phenylthio)-1-(trimethylsilyl)-1-octene (3n). IR (neat): 3072, 3060, 1585, 1476, 1439, 1247, 837, 738, 690; ^{1}H NMR: 0.21 (s, 9H), 1.05 (t, *J*=6.8 Hz, 3H), 1.36–1.65 (m, 8H), 2.57 (dt, *J*=7.7, 6.9 Hz, 2H), 6.77 (t, *J*=6.8 Hz, 1H), 7.23–7.44 (m, 5H); ^{13}C NMR: −1.2, 14.0, 22.6, 28.8, 29.0, 30.9, 31.6, 124.9, 127.8, 128.5, 133.1, 138.0, 153.5. Anal. Calcd for $C_{17}H_{28}SSi$: C, 69.79; H, 9.65. Found: C, 69.36; H, 9.79.

4.2.16. (*E*)-1-(4-Chlorophenylthio)-1-(trimethylsilyl)-1-octene (3o). IR (neat): 2956, 2925, 2855, 1474, 1247, 1092, 837, 815; ^{1}H NMR: 0.20 (s, 9H), 1.03 (t, *J*=6.8 Hz, 3H), 1.32–1.63 (m, 8H), 2.53 (dt, *J*=7.5, 7.1 Hz, 2H), 6.77 (t, *J*=6.8 Hz, 1H), 7.26 (d, *J*=6.8 Hz, 2H), 7.35 (d, *J*=6.6 Hz, 2H); ^{13}C NMR: −1.2, 14.0, 22.6, 28.7, 29.0, 31.0, 31.6, 128.6, 128.7, 130.6, 132.8, 136.7, 154.2. Anal. Calcd for $C_{17}H_{27}ClSSi$: C, 62.44; H, 8.32. Found: C, 62.59; H, 8.56.

4.2.17. 3-Benzyl-4-phenyl-1-butyne (7a). IR (neat): 3293, 3062, 3028, 2923, 1496, 1454, 752, 735, 699; ^{1}H NMR: 2.05 (d, *J*=2.4 Hz, 1H), 2.74–2.82 (m, 4H), 2.89–2.95 (m, 1H), 7.19–7.31 (m, 10H); ^{13}C NMR: 35.4, 40.6, 71.0, 86.5, 126.4, 128.2, 129.2, 139.1. Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.63; H, 7.31.

4.2.18. 1,8-Diphenyl-4-octyne (7b).[23] IR (neat): 3084, 3061, 3026, 2938, 2858, 1603, 1496, 1454, 1433, 745, 699; ^{1}H NMR: 1.82 (tt, *J*=7.3 Hz, 4H), 2.19 (t, *J*=7.0 Hz, 4H), 2.73 (t, *J*=7.6 Hz, 4H), 7.16–7.31 (m, 10H); ^{13}C NMR: 18.2, 30.7, 34.8, 90.3, 125.8, 128.3, 128.5, 141.8.

4.2.19. Cyclohexyl phenyl sulfide (10a).[8] IR (neat): 3053, 2972, 2925, 1564, 1502, 1262, 976, 788, 769; ^{1}H NMR: 1.15–1.45 (m, 5H), 1.51–1.66 (m, 1H), 1.69–1.85 (m, 2H), 1.89–2.06 (m, 2H), 3.11 (tt, *J*=10.4, 3.7 Hz, 1H), 7.17–7.32 (m, 3H), 7.36–7.42 (m, 2H); ^{13}C NMR: 25.7, 26.0, 33.3, 46.5, 126.6, 128.7, 131.8, 135.1.

4.2.20. Diphenyl sulfide (10b).[8] IR (neat): 3059, 1579, 1475, 1439, 1080, 1024, 737, 688; ^{1}H NMR: 7.21–7.49 (m, 10H); ^{13}C NMR: 127.0, 129.2, 131.0, 135.8.

