

The Claisen Rearrangement of 2-Phenylsulfinyl-2-propenyl Phenyl Ethers —A New Route to Functionalized Phenols and 2-Methylbenzofurans

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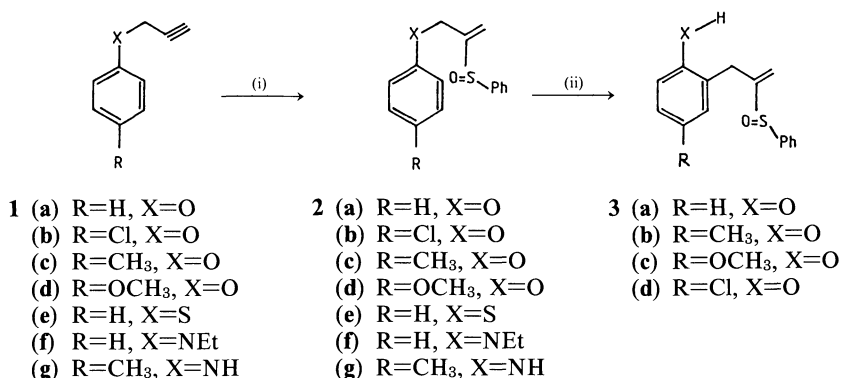
The hitherto unknown Claisen rearrangement of 2-phenylsulfinyl-2-propenyl phenyl ethers to the corresponding 2-(2-phenylsulfinyl-2-propenyl)phenols is reported. The latter compounds underwent Michael reactions with a variety of nucleophiles to provide functionalized phenolic adducts. *O*-Alkylation of the initial rearrangement products with 3-bromo-2-phenylsulfinyl-1-propene and 2,3-dibromo-1-propene followed by [3,3] sigmatropic rearrangement provided a promising route to 7-substituted 2-methylbenzofurans.

Although the [3,3] sigmatropic rearrangement of enol or phenol ethers to the corresponding *C*-alkylated products also known as the Claisen rearrangement¹⁾ has enjoyed widespread application in organic synthesis for over seven decades, it continues to be a rewarding reaction for the construction of carbon–carbon bonds. We report here in this context a hitherto unknown Claisen rearrangement of (phenoxy-substituted alkenyl) phenyl sulfoxides (**2a–d**). Alkenyl sulfoxides are versatile molecules in organic synthesis. They act as dienophiles, Michael acceptors, and as precursors to alkenyl sulfides, chloroalkyl sulfides, ketones, allenes, enamines, and enamides.²⁾ The alkenyl sulfoxides (**2a–g**) were prepared efficiently by the regiospecific addition of benzenesulfenic acid to the terminal alkynes (**1a–g**). The benzenesulfenic acid was generated in situ by the thermolysis of 1-cyano-2-(phenylsulfinyl) ethane.³⁾

The sulfoxides (**2a–d**) as solutions in mesitylene were very cleanly transformed upon reflux into the corresponding phenols (**3a–d**) (yields ca. 50%). The reaction progress was monitored by TLC which showed the

