Hydrohalogenation Reaction of 1,2-Allenic Sulfoxides with AlX_3 and H_2O: Efficient Synthesis of 2-Haloallyl Sulfoxides

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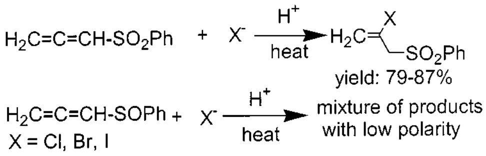
The hydrohalogenation reaction of 1,2-allenic sulfoxides **1** afforded 2-haloallyl sulfoxides **2** with yields ranging from 56 to 89%. The influence of the ratio of $AlCl_3$ and H_2O on this reaction is discussed and the optimized ratio of allenic sulfoxides, $AlCl_3$ and H_2O is 1:0.55:1. For the hydroiodination reaction, a combination of excess NaI, $AlCl_3$, and H_2O was used. The reaction is probably mediated by the species formed from the reaction of AlX_3 with H_2O. Because of the steric hindrance of the substrates, the hydrohalogenation of 1-methyl-1-(methylsulfinyl)-1,2-propadiene (**1e**), (1-methyl-1,2-propadienylsulfinyl)benzene (**1f**), and (3-methyl-1,2-butadienylsulfinyl)benzene (**1g**) did not proceed under the same reaction conditions.

Introduction

Water-promoted reactions have become increasingly important in recent years.[1] This is mainly due to their versatile merits, for example, the very low price of water, they are non-hazardous to the environment and easy to handle.[2] Water-stable Lewis acids have been used in carbon−carbon bond formation reactions[3] such as the aldol reaction,[4] allylation reaction,[4b] Diels−Alder reaction,[5] Michael addition reaction,[6] aromatic hydrocarbon nitration,[7] and isomerization of alkanes.[8] Although water-stable Lewis acid catalysis is becoming increasingly popular, active Lewis acids like BF_3, $TiCl_4$, and $AlCl_3$ react violently with water and thus lose their catalytic activities. A few literature reports state that water can accelerate the reaction catalyzed by water-unstable Lewis acids.[9] We show here that the hydrohalogenation reactions of 1,2-allenic sulfoxides can be conveniently achieved by mediation with $AlCl_3$ and H_2O. The optimized ratio of allenic sulfoxides, $AlCl_3$, and H_2O is 1:0.55:1.

The hydrohalogenation reaction of electron-deficient allenes, such as 1,2-allenyl carboxylic acids, esters and 1,2-allenyl ketones provided an efficient route to β-halo-β,γ-unsaturated enoic acids, enoates, and enones.[10−12] Recently, we have also developed the hydrohalogenation reactions of 1,2-allenyl sulfones;[13] however, under the same conditions, the hydrohalogenation reactions of the easily available 1,2-allenic sulfoxides, which are precursors to the 1,2-allenic sulfones employed in our early study,[13] failed to provide the expected 2-haloallylic sulfoxides (Scheme 1), probably due to the following two reasons: (i) the electron-withdrawing ability of the sulfinyl group (RSO) is much weaker than that of sulfonyl group (RSO_2),[14] and (ii) allenic sulfoxide is relatively unstable in acidic media such as HX at moderate temperatures (50−70 °C).[15]

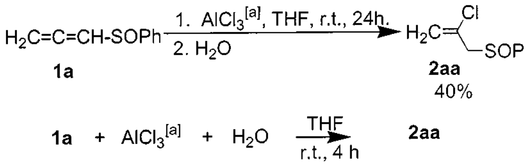


Scheme 1. Different reactivities of 1,2-allenyl sulfoxides and sulfones toward x⁻

Results and Discussion

Because of the synthetic importance of 2-haloallylic sulfoxides,[16] we screened numerous reaction conditions without any success. It is believed that Lewis acids might be able to activate the sulfinyl group.[17] Although $FeCl_3$, $ZnBr_2$, $MgCl_2$, Al_2O_3, and $Ti(O\textit{i}Pr)_4$ did not show any catalytic effect, $AlCl_3$ was found to show an obvious activity. After quenching the reaction with water, we successfully obtained the hydrochlorination product, i.e. [(2-chloro-2-propenyl)-sulfinyl]benzene (**2aa**) in 40% yield (Scheme in Table 1). However, the reaction is slow and the yield is unsatisfactory.

