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Studies on electrophilic reaction of Br_2 with 1,2-allenylic sulfones. A highly regio- and stereoselective synthesis of 1-phenylsulfonyl-2-bromo-1(*E*)-alken-3-ols and 1-phenylsulfonyl-2-bromo-1(*E*),3(*E*)-butadienes

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Abstract—The reaction of 1,2-allenyl sulfones with Br_2 afforded *E*-bromohydroxylation- or *E*-bromination–elimination products highly regio- and stereoselectively depending on the substitution pattern of the allene functionality. The five-membered intermediate *cis*-**3h** was isolated and characterized by X-ray diffraction study. The study on its reactivity of this intermediate revealed the origin of the regio- and stereoselectivity of this reaction.

1. Introduction

Electrophilic additions of allenes[1] would be very powerful reactions in organic synthesis since two functionalities are introduced with one of the carbon–carbon double bond intact.[2] However, in order to make these methodologies synthetically attractive, the issues of regio- and stereoselectivity must be addressed.[3–6] Recently, we have demonstrated the electrophilic halocyclization reaction of functionalized allenes.[7–9] In addition, we also established the highly regio- and stereoselective halohydroxylation of 1,2-allenyl sulfoxides[10,11] and sulfides or selenides affording *E*-2-halo-3-hydroxyalkenyl sulfoxides or *Z*-2-halo-3-hydroxyalkenyl sulfides or selenides, respectively.[12–14] Although rationales for the stereoselectivity observed in these reactions were provided, they all lack direct experimental proof. In addition, under the same reaction conditions used for 1,2-allenyl sulfoxides,[10,11] no reaction occurred with 1,2-allenyl sulfones probably due to the relatively stronger electron-withdrawing ability of the sulfone functionality.[15] In this paper, we wish to report the realization of highly regio- and stereoselective bromohydroxylation reaction of the electron-deficient 1,2-allenyl sulfones with Br_2 leading to *E*-2-bromo-3-hydroxyalkenyl sulfones or *E*-2-bromo-1,3-alkadienyl sulfones depending on the substitution pattern of the allene moiety. The intermediate responsible for the regio- and stereoselectivity observed was isolated and characterized by the X-ray diffraction study.

2. Results and discussion

After some screening, it was observed that the reaction of 3-monoalkyl substituted 1,2-allenyl phenyl sulfones **1** with Br_2 in MeCN followed by the addition of H_2O afforded *E*-2-bromo-3-hydroxyalkenyl sulfones **2** with very high regio- and stereoselectivity, which were established by the X-ray diffraction study of **2c**.[16] Some of the most typical results of this bromohydroxylation reaction are summarized in Table 1 (Fig. 1).

In order to search the origin of the regio- and stereoselectivity, after some trial and error, 1,2-butadienyl *p*-bromophenyl sulfone **1h** was prepared and its reaction with 1.2 equiv of Br_2 in MeCN at 0 °C afforded the expected product **2h** in 85% yield. However, when 2.0 equiv of Br_2 were applied, after careful handling, a five-membered intermediate with Br_3^- as the counter ion, i.e., *cis*-**3h** was isolated with the structure

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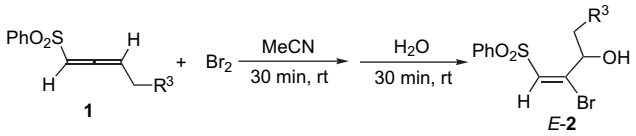
Table 1. *E*-Bromohydroxylation reaction of 1,2-allenyl sulfones



Entry	R^3	Br_2 (equiv)	Yield of *E*-**2** (%)
1[a]	H (**1a**)	1.2	85 (**2a**)
2	CH_3 (**1b**)	1.2	68 (**2b**)
3	C_2H_5 (**1c**)	2.0	60 (**2c**)
4	*n*-C_3H_7 (**1d**)	2.0	63 (**2d**)
5	*n*-C_4H_9 (**1e**)	1.2	63 (**2e**)
6	*n*-C_5H_{11} (**1f**)	1.5	58 (**2f**)
7[b]	*n*-C_5H_{11} (**1f**)	1.5	53 (**2f**)
8	Ph (**1g**)	2.0	71 (**2g**)

[a] The reaction was conducted at 0 °C.
[b] Solvent: MeCN/EtOH=40:1, 1.0 equiv of H_2O.