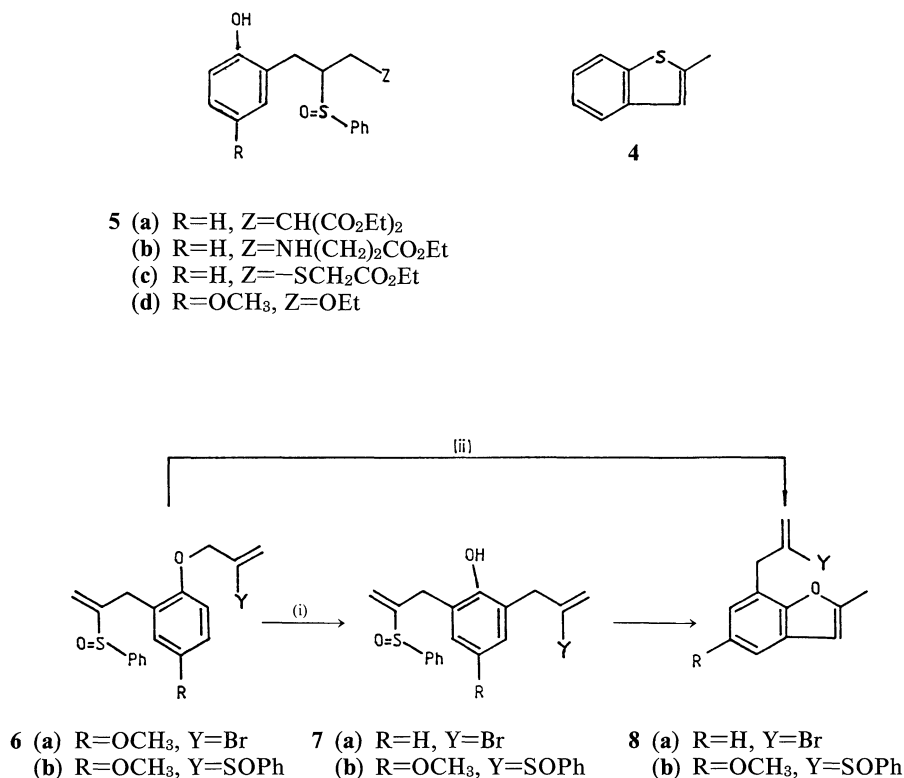
phenolic products (**3a–d**) to have relatively lower *R_f* values compared with the starting ethers (**2a–d**). Using 1,2-dichlorobenzene (DCB) as the reaction solvent the yields of the products (**3a–d**) were significantly improved (80%). ¹H NMR and IR spectroscopies tentatively established the product structures. The appearance of OH absorptions (ca. 3200 cm^{−1}) in the IR spectra of products (**3a–d**) and the change in the chemical shift of the diastereotopic allylic methylene protons from low field ($\delta=4.1$ – 4.5 in starting materials **2a–d**) to high field ($\delta=3.1$ – 3.5 in products **3a–d**) were the most noticeable spectroscopic features that witnessed the rearrangement process.

Under similar reaction conditions to above the thioether (**2e**) rearranged to yield 2-methylbenzothiophen (**4**) along with *O*-phenyl and *S*-phenyl benzenethiosulfinates (PhSSOPh), a product known to arise from the intermolecular condensation of benzenesulfenic acid. 2-Methylbenzo[*b*]thiophenes and 2-methylbenzofurans have previously been obtained from the Claisen rearrangement of 2-chloro-2-propenyl



Scheme 1. Reagents: (i) PhSCH₂CH₂CN, 110 °C, under N₂. (ii) As solutions in mesitylene or 1,2-dichlorobenzene, 180 °C (oil bath), 18–24 h, under N₂.

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Scheme 2. Reagents: (i) Solution in mesitylene, 180 °C (oil bath), under N_2 , 22 h. (ii) SiO_2 added to solution in mesitylene, 180 °C (oil bath), 22 h.

phenyl ethers and thioethers.⁴⁾

The corresponding amino-substituted sulfoxides (**2f**, **2g**) resisted rearrangement under similar reactions. Although it is known that the amino Claisen rearrangement is greatly accelerated by acids and Lewis acid catalysis,⁵⁾ the use of these reagents in our case was negated by the fact that sulfoxides are decomposed by such reagents.

The (phenoxy-substituted alkenyl) sulfoxides (**3a—d**) underwent Michael reactions in alcoholic solutions with diethyl sodiomalonate, thiolate anions, β -alanine ethyl ester and sodium ethoxide to furnish the adducts (**5a—d**) in good yields. Since suitably substituted phenolic compounds are pharmacologically rewarding compounds,⁶⁾ the Michael reactions of the phenols (**3a—d**) provides a method for synthesizing a great variety of new hetero derivatives such as (**5a—d**) that otherwise are difficult to produce.