Table 1. The influence of the amounts of $AlCl_3$ and H_2O on the hydrochlorination of **1a**



Experiment	1	2	3	4	5	6	7	8
$AlCl_3$[a]	1.1	1.1	1.1	1.1	1.1	0.38	0.55	0.77
H_2O[b]	1	2	3	4	6	1	1	1
yield (%)[c]	97	96	96	95	6	87	95	96

[a] Commercial $AlCl_3$ was used. Equivalents of $AlCl_3$ used (solution in THF, 0.55 M). − [b] Equivalents of H_2O used (solution in THF, 1 M). − [c] NMR yield determined by using CH_2Br_2 as internal standard.

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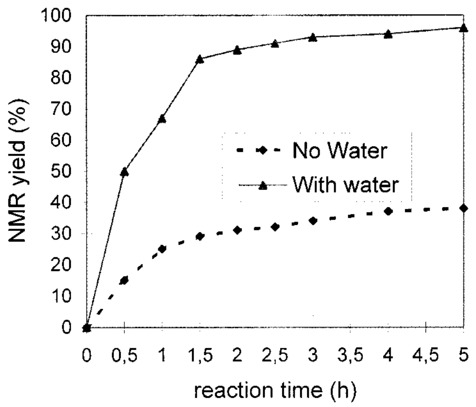
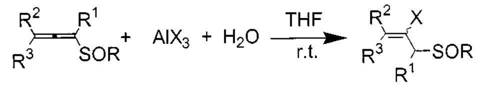


Figure 1. The influence of water on the speed of the reaction

Fortunately, after some trial and error, we observed with surprise that a certain amount of water promoted this reaction to afford **2aa** in 95% yield within 4 h. The presence of H_2O greatly influenced the speed of the reaction. We monitored the reaction of allenic sulfoxide **1a** (1.0 mmol) with commercially available $AlCl_3$ (0.55 mmol in 1 mL of THF) in the presence of H_2O (1.0 mmol) or in absence of H_2O, and the results shown in Figure 1 clearly indicate the difference. The ratio of $AlCl_3$ and H_2O also has influence on the speed of this conversion. The result shown in experiment 7 of Table 1 is the best, i.e. 0.55 equiv. of $AlCl_3$ and 1 equiv. of water are sufficient. With a ratio of H_2O and $AlCl_3$ greater than 6, the reaction is very slow (compare experiment 4 with experiment 5, Table 1). When commercially available $AlCl_3$ was further purified and dried by sublimation, the corresponding reaction in absence of H_2O produced **2aa** in only 5% yield and 90% of **1a** was recovered after 5 h.

Solvents also influence this reaction greatly. When CH_3CN was used instead of THF, the reaction proceeded slowly at room temperature to afford **2aa** in 55% yield and 40% of allenic sulfoxide **1a** remained even after 18 hours. Some typical examples in THF (Scheme 2) are listed in Table 2. It should be noted that the hydrobromination reaction with $AlBr_3$ was less efficient than the hydrochlorination reaction with $AlCl_3$ (compare entries 1 with 2, 3 with 4, 5 with 6 and 7 with 8, Table 2), probably due to the fact that allenyl sulfoxides were more sensitive to the small amounts of HBr generated in situ from $AlBr_3/H_2O$ than to the HCl formed by reaction of $AlCl_3$ with H_2O.[15] The structure of allenic sulfoxide is important: The reaction of some allenic sulfoxides, i.e. **1e**, **1f** and **1g**, did not proceed, probably due to the steric hindrance of the allenic sulfoxides. The yields for **1a** are usually higher than those for **1b** (compare entries 1, 2 with 3, 4, Table 2), probably due to the higher stability of **1a** in the reaction media, since the control experiment showed that the reaction of **1b** was faster than that of **1a**.