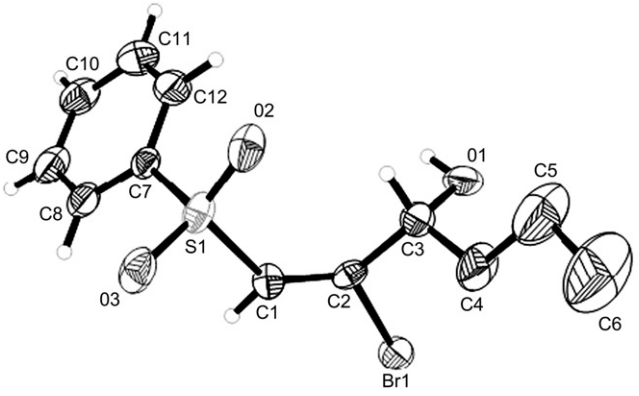


Figure 1. ORTEP representation of **2c**.

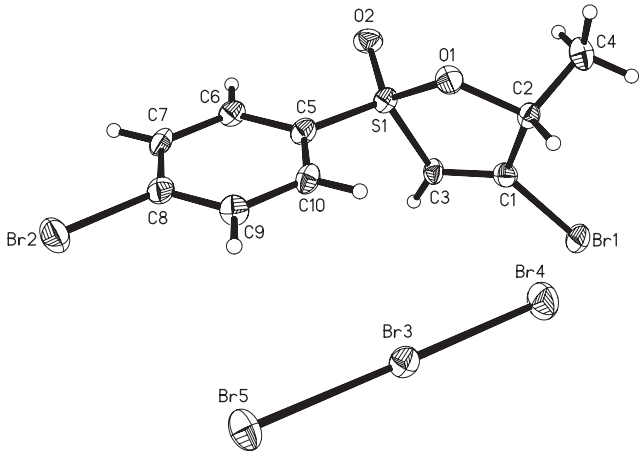
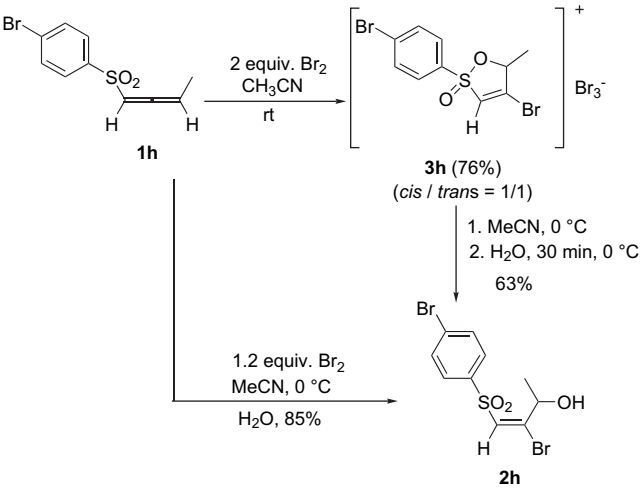


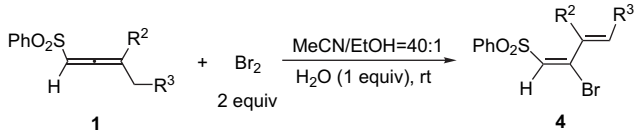
Figure 2. ORTEP representation of *cis*-**3h**.

being established by X-ray diffraction study[17] (Fig. 2). Its reaction with H_2O in MeCN afforded **2h** as the single product cleanly (Scheme 1)! The intermediacy of **3h** explains the regio- and stereoselectivity and provides strong proof for the rationale that the sulfoxide functionality was involved to form a similar five-membered intermediate in the highly regio- and stereoselective *E*-halohydroxylation of 1,2-allenyl sulfoxides (Fig. 2).[11,18]



Scheme 1.