O-Alkylation of **3** with synthons 2,3-dibromo-1-propene and 2-bromo-2-phenylsulfinyl-1-propene²⁾ gave the ethers (**6a**) and (**6b**) respectively which underwent [3,3] sigmatropic rearrangement upon reflux in mesitylene to afford the acyclic adducts (**7a**) and (**7b**) as the only reaction products. However, rearrangement of the ethers (**6a**) and (**6b**) under catalysis by SiO_2 (Fluka 60H) resulted in the formation of 2-methylbenzofurans (**8a**) and (**8b**) respectively. Repeating the SiO_2 -catalyzed reactions in DCB as the solvent resulted in decomposition and polymerization. Dark oily compounds in

the case of **7b** were obtained that crystallized upon the addition of diethyl ether. Although soluble in chloroform the identification of the solid proved difficult, however. Benzofurans are biologically important molecules.⁷⁾ The Michael reactions of the 7-(phenylsulfinyl-substituted alkenyl) benzofuran (**8b**) with various nucleophiles should provide a route to a wide variety of hetero derivatives that might have interesting physiological properties.

Experimental

NMR spectra were recorded on either JEOL EX90 FT or Perkin-Elmer R34 (220 MHz) NMR spectrometers for solutions in $CDCl_3$ with $SiMe_4$ as an internal standard. IR spectra were recorded on a Perkin-Elmer 520B spectrophotometer. Mass spectra were obtained on either Finnigan MAT 311A or Nermag R10-10 connected to a Varian Vista 6000 GC. Analytical TLC was performed on Eastman Kodak Silica Chromatogram sheets using diethyl ether (ether) as the eluent. Column chromatography was performed on Fluka SiO_2 60H under pressure using the short path technique.

Preparation of Acetylenic Precursors (1a—g). The preparations of compounds **1a**,⁸⁾ **1e**,⁸⁾ **1f**,⁸⁾ and **1g**,²⁾ are described elsewhere.

3-(4-Chlorophenoxy)-1-propyne (1b). This was prepared (11.7 g, 70%) from NaOEt (0.1 mol) in dry EtOH (45 ml), 4-chlorophenol (12.86 g, 0.1 mol) and 3-bromo-1-propyne (12.9 g, 0.108 mol); bp 60 °C/0.2 mm Hg (1 mmHg=133.322 Pa); IR (neat) 3295 ($HC\equiv C-$), 2115 ($-C\equiv C-$) cm^{-1} ; 1H NMR δ =2.50

(1H, t, $J=2$ Hz acetylenic proton), 4.60 (2H, d, $J=2$ Hz, $-\text{OCH}_2-$), 6.80 (2H, d, $J=9$ Hz, ArH *ortho* to oxygen), 7.22 (2H, d, $J=9$ Hz, ArH *ortho* to Cl). Found: C, 64.7; H, 4.1%. Calcd. for $\text{C}_9\text{H}_7\text{OCl}$: C, 64.86; H, 4.20%.

3-(*p*-Tolyloxy)-1-propyne (1c). It was prepared in a similar way to above from *p*-cresol (10.8 g, 0.1 mol), 3-bromo-1-propyne (12.9 g, 0.108 M) (1 M=1 mol dm $^{-3}$) and NaOEt (0.1 mol); bp 50 °C/0.2 mm Hg; IR (neat) 3290 ($\text{HC}\equiv\text{C}-$), 2110 ($-\text{C}\equiv\text{C}-$) cm^{-1} ; ^1H NMR $\delta=2.23$ (3H, s, $-\text{CH}_3$), (1H, t, $J=2$ Hz, acetylenic proton), 4.57 (2H, d, $J=2$ Hz, $-\text{OCH}_2-$), 6.76 (2H, d, $J=9$ Hz, ArH *ortho* to oxygen), 7.03 (2H, d, $J=9$ Hz, ArH *ortho* to CH_3). Found: C, 82.0; H, 6.7%. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}$: C, 82.19; H, 6.85%.