4.2.21. Benzyl phenyl sulfide (10c).[8] IR (neat): 3058, 3046, 1480, 1454, 1438, 730, 715, 686; ^{1}H NMR: 4.12 (s, 2H), 7.10–7.30 (m, 10H); ^{13}C NMR: 39.0, 126.3, 127.1, 128.5, 128.79, 128.81, 129.8.

4.2.22. 4-Chlorophenyl phenyl sulfide (10d).[18] IR (neat): 1475, 1094, 952, 820, 741, 690; ^{1}H NMR: 7.20–7.35 (m, 9H); ^{13}C NMR: 127.4, 129.29, 129.32, 131.3, 132.0, 133.0, 134.6, 135.1.

4.2.23. Ethyl naphthyl sulfide (10e).[24] IR (neat): 3072, 2928, 2852, 1583, 1479, 1447, 750, 735, 691; ^{1}H NMR: 1.33 (t, *J*=7.4 Hz, 3H), 3.01 (q, *J*=7.4 Hz, 2H), 7.41 (dd, *J*=7.2, 8.1 Hz, 1H), 7.47–7.58 (m, 3H), 7.73 (d, *J*=8.4 Hz, 1H), 7.85 (d, *J*=7.5 Hz, 1H), 8.40 (d, *J*=7.8 Hz, 1H); ^{13}C NMR: 14.4, 28.2, 125.0, 125.5, 126.1, 126.2, 126.9, 127.7, 128.5.

4.3. In situ oxidation of the alkenyl sulfides 3

Typical procedure: the alkenyl sulfide **3a** was prepared in the dark in a similar manner as described above. After completion of the reaction, the reaction mixture was cooled to 0 °C. A CH_2Cl_2 (2.7 mL) solution of MCPBA (672 mg, 3.0 mmol) was added and the reaction mixture was stirred for 11 h in the dark. The reaction was quenched by the addition of 1 M NaOH and the organic materials were extracted with CH_2Cl_2. The organic layer was washed with 1 M NaOH and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by PTLC (hexane/EtOAc=2:1, v/v) to give **5a** (64 mg, 93%).

4.3.1. (*E*)-1-Phenyl-2-(phenylsulfinyl)ethene (5a).[25] IR (neat): 3058, 3025, 1494, 1476, 1084, 1045, 998, 739, 689; ^{1}H NMR: 6.84 (d, *J*=15.6 Hz, 1H), 7.30–7.56 (m, 9H), 7.64–7.72 (m, 2H); ^{13}C NMR: 124.7, 127.8, 128.9, 129.4, 129.9, 131.1, 133.0, 133.7, 136.4, 143.9.

4.3.2. (*E*)-1-(Phenylsulfinyl)octene (5b).[25] IR (neat): 2926, 2855, 1466, 1443, 1085, 1046, 958, 920, 746; ^{1}H NMR: 0.87 (t, *J*=6.8 Hz, 3H), 1.16–1.37 (m, 6H), 1.46 (tt, *J*=7.4 Hz, 2H), 2.23 (dt, *J*=7.2, 7.2 Hz, 2H), 6.23 (dt, *J*=15.0, 1.4 Hz, 1H), 6.62 (dt, *J*=15.0, 6.8 Hz, 1H), 7.43–7.54 (m, 3H), 7.59–7.63 (m, 2H); ^{13}C NMR: 14.0, 22.5, 28.0, 28.7, 31.5, 32.0, 124.4, 129.2, 130.8, 134.9, 141.6, 144.3.

4.3.3. (*E*)-1-(Ethylsulfonyl)-2-phenylethene (6).[21] IR (neat): 3054, 2979, 1616, 1450, 1304, 1126, 979, 856, 822, 747, 688; ^{1}H NMR: 1.40 (t, *J*=7.4 Hz, 3H), 3.10 (q,

J=7.5 Hz, 2H), 6.82 (d, J=15.6 Hz, 1H), 7.39–7.48 (m, 3H), 7.48–7.57 (m, 2H), 7.61 (d, J=14.4 Hz, 1H); ^{13}C NMR: 7.3, 49.4, 123.9, 128.5, 129.1, 131.4, 132.2, 145.2.

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