Table 2. Synthesis of 1-phenylsulfonyl-2-bromo-1,3-butadienes (*E*,*E*)-4 via the reactions of 1,2-allenyl sulfones



Entry	R^2	R^3	Yield of *E*,*E*-**4**	*E*/*Z*	
				C=C (1)	C=C (3)
1	CH_3	H (**1i**)	76 (**4i**)	>99:1	—
2[a]	$(CH_2)_4$ (**1j**)		63 (**4j**)	>99:1	>99:1
3	Ph	CH_3 (**1k**)	80 (**4k**)	>99:1	>99:1

[a] The reaction was conducted at −40 °C.

Furthermore, when 3,3-disubstituted 1,2-allenyl sulfones were applied, the reaction under the conditions given in Table 1 was either not clean or low-yielding. After screening, it was observed that the reaction in MeCN/EtOH (40:1) *in the presence of 1 equiv of water* afforded 2-bromo-1,3-alkadienyl sulfones (*E*,*E*)-**4** highly stereoselectively, indicating a further elimination reaction following the bromination yielding the second carbon–carbon double bond highly stereoselectively[12–14] (Table 2). However, under this set of conditions, the reaction of **1f** still afforded the bromohydroxylation product *E*-**2f** (entry 7, Table 1).

3. Conclusion

In conclusion, a highly regio- and stereoselective *E*-bromohydroxylation or *E*-bromination–elimination reaction has been established. The reaction pathway depends largely on the substitution pattern of the allene functionality. The intermediacy of these reactions has been established by the isolation, X-ray diffraction characterization, and the reactivity study of the five-membered intermediate *cis*-**3h**, which provide a proof for the rationale that the participation of sulfoxide or sulfone functionality[18] forming a five-membered intermediate determines the stereoselectivity of these halohydroxylation reactions. Further studies in this area are being conducted in our laboratory.

4. Experimental section

4.1. Synthesis of *E*-2-bromo-3-hydroxyalkenyl sulfones via the *E*-bromo-hydroxylation reaction of 1,2-allenyl sulfones

4.1.1. 3-Bromo-4-(phenylsulfonyl)but-3(*E*)-en-2-ol (2a). Typical procedure: to a solution of **1a** (58.5 mg, 0.3 mmol) in 3.3 mL of MeCN was added with stirring 0.72 mL of Br_2 (0.5 M in MeCN, 0.36 mmol) at 0 °C. After the addition, the reaction was stirred at 0 °C for 0.5 h. The resulting mixture was treated with 6 mL of water and stirred for another 0.5 h. Then it was extracted with diethyl ether (50+25×2 mL), washed with brine, and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate=5:1) afforded **2a** (73.9 mg, 85%) as a solid, mp 78–79 °C (hexane and diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J=8.4 Hz, 2H), 7.67 (t, J=8.0 Hz, 1H), 7.58 (t, J=8.0 Hz, 2H), 6.78 (s, 1H), 5.51 (t, J=6.6 Hz, 1H), 2.78 (d, J=6.8 Hz, 1H), 1.37 (d, J=6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 140.1, 134.1, 131.3, 129.6, 127.4, 65.4, 22.2; IR (neat) ν (cm^{-1}) 3479, 3046, 1601, 1302, 1120; MS (70 eV, EI) *m/z* (%): 293 (M^+(^{81}Br), 9.91), 291 (M^+(^{79}Br), 9.92), 77 (100). Elemental analysis Calcd for $C_{10}H_{11}BrO_3S$: C, 41.25; H, 3.81. Found: C, 41.21; H, 3.78.

4.1.2. 2-Bromo-1-(phenylsulfonyl)pent-1(*E*)-en-3-ol (2b). The reaction of 62.4 mg (0.3 mmol) of **1b** and 0.72 mL (0.5 M in MeCN, 0.36 mmol) of Br_2 at rt afforded 62.0 mg (68%) of **2b** as an oil. ^{1}H NMR δ 7.91 (d, J=6.8 Hz, 2H), 7.66 (t, J=6.8 Hz, 1H), 7.57 (t, J=6.8 Hz, 2H), 6.83 (s, 1H), 5.33 (t, J=6.8 Hz, 1H), 2.74 (br s, 1H), 1.70–1.79 (m, 1H), 1.56–1.65 (m, 1H), 0.93 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 140.3, 134.1, 132.5, 129.6, 127.5, 70.2, 29.1, 9.4; IR (neat) ν (cm^{-1}) 3487, 3043, 1601, 1447, 1310, 1115; MS (70 eV, EI) *m/z* (%): 277 (M^+(^{81}Br)−C_2H_5, 5.23), 275 (M^+(^{79}Br)−C_2H_5, 8.71), 151 (100). Elemental analysis Calcd for $C_{11}H_{13}BrO_3S$: C, 43.29; H, 4.27. Found: C, 43.29; H, 4.36.