3-(4-Methoxyphenoxy)-1-propyne (1d). This was prepared (65 g, 86%) from *p*-anisole (58 g, 0.47 mol), 3-bromo-1-propyne (57 g, 0.48 mol), and NaOEt (0.47 M); bp 112–114 °C/7 mmHg; IR (neat) 3295 ($\text{HC}\equiv\text{C}-$), 2125 ($-\text{C}\equiv\text{C}-$) cm^{-1} ; ^1H NMR $\delta=2.45$ (1H, t, $J=2$ Hz, acetylenic proton), 3.63 (3H, s, $-\text{OCH}_3$), 4.50 (2H, d, $J=2$ Hz, $-\text{OCH}_2-$), 6.73 (4H, m, ArH). Found: C, 74.0; H, 6.1%. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.07; H, 6.17%.

Preparation of Alkenyl Sulfoxides (2a–g). The alkenyl sulfoxides **2a**,⁸⁾ **2e**,⁸⁾ **2f**,⁸⁾ and **2g**,²⁾ have been prepared by us and described elsewhere.

3-(4-Chlorophenoxy)-2-phenylsulfinyl-1-propene (2b). Thermolysis of 1-cyano-2-(phenylsulfinyl)ethane (4.0 g, 22.3 mmol) in the acetylene **1b** (15 g, 90 mmol) for 3 h under N_2 at 110 °C in a toluene vapor jacket gave an oily residue, after distillation to remove excess **1b**, which was purified by column chromatography [(a) (1 : 1) ether–petroleum ether (40 : 60) (b) ether] to give **2** (5.8 g, 89%) as an oil which solidified on keeping. Recrystallization [acetone–petroleum ether (40 : 60)] yielded pure **2b** as a white powder, mp 92–95 °C; IR (KBr) 1040 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=4.33$ (1H, d, $J=13.5$ Hz, diastereotopic allylic proton), 4.70 (1H, d, $J=13.5$ Hz, diastereotopic allylic proton), 5.93 (1H, s, olefinic proton *trans* to $-\text{SOPh}$), 6.25 (1H, s, olefinic proton *cis* to $-\text{SOPh}$), 6.65 (2H, d, $J=8$ Hz, ArH *ortho* to oxygen), 7.16 (2H, d, $J=8$ Hz, ArH *ortho* to Cl), 7.36–7.93 (5H, m, $-\text{SOPh}$); MS m/z 293 (M^+), 277, 167, 126. Found: C, 61.3; H, 4.3%. Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{SCl}$: C, 61.54; H, 4.44%.

3-(*p*-Tolyloxy)-2-phenylsulfinyl-1-propene (2c). Thermolysis of 1-cyano-2-(phenylsulfinyl)ethane (2.0 g, 11.1 mmol) in **1c** (11 g, 75.3 mmol) in the above manner gave pure **2c** (2.8 g, 93%) as an oil which solidified on keeping. Recrystallization [acetone–petroleum ether (40 : 60)] yielded a white powder, mp 48–50 °C; IR (KBr) 1040 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=2.25$ (3H, s, $-\text{CH}_3$), 4.30 (1H, d, $J=13.5$ Hz, diastereotopic allylic proton), 4.68 (1H, d, $J=13.5$ Hz, diastereotopic allyl proton), 5.93 (1H, s, olefinic proton *trans* to $-\text{SOPh}$), 6.20 (1H, s, olefinic proton *cis* to $-\text{SOPh}$), 6.63 (2H, d, $J=8$ Hz, ArH *ortho* to oxygen), 7.0 (2H, d, $J=8$ Hz, ArH *ortho* to CH_3), 7.36–7.75 (5H, m, $-\text{SOPh}$); MS m/z 272. Found: C, 70.4; H, 5.8%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$: C, 70.59; H, 5.88%.