Hydroiodination can be realized by using a combination of $AlCl_3$ and NaI (Scheme 3). When four equivalents of NaI and 0.55 equivalents of $AlCl_3$ were used, we did not observe the formation of any hydrochlorination product. However, when we used one equivalent of **1a**, one equivalent of NaI, and 0.55 equivalents of $AlCl_3$, 20% of the hydrochlorination product **2aa** was formed.



1a R = Ph, $R^1 = R^2 = R^3 = H$
1b R = CH_3, $R^1 = R^2 = R^3 = H$
1c R = Ph, $R^1 = R^2 = H$, $R^3 = CH_3$
1d R = Ph, $R^1 = R^2 = H$, $R^3 = n\text{-}C_4H_9$
1e R = CH_3, $R^1 = CH_3$, $R^2 = R^3 = H$
1f R = Ph, $R^1 = CH_3$, $R^2 = R^3 = H$
1g R = Ph, $R^1 = H$, $R^2 = R^3 = CH_3$

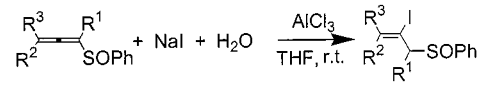
2aa X = Cl, **2ab** X = Br
2ba X = Cl, **2bb** X = Br
2ca X = Cl, **2cb** X = Br
2da X = Cl, **2db** X = Br

Scheme 2. Hydrohalogenation (X = Br, Cl) reaction of 1,2-allenyl sulfoxides

Table 2. Hydrohalogenation reactions of 1,2-allenic sulfoxides under conditions A

Entry	Sulfoxide **1**	AlX_3	Product **2**	Time [h]	Yield (%)[a]	(*Z*)/(*E*)[b]
1	**1a**	$AlCl_3$	**2aa**	4	89	–
2	**1a**	$AlBr_3$	**2ab**	1	81	–
3	**1b**	$AlCl_3$	**2ba**	1.5	71	–
4[c]	**1b**	$AlBr_3$	**2bb**	29	64	–
5	**1c**	$AlCl_3$	**2ca**	4	81	65:35
6	**1c**	$AlBr_3$	**2cb**	8.5	75	83:17
7	**1d**	$AlCl_3$	**2da**	7	82	60:40
8	**1d**	$AlBr_3$	**2db**	3.5	56	83:17

[a] Isolated yield. – [b] The ratio of (*Z*) isomer and (*E*) isomer was determined from the ^1H NMR spectra of the crude product. – [c] Water was not used in this reaction.

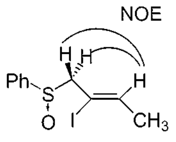


1a, $R^1 = R^2 = R^3 = H$
1c, $R^1 = R^2 = H$, $R^3 = CH_3$

2ac, yield: 79% (4 h)
2cc, yield: 69% (3h)
Z/E=92/8

Scheme 3. Hydroiodination Reaction of 1,2-allenyl sulfoxides

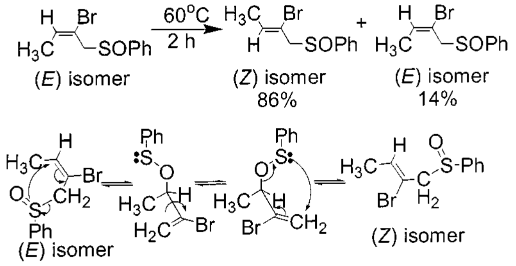
The stereoselectivity of this reaction is substrate-dependent and the two isomers can be separated by careful chromatography on silica gel; the (*Z*) isomers are predominant. The hydroiodination reaction of PhS(O)CH=C=CHCH$_3$ (**1c**) afforded the corresponding 2-iodoallyl sulfoxide **2cc** in an isomeric (*Z*)/(*E*) ratio of 92:8. The configuration of the C=C bond was determined by a 2D ^1H-^1H NOESY experiment of (*Z*)-**2cc** (Figure 2).