4.1.3. 2-Bromo-1-(phenylsulfonyl)hex-1(*E*)-en-3-ol (2c). The reaction of 66.3 mg (0.3 mmol) of **1c** and 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 at rt afforded 57.2 mg (60%) of **2c** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J=7.8 Hz, 2H), 7.66 (t, J=7.8 Hz, 1H), 7.57 (t, J=7.8 Hz, 2H), 6.80 (s, 1H), 5.40 (t, J=6.2 Hz, 1H), 2.74 (br s, 1H), 1.67–1.75 (m, 1H), 1.40–1.66 (m, 2H), 1.23–1.35 (m, 1H), 0.93 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 140.2, 134.0, 131.9, 129.5, 127.4, 68.7, 37.9, 18.2, 13.7; IR (KBr) ν (cm^{-1}) 3492, 3044, 1604, 1309, 1152; MS (70 eV, EI) *m/z* (%): 303 (M^+(^{81}Br)−OH, 0.73), 301 (M^+(^{79}Br)−OH, 0.83), 77 (100); HRMS calcd for $C_{12}H_{15}{}^{79}BrO_3S$ (M^+): 317.9925, found: 317.9938.

4.1.4. 2-Bromo-1-(phenylsulfonyl)hept-1(*E*)-en-3-ol (2d). The reaction of 71.5 mg (0.3 mmol) of **1d** and 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 at rt afforded 62.8 mg (63%) of **2d** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J=7.8 Hz, 2H), 7.66 (t, J=7.8 Hz, 1H), 7.55 (t, J=7.8 Hz, 2H), 6.81 (s, 1H), 5.38 (t, J=6.2 Hz, 1H), 2.96 (br s, 1H), 1.63–1.74 (m, 1H), 1.45–1.59 (m, 1H), 1.18–1.42 (m, 4H), 0.88 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 140.2, 134.0, 132.0, 129.5, 127.4, 68.7, 35.5, 26.9, 22.3, 13.8; IR (KBr) ν (cm^{-1}) 3490, 3044, 1603, 1447, 1310, 1152; MS (70 eV, EI) *m/z* (%): 335 (M^++1(^{81}Br), 0.58), 333 (M^++1(^{79}Br), 0.80), 125 (100); HRMS calcd for $C_{13}H_{17}{}^{79}BrO_3S$ (M^+): 332.0082, found: 332.0099.

4.1.5. 2-Bromo-1-(phenylsulfonyl)oct-1(*E*)-en-3-ol (2e). The reaction of 73.8 mg (0.3 mmol) of **1e** and 0.72 mL (0.5 M in MeCN, 0.36 mmol) of Br_2 at rt afforded 64.0 mg (63%) of **2e** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J=7.2 Hz, 2H), 7.65 (t, J=7.2 Hz, 1H), 7.56 (t, J=7.2 Hz, 2H), 6.81 (s, 1H), 5.38 (t, J=6.8 Hz, 1H), 2.84 (br s, 1H), 1.65–1.72 (m, 1H), 1.49–1.59 (m, 1H), 1.35–1.45 (m, 1H), 1.20–1.34 (m, 5H), 0.86 (t, J=6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 140.3, 134.0, 132.0, 129.5, 127.4, 68.9, 35.8, 31.3, 24.5, 22.3, 13.9; IR (KBr) ν (cm^{-1}) 3492, 3039, 1603, 1309, 1152; MS (70 eV, EI) *m/z* (%): 277 (M^+(^{81}Br)−C_5H_{11}, 25.5), 275 (M^+(^{79}Br)−C_5H_{11}, 24.9), 125 (100); HRMS calcd for $C_{14}H_{19}BrO_3SNa$ (M^++Na): 371.0115 (^{81}Br), 369.0136 (^{79}Br), found: 371.0094 (^{81}Br), 369.0116 (^{79}Br).