3-(4-Methoxyphenoxy)-2-phenylsulfinyl-1-propene (2d). Thermolysis of 1-cyano-2-(phenylsulfinyl)ethane (7.0 g, 39.1 mmol) in **1d** (33 g, 6.204 mol) in the above manner yielded pure **2d** (9.6 g, 85%) as a thick brown oil which solidified after prolonged keeping. Recrystallization (as above) yielded a white powder, mp 90–94 °C; IR (KBr) 1050 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=3.70$ (3H, s, $-\text{OCH}_3$), 4.33 (1H, d, $J=14.5$ Hz, $-\text{OCH}_2-$), 4.65 (1H, d, $J=14.5$ Hz, $-\text{OCH}_2-$), 5.95 (1H, s, olefinic H *trans* to $-\text{SOPh}$), 6.23 (1H, s, olefinic H *cis* to

$-\text{SOPh}$), 6.66 (2H, d, $J=7.5$ Hz, ArH *ortho* to oxygen), 6.75 (2H, d, $J=7.5$ Hz, ArH *ortho* to OCH_3), 7.43–7.53 (5H, m, SOPh); MS m/z 288 (M^+), 195, 162, 141, 77 (100%). Found: C, 66.5; H, 5.4%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$: C, 66.67; H, 5.55%.

Claisen Rearrangement of the Sulfoxides (2a–e). The following procedure illustrated for **2a** was typical. A solution of the sulfoxide **2a** (1.9 g, 7.36 mmol) in dry mesitylene (19 ml) was heated under N_2 in an oil bath maintained at 180 °C for 20–24 h. After removal of the solvent under reduced pressure an oily residue was obtained which was chromatographed [(a) (1 : 1) ether–petroleum ether (40 : 60) (b) ether] to yield mesitylene followed by unchanged **2a** (480 mg, 25%), and finally 2-(2-phenylsulfinyl-2-propenyl)phenol **3a** (1.33 g, 70%) as a pale yellow oil which solidified on keeping. Recrystallization [(CH_2Cl_2 –petroleum ether (40 : 60))] afforded pure **3a** as a white powder, mp 94–95 °C; IR (KBr) 3200 (OH, broad), 1020 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=3.10$ (d, $J=16$ Hz, 1H, diastereotopic allylic $-\text{OCH}_2-$), 3.50 (d, $J=16$ Hz, 1H, diastereotopic allylic $-\text{OCH}_2-$), 5.65 (s, 1H, olefinic H *trans* to $-\text{SOPh}$), 6.00 (s, 1H, olefinic H *cis* to SOPh), 6.6–7.20 (m, 4H, ArH), 7.25–7.90 (m, 3H, $-\text{SOPh}$); MS m/z 258 (M^+), 218, 131 (100%). Found: C, 69.6; H, 5.3; S, 12.3%. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}$: C, 69.77; H, 5.43; S, 12.40%. Rearrangement of **2a** in 1,2-dichlorobenzene (DCB) gave in **3a** in a higher yield (86%).

4-Chloro-2-(2-phenylsulfinyl-2-propenyl)phenol (3b). Similar to above the sulfoxide **2b** (550 mg, 1.88 mmol) in mesitylene (6 ml) yielded upon heating **3b** (281 mg, 51%) together with unchanged **2b** (260 mg, 47%). The pale yellow oily phenol **3b** solidified upon keeping. Recrystallization (as above) afforded **3b** as a white powder, mp 130–131 °C; IR (KBr) 3195 (OH, broad), 1025, 1030 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=3.05$ (d, $J=15$ Hz, 1H, $-\text{OCH}_2-$), 3.45 (d, $J=15$ Hz, 1H, $-\text{OCH}_2-$), 5.63 (s, 1H, olefinic H *trans* to SOPh), 6.00 (s, 1H, olefinic H *cis* to SOPh), 6.5–7.15 (m, 3H, ArH), 7.3–7.7 (m, 5H, $-\text{SOPh}$); MS m/z 292 (M^+), 277, 165 (100%), 126. Found: C, 61.4; H, 4.3; S, 11.0%. Calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{SCl}$: C, 61.54; H, 4.44; S, 10.94%. Rearrangement of **2b** in DCB gave **3b** in 80% yield.