Z-**2cc**

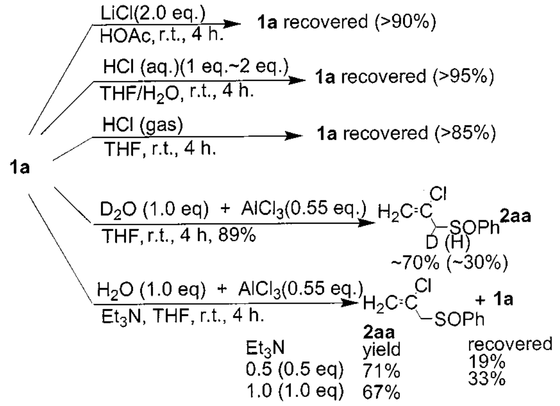
Figure 2. NOE experiment of *Z*-**2cc**

In addition, the (*Z*) isomers are thermodynamically more stable: the (*E*) isomers could be converted to the (*Z*) isomers slowly at room temperature or quickly by heating[16d] by a [2,3]-sigmatropic rearrangement.[18] For example, when the (*E*) isomer of product **2cb** was heated at 60 °C for 2 hours, 86% of the (*E*) isomer was converted into the (*Z*) isomer (Scheme 4).



Scheme 4. Isomerization of *E*-**2cb**

The reaction of **1a** with NaCl or LiCl in HOAc at room temperature did not yield the hydrochlorination product **2aa** in decent yields and **1a** was recovered in >95% or >90% yields, respectively (Scheme 5). When the hydrochlorination reaction of **1a** was carried out with LiCl in HOAc at 95–100 °C, or with LiCl and aqueous H_2SO_4 (2 equiv.) in THF at room temp., **1a** was completely consumed affording a complex mixture of products with low polarity. Furthermore, when **1a** was treated with gaseous HCl or aqueous HCl (1–2 equiv.) at room temp., most of **1a** was recovered, indicating that the current reaction did not proceed through the hydrochlorination of 1,2-allenyl sulfoxides with the HCl generated in situ from the reaction of $AlCl_3$ with H_2O.[19] The reaction of **1a** with $AlCl_3/D_2O$ afforded a mixture of non-deuterated (30%) and deuterated **2aa** (70%) in 89% combined yield. The addition of triethyl amine did slow down the reaction, probably due to its complexation with Al^{III}. Thus, the mechanism of this reaction is the Al^{III}-mediated nucleophilic attack of X^- at the middle carbon atom of the electron-deficient allenes.[10–13]



Scheme 5. Hydrochlorination reaction of **1a** under different conditions

In conclusion, the hydrohalogenation reactions of 1,2-allenic sulfoxides can be achieved using a combination of AlX_3 and H_2O (for hydroiodination, NaI is required) to afford synthetically important 2-haloallylic sulfoxides.

Experimental Section

General: $AlCl_3$ and NaI are commercially available and were used as received. THF was distilled from sodium benzophenone ketyl. $AlBr_3$ was prepared from the reaction of Al with Br_2 in CS_2 under reflux for 3 h.[20] $AlCl_3$ and H_2O were used as solutions in THF. ^1H NMR spectra were measured with $CDCl_3$ as solvent and Me_4Si as internal standard. The NMR yields were measured using CH_2Br_2 as the internal standard. (1,2-Propadienylsulfinyl)benzene (**1a**), 1-(methylsulfinyl)-1,2-propadiene (**1b**), (1,2-butadienylsulfinyl)benzene (**1c**), (1,2-heptadienylsulfinyl)benzene (**1d**), 1-methyl-1-(methylsulfinyl)-1,2-propadiene (**1e**), (1-methyl-1,2-propadienylsulfinyl)benzene (**1f**), and (3-methyl-1,2-butadienylsulfinyl)benzene (**1g**) were prepared according to published procedures.[21]