4.1.6. 2-Bromo-1-(phenylsulfonyl)non-1(*E*)-en-3-ol (2f). The reaction of 79.3 mg (0.3 mmol) of **1f** and 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 at rt afforded 62.6 mg (58%) of **2f** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J=7.8 Hz, 2H), 7.65 (t, J=7.8 Hz, 1H), 7.56 (t, J=7.8 Hz, 2H), 6.81 (s, 1H), 5.38 (t, J=6.8 Hz, 1H), 2.79 (br s, 1H), 1.64–1.75 (m, 1H), 1.49–1.60 (m, 1H), 1.25–1.44 (m, 8H), 0.87 (t, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 140.3, 134.0, 132.1, 129.5, 127.4, 69.0, 35.9, 31.5, 28.9, 24.8, 22.4, 14.0; IR (KBr) ν (cm^{-1}) 3491, 2928, 1604, 1310, 1152; MS (70 eV, EI) *m/z* (%): 363 (M^++1(^{81}Br), 0.52), 361 (M^++1(^{79}Br), 0.56), 125 (100); HRMS calcd for $C_{15}H_{21}{}^{79}BrO_3S$ (M^+): 360.0395, found: 360.0407.

4.1.7. 2-Bromo-1-(phenylsulfonyl)non-1(*E*)-en-3-ol (2f). To a solution of **1f** (80.0 mg, 0.3 mmol) in 2.8 mL of MeCN were added with stirring 0.1 mL of EtOH and 5.4 μL (5.4 mg, 0.3 mmol) of H_2O. Then 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 was added at rt. After the addition, the reaction was stirred at rt for 0.5 h. The resulting mixture was treated with 6 mL of water and stirred for another 0.5 h. Then it was extracted with diethyl ether (50+25×2 mL), washed with brine, and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate=5:1) afforded *E*-**2f** (58.5 mg, 53%).

4.1.8. 3-Bromo-1-phenyl-4-(phenylsulfonyl)but-3(*E*)-en-2-ol (2g). The reaction of 80.8 mg (0.3 mmol) of **1g** and 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 at rt afforded 77.5 mg (71%) of **2g** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J=7.6 Hz, 2H), 7.63 (t, J=7.6 Hz, 1H), 7.51 (t, J=7.6 Hz, 2H), 7.25–7.34 (m, 5H), 6.77 (s, 1H), 5.76 (t, J=6.6 Hz, 1H), 3.01 (d, J=7.2 Hz, 2H), 2.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.9, 135.8, 133.9, 132.3, 129.7, 129.5, 128.6, 127.4, 127.0, 69.7, 42.4; IR (KBr) ν (cm^{-1}) 3489, 3031, 1603, 1308, 1152; MS (70 eV, EI) *m/z* (%): 277 (M^+(^{81}Br)−Bn, 10.5), 275 (M^+(^{79}Br)−Bn, 10.5), 91 (100); HRMS calcd for

$C_{16}H_{15}BrNaO_3S$ (M^++Na): 390.9802 (^{81}Br), 388.9823 (^{79}Br), found: 390.9793 (^{81}Br), 388.9812 (^{79}Br).

4.1.9. 3-Bromo-4-(4′-bromophenylsulfonyl)but-3(*E*)-en-2-ol (2h). The reaction of 54.1 mg (0.2 mmol) of **1h** and 0.48 mL (0.5 M in MeCN, 0.24 mmol) of Br_2 at 0 °C afforded 53.4 mg (73%) of **2h** as a solid, mp 98–100 °C (hexane and diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J=9.2 Hz, 2H), 7.72 (d, J=9.2 Hz, 2H), 6.75 (s, 1H), 5.54 (q, J=6.3 Hz, 1H), 2.72 (br s, 1H), 1.37 (d, J=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 139.2, 132.9, 130.9, 129.5, 129.0, 65.5, 22.3; IR (KBr) ν (cm^{-1}) 3484, 2972, 1598, 1572, 1314, 1148; MS (70 eV, EI) *m*/*z* (%): 357 (M^+(^{81}Br, ^{81}Br)−CH_3, 2.6), 355 (M^+(^{81}Br, ^{79}Br)−CH_3, 3.9), 353 (M^+ (^{79}Br, ^{79}Br)−CH_3, 2.3), 149 (100). Elemental analysis Calcd for $C_{10}H_{10}Br_2O_3S$: C, 32.46; H, 2.72. Found: C, 32.60; H, 2.81.