4-Methyl-2-(2-phenylsulfinyl-2-propenyl)phenol (3c). Thermal rearrangement of **2c** (550 mg, 2.02 mmol) in mesitylene (6 ml) in the above manner afforded **3c** (440 mg, 80%) as an oil which solidified on keeping. Recrystallization (as above) yielded **3c** as a white powder, mp 128–130 °C; IR (KBr) 3195 (OH, broad), 1030, 1040 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=2.15$ (d, $J<2$ Hz, 3H, CH_3), 3.12 (d, $J=15$ Hz, 1H, $-\text{OCH}_2-$), 3.53 (d, $J=15$ Hz, 1H, $-\text{OCH}_2-$), 5.70 (s, 1H, olefinic H *trans* to SOPh), 6.05 (s, 1H, olefinic H *cis* to $-\text{SOPh}$), 6.65–7.05 (m, 3H, ArH), 7.4–7.7 (m, 5H, $-\text{SOPh}$); MS m/z 272 (M^+). Found: C, 70.5; H, 5.7; S, 11.6%. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2\text{S}$: C, 70.59; S, 11.76%. Rearrangement of **2c** in DCB yielded **3c** in higher yield (95%).

4-Methoxy-2-(2-phenylsulfinyl-2-propenyl)phenol (3d). The thermal rearrangement of **2d** (3.0 g, 16.4 mmol) in mesitylene (30 ml) in the above manner produced **3d** (2.55 g, 85%) as a thick dark brown oil; IR (neat) 3190 (OH, broad), 1035 ($>\text{S}=\text{O}$) cm^{-1} ; ^1H NMR $\delta=3.13$ (d, $J=16$ Hz, 1H, $-\text{OCH}_2-$), 3.45 (d, $J=16$ Hz, 1H, $-\text{OCH}_2-$), 3.67 (s, 3H, $-\text{OCH}_3$), 5.67 (s, 1H, olefinic H *trans* to $-\text{SOPh}$), 6.07 (s, 1H, olefinic H *cis* to $-\text{SOPh}$), 6.50 (d, $J=2$ Hz, 1H, H-3), 6.65 (dd, $J=2$ Hz and 8 Hz, 1H, H-5), 6.77 (d, $J=8$ Hz, 1H, H-6), 7.4–7.55 (m, 3H, $-\text{SOPh}$), 7.55–7.70 (m, 2H, $-\text{SOPh}$); MS m/z 288 (M^+), 162 (100%). Found: C, 66.6; H, 6.5; S, 11.0%. Calcd for

$C_{16}H_{16}O_3S$: C, 66.67; H, 5.55; S, 11.11%. Rearrangement of **2d** in DCB afforded **3d** in higher yield (95%).

2-Methylbenzothiophene (4). Thermal rearrangement of **2e** (210 mg, 7.66 mmol) in mesitylene (3 ml) gave **4** (135 mg, 64%), as a pale brown solid; mp 50–52 °C (lit.⁴) mp 51–52 °C). The compound had identical 1H NMR with that reported in the literature. The other product obtained from column chromatography of reaction mixture was *S*-phenyl benzenethiosulfonates (PhSSOPh).

The Michael Reactions of the Alkenyl Sulfoxides (3a–d).
2-[4,4-Bis(ethoxycarbonyl)-2-(phenylsulfinyl)butyl]phenol (5a). A solution of **3a** (1.0 g, 3.87 mmol) in absolute EtOH (1 ml) was added to a solution of diethyl sodiomalonate (1.24 g, 7.75 mmol) in absolute EtOH (2.5 ml) and the mixture heated under N_2 in EtOH vapor jacket (ca. 80 °C) for 14 h. The EtOH was evaporated and the residue, after acidification with H_2SO_4 (2 M), was extracted with CH_2Cl_2 (60 ml) and washed with H_2O once. After drying ($MgSO_4$) the organic layer, the solvent was evaporated to yield an oily residue which crystallized upon addition of ether. Recrystallization [CH_2Cl_2 –petroleum ether (40:60)] yielded pure **5a** (955 mg, 59%) as a cream colored powder that was racemic modification; mp 127–130 °C; IR (KBr) 3240 (OH, broad), 1735 ($>S=O$, broad, W. 1/2 1.5 cm), 1030 ($>S=O$) cm^{-1} ; 1H NMR δ =0.9–1.40 (m, 6H, $2\times CH_3$), 2.0–2.30 (m, 2H, $H_2C-C(CO_2Et)_2$), 2.7–3.2 (m, 3H, $-CH_2CHSOPh$), 3.3–3.7 (m, 1H, $-CH(CO_2Et)_2$), 3.9–4.4 (m, 4H, $2\times -OCH_2-$), 6.4–7.30 (m, 4H, ArH), 7.35–7.80 (m, 6H, $-SOPh$ and OH); MS m/z 292 ($M-PhSOH$). Found: C, 63.1; H, 6.1; S, 7.5%. Calcd for $C_{22}H_{26}O_6S$: C, 63.16; H, 6.22; S, 7.65%.