Hydrohalogenation Reactions of 1,2-Allenic Sulfoxides

(a) Synthesis of [(2-Chloro-2-propenyl)sulfinyl]benzene (2aa). – General Procedure. – Conditions A: To a dried reaction flask were added (1,2-propadienylsulfinyl)benzene (**1a**) (164 mg, 1.0 mmol), THF (3 mL), H_2O (1 M in THF, 1 mL, 1 mmol), and $AlCl_3$ (0.55 M in THF, 1 mL, 0.55 mmol). This mixture was stirred at room temperature for 4 h. After complete conversion of the starting material as monitored by TLC (eluent: 1,2-dichloroethane/THF, 20:1), the mixture was quenched with water (2 mL), and extracted with diethyl ether (2 × 10 mL). The combined ether layer was dried with $MgSO_4$. Evaporation of the solvent and flash chromatography on silica gel (eluent: hexane/ethyl acetate, 2:1) afforded **2aa** (177 mg, 89%): solid, m.p. 46–47 °C (dichloromethane/petroleum ether). – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.60$ (A part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 57 Hz, 1 H, 1-CH_2), 3.79 (B part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 57 Hz, 1 H, 1-CH_2), 5.27 (d, J = 1.5 Hz, 1 H, 3-H_{trans}), 5.42 (d, J = 1.5 Hz, 1 H, 3-H_{cis}), 7.40–7.58 (m, 3 H, 3-H, 4-H, 5-H arom), 7.58–7.70 (m, 2 H, 2-H, 6-H arom). – EI-MS: *m*/*z* (%) = 202 (6) [M^+ (^{37}Cl)], 200 (15) [M^+ (^{35}Cl)], 125 (100). – IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1}, 1030. – C_9H_9ClOS (200.7): calcd. C 53.84, H 4.52; found C 53.43, H 4.35.

The following compounds were prepared similarly.

(b) [(2-Bromo-2-propenyl)sulfinyl]benzene (2ab): Reaction of **1a** (164 mg, 1 mmol), $AlBr_3$ (1 M in CS_2, 1 mL, 1 mmol), and H_2O (1 M in THF, 1 mL, 1 mmol) afforded **2ab** (199 mg, 81%) as a liquid. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.71$ (A part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 60 Hz, 1 H, 1-CH_2), 3.91 (B part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 60 Hz, 1 H, 1-CH_2), 5.67 (d, J = 2.1 Hz, 1 H, 3-H_{trans}), 5.71 (br. s, 1 H, 3-H_{cis}), 7.43–7.60 (m, 3 H, 3-H, 4-H, 5-H arom), 7.60–7.75 (m, 2 H, 2-H, 6-H arom). – EI-MS: *m*/*z* (%) = 246 (0.44) [M^+ (^{81}Br)], 244 (0.63) [M^+ (^{79}Br)], 149 (100). – IR (neat): $\tilde{\nu}$ = 1618 cm^{-1}, 1036. – HRMS ($C_9H_9{}^{81}BrOS$): calcd. 245.9538; found 245.9525. – HRMS ($C_9H_9{}^{79}BrOS$): calcd. 243.9558; found 243.9553.

(c) 2-Chloro-3-(methylsulfinyl)-1-propene (2ba): Reaction of **1b** (51 mg, 0.5 mmol), $AlCl_3$ (0.55 M in THF, 0.5 mL, 0.27 mmol), and H_2O (0.5 M in THF, 1 mL, 0.5 mmol) afforded **2ba** (49 mg, 71%) as a liquid. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.59$ (s, 3 H, CH_3), 3.53 (A part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 48 Hz, 1 H, 3-CH_2), 3.69 (B part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 48 Hz, 1 H, 3-CH_2), 5.40–5.48 (m, 2 H, =CH_2). – EI-MS: *m*/*z* (%) = 140 (17) [M^+ (^{37}Cl)], 138 (43) [M^+ (^{35}Cl)], 75 (100). – IR (neat): $\tilde{\nu}$ = 1628 cm^{-1}, 1022. – HRMS ($C_4H_7{}^{37}ClOS$): calcd. 139.9877; found 139.9870. – HRMS ($C_4H_{77}{}^{35}ClOS$): calcd. 137.9906; found 137.9901.