4.2. Synthesis of 1-phenylsulfonyl-2-bromo-1,3-butadienes via the reactions of 3,3-disubstituted 1,2-allenyl sulfones

4.2.1. *E*-(2-Bromo-3-methylbuta-1,3-dienyl) phenyl sulfone (4i). Typical procedure: to a solution of **1i** (62.1 mg, 0.3 mmol) in 2.8 mL of MeCN were added with stirring 0.1 mL of EtOH and 5.4 μL (5.4 mg, 0.3 mmol) of H_2O. Then 1.2 mL (0.5 M in MeCN, 0.6 mmol) of Br_2 was added at rt. After being stirred for 5 min, the resulting mixture was treated with 6 mL of water, extracted with diethyl ether (30+25×2 mL), washed with brine, and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate=20:1) afforded **4i** (65.3 mg, 76%) as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J=7.8 Hz, 2H), 7.63 (t, J=7.2 Hz, 1H), 7.53 (t, J=7.6 Hz, 2H), 6.83 (s, 1H), 5.15 (s, 2 H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 140.7, 140.6, 133.7, 132.7, 129.2, 128.0, 119.6, 20.6; IR (neat) ν (cm^{-1}) 3051, 1600, 1325, 1152; MS (70 eV, EI) *m*/*z* (%): 285 (M^+(^{79}Br), 1.2), 287 (M^+(^{81}Br), 1.0), 161 (100); HRMS calcd for $C_{11}H_{11}BrNaO_2S$ (M^++Na): 310.9540 (^{81}Br), 308.9561 (^{79}Br), found: 310.9549 (^{81}Br), 308.9569 (^{79}Br).

4.2.2. *E*-1-Phenylsulfonyl-2-bromo-2-cyclohexenylethene (4j). The reaction of 49.1 mg (0.2 mmol) of **1j**, 67.5 μL of EtOH, 3.6 μL of H_2O, and 0.8 mL (0.5 M in MeCN, 0.4 mmol) of Br_2 at −40 °C afforded 42.1 mg (65%) of **4j** as an oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J=7.6 Hz, 2H), 7.62 (t, J=7.6 Hz, 1H), 7.53 (t, J=7.6 Hz, 2H), 6.87 (s, 1H), 5.94–5.96 (m, 1H), 2.03–2.08 (m, 2H), 1.86–1.88 (m, 2H), 1.45–1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.1, 134.3, 133.5, 133.2, 132.5, 129.0, 127.9, 26.3, 25.2, 21.5, 20.9; IR (neat) ν (cm^{-1}) 3049, 1641, 1596, 1320, 1149; MS (70 eV, EI) *m*/*z* (%): 328 (M^+(^{81}Br), 5.8), 326 (M^+(^{79}Br), 5.6), 105 (100); HRMS calcd for $C_{14}H_{15}BrNaO_2S$ (M^++Na): 350.9853 (^{81}Br), 348.9874 (^{79}Br), found: 350.9840 (^{81}Br), 348.9859 (^{79}Br).