2-[3-[2-(Ethoxycarbonyl)ethylamino]-2-(phenylsulfinyl)propyl]phenol (5b). A solution of **3a** (1.13 g, 4.38 mmol) in absolute EtOH (2 ml) was added to a solution of 2-(ethoxycarbonyl)ethylammonium chloride (700 mg, 4.56 mmol) in absolute EtOH (13 mmol) containing triethylamine (0.7 ml, 1 equiv). The reaction was conducted in an analogous manner to above to yield crude oily product which was purified by column chromatography [(a) ether (b) ether–EtOH (2:1)] to give **5b** (1.07 g, 65%) as a pale brown oil; IR (neat) 3440 (NH), 3300 (OH), 1730 ($>S=O$) cm^{-1} ; 1H NMR δ =1.23 (t, $J=7$ Hz, 3H, CH_3), 2.3–2.8 (m, 5H, $-CH_2CHSOPh-$ and $-CH_2CO_2Et$), 2.8–3.2 (m, 4H, $-CH_2-N-CH_2-$), 4.10 (q, $J=7$ Hz, 2H, $-OCH_2-$), 6.7–7.3 (m, 5H, ArH and OH), 7.33–7.76 (m, 5H, $-SOPh$). Found: C, 63.8; H, 6.6; N, 3.6; S, 8.5%. Calcd for $C_{20}H_{25}NO_4S$: C, 64.00; H, 6.67; N, 3.78; S, 8.53%.

2-[3-[Ethoxycarbonyl)methylthio]-2-(phenylsulfinyl)propyl]phenol (5c). In a similar manner to above the alkenyl sulfoxide **3a** (620 mg, 2.40 mmol), sodium ethoxide (2.4 mmol) and ethyl mercaptoacetate (0.6 ml, an excess) in EtOH (1.5 ml) yielded an oily mixture which was chromatographed [(a) (1:1) ether–petroleum ether (40:60) (b) ether] to yield **5c** (745 mg, 82%) as a light brown oil; IR (neat) 3400 (OH, broad), 1740 ($>C=O$), 1025 ($>S=O$) cm^{-1} ; 1H NMR δ =1.26 (t, $J=7$ Hz, 3H, CH_3), 2.2–2.5 (m, 2H, $-CH_2S-$), 2.66–3.30 (m, 3H, $ArCH_2CHSO$), 3.45 (s, 2H, $-SCH_2CO_2Et$), 4.13 (q, $J=7$ Hz, 2H, $-OCH_2-$), 6.6–7.3 (m, 4H, ArH), 7.3–7.6 (m, 5H, $-SOPh$), 7.9 (s, 1H, OH). Found: C, 60.2; H, 5.6; S, 16.8%. Calcd for $C_{19}H_{22}O_4S_2$: C, 60.32; H, 5.82; S, 16.93%.