(d) 2-Bromo-3-(methylsulfinyl)-1-propene (2bb): Reaction of **1b** (51 mg, 0.5 mmol), $AlBr_3$ (1 M in CS_2, 0.5 mL, 0.5 mmol), and THF (1 mL) afforded **2bb** (58 mg, 64%): liquid. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.64$ (s, 3 H, CH_3), 3.69 (A part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 51 Hz, 1 H, 3-CH_2), 3.86 (B part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 51 Hz, 1 H, 3-CH_2), 5.75 (d, J = 2 Hz, 1 H, 1-H_{trans}), 5.93

(br. s, 1 H, 1-H_{cis}). − EI-MS: *m/z* (%) = 184 (10) [M^+ (^{81}Br)], 182 (10) [M^+ (^{79}Br)], 64 (100). − IR (neat): $\tilde{\nu}$ = 1622 cm^{-1}, 1047. − HRMS ($C_4H_7{}^{81}BrOS$): calcd. 183.9381; found 183.9373. − HRMS ($C_4H_7{}^{79}BrOS$): calcd. 181.9401; found 181.9390.

(e) [(2-Chloro-2-butenyl)sulfinyl]benzene (2ca): Reaction of **1c** (534 mg, 3 mmol), $AlCl_3$ (0.55 M in THF, 3 mL, 1.65 mmol), and H_2O (1 M in THF, 3 mL, 3 mmol) afforded **2ca** (522 mg, 81%, *Z*/*E* = 65:35).

(*Z*) Isomer: Solid; m.p. 52.5−53.5 °C (dichloromethane/petroleum ether). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.74 (d, *J* = 6.7 Hz, 3 H, CH_3), 3.56 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 60 Hz, 1 H, 1-CH_2), 3.76 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 60 Hz, 1 H, 1-CH_2), 5.66 (q, *J* = 6.7 Hz, 1 H, =C*H*CH_3), 7.40−7.56 (m, 3 H, 3-H, 4-H, 5-H arom), 7.56−7.70 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 216 (0.32) [M^+ (^{37}Cl)], 214 (0.66) [M^+ (^{35}Cl)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1662 cm^{-1}, 1040. − $C_{10}H_{11}ClOS$ (214.7): calcd. C 55.92, H 5.17; found: C 55.82, H 5.09.

(*E*) Isomer: Liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.3 Hz, 3 H, CH_3), 3.64 (A part of AB, J_{AB} = 12.7 Hz, $\Delta\nu$ = 66 Hz, 1 H, 1-CH_2), 3.97 (B part of AB, J_{AB} = 12.7 Hz, $\Delta\nu$ = 66 Hz, 1 H, 1-CH_2), 5.92 (q, *J* = 7.3 Hz, 1 H, =C*H*CH_3), 7.42−7.62 (m, 3 H, 3-H, 4-H, 5-H arom), 7.62−7.77 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 216 (0.48) [M^+ (^{37}Cl)], 214 (0.89) [M^+ (^{35}Cl)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1654 cm^{-1}, 1040.

(f) [(2-Bromo-2-butenyl)sulfinyl]benzene(2cb): Reaction of **1c** (178 mg, 1 mmol), $AlBr_3$ (0.55 M in CS_2, 2 mL, 1 mmol), and H_2O (1 M in THF, 0.5 mL, 0.5 mmol) afforded **2cb** [195 mg, 75%, (*Z*)/(*E*) = 83:17].

(*Z*) Isomer: Liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 6.5 Hz, 3 H, CH_3), 3.70 (A part of AB, J_{AB} = 13.7 Hz, $\Delta\nu$ = 63 Hz, 1 H, 1-CH_2), 3.91 (B part of AB, J_{AB} = 13.7 Hz, $\Delta\nu$ = 63 Hz, 1 H, 1-CH_2), 5.86 (q, *J* = 6.5 Hz, 1 H, =C*H*CH_3), 7.44−7.57 (m, 3 H, 3-H, 4-H, 5-H arom), 7.57−7.72 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 260 (0.68) [M^+ (^{81}Br)], 258 (0.85) [M^+ (^{79}Br)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1648 cm^{-1}, 1042. − HRMS ($C_{10}H_{11}{}^{81}BrOS$): calcd. 259.9694; found 259.9700. − HRMS ($C_{10}H_{11}{}^{79}BrOS$): calcd. 257.9714; found 257.9733.