4.2.3. 1-Phenylsulfonyl-2-bromo-3-phenyl-1(*E*),3(*E*)-pentadiene (4k). The reaction of **1k** (56.2 mg, 0.2 mmol) in 1.9 mL of MeCN, 67.5 μL of EtOH, and 3.6 μL of H_2O (3.6 mg, 0.2 mmol) with 0.8 mL of Br_2 (0.5 M in MeCN, 0.4 mmol) at rt afforded **4k** (57.2 mg, 80%). The reaction mixture was submitted to chromatography on silica gel without workup. Compound **4k**: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J=8.0 Hz, 2H), 7.53 (t, J=8.0 Hz, 1H), 7.40 (t, J=8.0 Hz, 2H), 7.26–7.31 (m, 5H), 7.14 (s, 1H), 6.28 (q, J=7.0 Hz, 1H), 1.84 (d, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 137.2, 136.8, 135.8, 134.5, 133.7, 129.1, 128.6, 128.5, 127.9, 127.7, 125.8, 16.0; IR (neat) ν (cm^{-1}) 3045, 1631, 1592, 1327, 1153; MS (70 eV, EI) *m*/*z* (%): 364 (M^+(^{81}Br), 0.72), 362 (M^+(^{79}Br), 1.0), 103 (100); HRMS calcd for $C_{17}H_{15}BrNaO_2S$ (M^++Na): 386.9852 (^{81}Br), 384.9874 (^{79}Br), found: 386.9852 (^{81}Br), 384.9872 (^{79}Br).

4.3. Isolation and reaction of the intermediate *cis*-3h and study of the mechanism

4.3.1. Isolation and reaction of intermediate *cis*-3h. To a solution of **1h** (546 mg, 2.0 mmol) in 4.0 mL of anhydrous MeCN was added with stirring 8.0 mL (0.5 M in anhydrous MeCN, 4.0 mmol) of Br_2 at rt. After evaporation of the solvent, an orange solid was collected by filtration. It was washed with 10×3 mL of anhydrous diethyl ether and dried under vacuum to afford 940.7 mg (79%, *cis*/*trans* isomer 1:1) of **3h**. This solid was dissolved in anhydrous MeCN at 40 °C and then recrystallized at 0 °C to afford pure *cis*-**3h** as a solid, mp 103–105 °C (MeCN) (decomposition). ^{1}H NMR (400 MHz, CD_3CN) δ 8.07 (d, J=8.8 Hz, 2H), 8.01 (d, J=8.8 Hz, 2H), 7.68 (d, J=1.6 Hz, 1H), 6.45 (dq, J=7.2 and 1.6 Hz, 1H), 1.99 (d, J=7.2 Hz, 3H); IR (KBr) ν (cm^{-1}) 3083, 1565, 1308, 1278; MS (70 eV, EI) *m*/*z* (%): 355 (M^+(^{81}Br, ^{81}Br), 4.8), 353 (M^+(^{79}Br, ^{81}Br), 2.8), 351 (M^+(^{79}Br, ^{79}Br), 0.27), 149 (100); HRMS calcd for $C_{10}H_9BrO_3S$ (M^+): 354.8649 (^{81}Br, ^{81}Br), 352.8669 (^{79}Br, ^{81}Br), 350.8690 (^{79}Br, ^{79}Br), found: 354.8645 (M^+(^{81}Br, ^{81}Br), 352.8668 (M^+(^{79}Br, ^{81}Br), 350.8689 (^{79}Br, ^{79}Br).

4.3.2. The reaction of 3h with H_2O affording 2h. To a solution of **3h** (118.6 mg, 0.2 mmol, *cis*/*trans* ratio: 1:1) in 2.7 mL of MeCN was added with stirring 4.0 mL of water at 0 °C. After being stirred for 0.5 h at 0 °C as monitored by TLC, it was extracted with diethyl ether (30+25×2 mL), washed with brine, and dried over *anhydrous* Na_2SO_4. Evaporation and column chromatography on silica gel (petroleum ether/ethyl acetate=4:1) afforded **2h** (46.3 mg, 63%).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.05.039.

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17. Crystal data for compound *cis*-**3h**: $C_{10}H_9Br_5O_2S$, M_w 592.78, monoclinic, *P*2(1)/*n*, Mo Kα, final *R* indices [$I>2\sigma(I)$], R=0.0825, *wR*2=0.1776, a=9.8897(11) Å, b=10.7078(12) Å, c=14.8225(16) Å, α=90°, β=93.634(2)°, γ=90°, V=1566.5(3), Z=4, number of reflections measured/unique 9049/3414 (R_{int}=0.1978) number of observations 2152 [$I>2\sigma(I)$], parameter 164, CCDC 614241.
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