(*E*) Isomer: δ = 1.21 (d, *J* = 6.5 Hz, 3 H, CH_3), 3.69 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 96 Hz, 1 H, 1-CH_2), 4.01 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 96 Hz, 1 H, 1-CH_2), 6.07 (q, *J* = 7 Hz, 1 H, =C*H*CH_3), 7.35−7.66 (m, 3 H, 3-H, 4-H, 5-H arom), 7.50−7.66 (m, 2 H, 2-H, 6-H arom).

(g) [(2-Chloro-2-heptenyl)sulfinyl]benzene (2da): Reaction of **1d** (220 mg, 1 mmol), $AlCl_3$ (0.55 M in THF, 1 mL, 0.55 mmol), and H_2O (0.5 M in THF, 2.5 mL, 1.25 mmol) afforded **2da** [211 mg, 82%, (*Z*)/(*E*) = 60:40].

(*Z*) Isomer: Liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 3 H, CH_3), 1.16−1.42 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 2.04−2.25 (m, 2 H, =CHC*H*$_2$), 3.56 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 72 Hz, 1 H, 1-CH_2), 3.80 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 72 Hz, 1 H, 1-CH_2), 5.54 (t, *J* = 7 Hz, 1 H, =C*H*CH_2), 7.40−7.57 (m, 3 H, 3-H, 4-H, 5-H arom), 7.57−7.70 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 259 (6) [M^+ + 1 (^{37}Cl)], 257 (14) [M^+ + 1 (^{35}Cl)], 126 (100). − HRMS ($C_{13}H_{17}{}^{35}ClOS$): calcd. for 256.0689; found 256.0683.

(*E*) Isomer: Liquid [contaminated by a trace amount of (*Z*) isomer]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7 Hz, 3 H, CH_3), 0.97−1.30 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 1.56−1.71 (m, 1 H, = CHC*H*HCH_2), 1.71−1.90 (m, 1 H, =CHCH*H*CH_2), 3.65 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 99 Hz, 1 H, 1-CH_2), 3.98 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 99 Hz, 1 H, 1-CH_2), 5.86 (t, *J* = 7.8 Hz, 1 H, =C*H*CH_2), 7.46−7.60 (m, 3 H, 3-H, 4-H, 5-H arom), 7.60−7.76 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 256 (1) [M^+ (^{35}Cl)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1646 cm^{-1}, 1034. − HRMS ($C_{13}H_{17}{}^{35}ClOS$): calcd. 256.0689; found 256.0719.

(h) [(2-Bromo-2-heptenyl)sulfinyl]benzene (2db): Reaction of **1d** (220 mg, 1 mmol), THF (2 mL), $AlBr_3$ (1 M in CS_2, 1 mL, 1 mmol), and H_2O (0.5 M in THF, 2.5 mL, 1.25 mmol) afforded **2db** [169 mg, 56%, (*Z*)/(*E*) = 83:17].

(*Z*) Isomer: Liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 3 H, CH_3), 1.18−1.42 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 2.07−2.23 (m, 2 H, =CHC*H*$_2$), 3.72 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 69 Hz, 1 H, 1-CH_2), 3.95 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 69 Hz, 1 H, 1-CH_2), 5.73 (t, *J* = 7 Hz, 1 H, =C*H*CH_2), 7.43−7.57 (m, 3 H, 3-H, 4-H, 5-H arom), 7.57−7.73 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 302 (10) [M^+ (^{81}Br)], 300 (10) [M^+ (^{79}Br)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1036 cm^{-1}. − HRMS ($C_{13}H_{17}BrOS$): calcd. 300.0183; found 300.0199.

(*E*) Isomer: [Contaminated by a trace amount of (*Z*) isomer]. − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (t, *J* = 7 Hz, 3 H, CH_3), 1.00−1.40 (m, 4 H, C*H*$_2$C*H*$_2$$CH_3$), 1.50−1.70 (m, 1 H, = CHC*H*HCH_2), 1.70−1.90 (m, 1 H, =CHCH*H*CH_2), 3.78 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 93 Hz, 1 H, 1-CH_2), 4.09 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 93 Hz, 1 H, 1-CH_2), 6.11 (t, *J* = 7 Hz, 1 H, =C*H*CH_2), 7.45−7.61 (m, 3 H, 3-H, 4-H, 5-H arom), 7.61−7.80 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 300 (12) [M^+ (^{79}Br)], 302 (13) [M^+ (^{81}Br)], 126 (100). − IR (neat): $\tilde{\nu}$ = 1046 cm^{-1}. − HRMS ($C_{13}H_{17}BrOS$): calcd. 300.0183; found 300.0169.

Hydroiodination Reactions of 1,2-Allenic Sulfoxides

(a) Synthesis of [(2-Iodo-2-propenyl)sulfinyl]benzene (2ac). − Typical Procedure. − Conditions B: To a reaction flask containing dry NaI (600 mg, 4 mmol), were added (1,2-propadienylsulfinyl)benzene (**1a**) (164 mg, 1 mmol), THF (2 mL), H_2O (1 M in THF, 1 mL, 1 mmol), and $AlCl_3$ (0.55 M in THF, 1 mL, 0.55 mmol) under nitrogen. The mixture was stirred at room temperature for 4 h. After complete conversion of the starting material as monitored by TLC (eluent: 1,2-dichloroethane/THF, 20:1), the mixture was quenched with water (2 mL) and extracted with diethyl ether (2 × 10 mL). The combined ether layers were dried with $MgSO_4$. Evaporation of the solvent and flash chromatography on silica gel (eluent: hexane/ethyl acetate, 2:1) afforded **2ac** (230 mg, 79%) as a liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 3.77 (A part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 57 Hz, 1 H, 1-CH_2), 3.96 (B part of AB, J_{AB} = 13.1 Hz, $\Delta\nu$ = 57 Hz, 1 H, 1-CH_2), 5.97 (d, *J* = 1.7 Hz, 1 H, 3-H_{trans}), 6.17 (br. s, 1 H, 3-H_{cis}), 7.43−7.59 (m, 3 H, 3-H, 4-H, 5-H arom), 7.59−7.74 (m, 2 H, 2-H, 6-H arom). − EI-MS: *m/z* (%) = 292 (13) [M^+], 125 (100). − IR (neat): $\tilde{\nu}$ = 1608 cm^{-1}, 1049. − HRMS (C_9H_9IOS): calcd. 291.9418; found 291.9436.

Product **2cc** was prepared similarly.

(b) [(2-Iodo-2-butenyl)sulfinyl]benzene (2cc): Reaction of **1c** (89 mg, 0.5 mmol), NaI (300 mg, 2 mmol), $AlCl_3$ (0.55 M in THF, 0.5 mL, 0.27 mmol), and H_2O (1 M in THF, 0.5 mL, 0.5 mmol) afforded **2cc** (105 mg, 69%, *Z*/*E* = 92/8).

(*Z*) Isomer: Liquid. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 6.3 Hz, 3 H, CH_3), 3.83 (A part of AB, 1 H, 1-CH_2, J_{AB} = 13 Hz, $\Delta\nu$ = 66 Hz), 4.05 (B part of AB, 1 H, 1-CH_2, J_{AB} = 13 Hz, $\Delta\nu$ = 66 Hz), 5.74 (q, *J* = 6.3 Hz, 1 H, =C*H*CH_3), 7.45−7.56 (m, 3 H, 3-H, 4-H, 5-H arom), 7.56−7.68 (m, 2 H, 2-H, 6-H arom). −

EI-MS: m/z (%) = 306 (2) [M$^+$], 126 (100). − IR (neat): $\tilde{\nu}$ = 1634 cm^{-1}, 1036. − HRMS ($C_{10}H_{11}IOS$): calcd. 305.9574; found 305.9557.

(*E*) Isomer: Crude product. − ^{1}H NMR(300 MHz, $CDCl_3$): δ = 1.30 (d, J = 7 Hz, 3 H, CH_3), 3.86 (A part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 51 Hz, 1 H, 1-CH_2), 4.13 (B part of AB, J_{AB} = 13 Hz, $\Delta\nu$ = 51 Hz, 1 H, 1-CH_2), 6.50 (q, J = 7 Hz, 1 H, =C*H*CH_3), 7.43−7.58 (m, 3 H, 3-H, 4-H, 5-H arom), 7.58−7.75 (m, 2 H, 2-H, 6-H arom).

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