2-[3-Ethoxy-2-(phenylsulfinyl)propyl]-4-methoxyphenol (5d). This was obtained in a similar manner from **3d** (630 mg, 20.19 mmol) and sodium ethoxide (2.2 mmol) in EtOH (16 ml) as an oil (548 mg, 75%) after column chromatography [ether]; IR (neat) 3320 (OH), 1030 ($>S=O$) cm^{-1} ; 1H NMR δ =1.27 (m,

3H, CH_3), 2.3–2.8 (m, 3H, $-OCH_2CHSO$), 3.76, (s, 3H, $-OCH_3$), 6.4–7.0 (m, 3H, PhH), 7.3–7.6 (m, 6H, $-SOPh$ and OH); MS m/z 334 (M^+). Found: C, 64.6; H, 6.4; S, 9.4%. Calcd for $C_{18}H_{22}O_4S$: C, 64.67; H, 6.59; S, 9.59%.

2-Bromo-2-propenyl-4-methoxy-2-(2-phenylsulfinyl-2-propenyl)phenyl Ether (6a). This was made by the Williamson synthesis from **3c** (1.35 g, 4.69 mmol), 2,3-dibromo-1-propene (1.1 g, 5.5 mmol) and sodium ethoxide (4.69 mmol) in EtOH (25 ml) to give, after chromatography [ether], **6a** (1.24 g, 68%) as a dark gum; IR (neat) 1040 cm^{-1} ; 1H NMR δ =3.25 (d, $J=17$ Hz, 1H, diastereotopic $-OCH-$), 3.45 (d, $J=17$ Hz, 1H, diastereotopic $-OCH-$), 3.70 (s, 3H, $-OCH_3$), 4.45 (s, 2H, $-OCH_2-$), 5.36 (s, 1H, $-C=CH$ *trans* to Br), 5.60 (s, 1H, $C=CH$ *cis* to Br), 5.80 (s, 1H, $-C=CH$ *trans* to $-SOPh$), 6.10, (s, 1H, $-C=CH$ *cis* to $SOPh$), 6.56 (s, 1H, ArH-3), 6.70 (s, 2H ArH-5,6), 7.50 (m, 3H, $-SOPh$), 7.66 (m, 2H, *ortho* $SOPh$); MS m/z 408 ($M+1$, 4%), 280 (58), 161 (1). Found: C, 55.8; H, 4.5; S, 7.6%. Calcd for $C_{19}H_{19}O_3SBr$: C, 56.02; H, 4.67; S, 7.86%.

4-Methoxy-2-(2-phenylsulfinyl-2-propenyl)phenyl 2-Phenylsulfinyl-2-propyl Ether (6b). 3-Bromo-2-phenylsulfinyl-1-propene (650 mg, 2.6 mmol) was reacted in a similar manner to above with a solution of **3c** (730 mg, 2.53 mmol) and sodium ethoxide (2.53 mmol) in EtOH (15 ml) to give, after chromatographic purification [(a) ether (b) ether : MeOH (2:1:1)], **6b** (1.03 g, 90%) as a thick dark oil; IR (neat) 1030 ($>S=O$) cm^{-1} ; 1H NMR δ =3.08 (d, $J=15$ Hz, 1H, diastereotopic $-CH-$), 3.40, (d, $J=15$ Hz, 1H, diastereotopic $-CH-$), 3.66 (s, 3H, $-OCH_3$), 4.15 (d, $J=16$ Hz, 1H, diastereotopic $-OCH-$), 4.56 (d, $J=16$ Hz, 1H, diastereotopic $-OCH-$), 5.27 (fine t, $J=2$ Hz, 1H, $-C=CH$ *trans* to $SOPh$ in allylic group), 5.77 (fine t, $J=2$ Hz, 1H, $-C=CH$ *trans* to $SOPh$ in allyloxy group), 6.05 (s, 1H, $-C=CH$ *cis* to $SOPh$ in allyloxy group), 6.13 (s, 1H, $-C=CH$, *cis* to $SOPh$ in allyloxy group), 6.4–6.75 (m, 3H, ArH-3,5,6), 7.35–7.75 (m, 10H, $-SOPh$); MS m/z 452 (M^+ , 12%), 327 (42), 200 (100). Found: C, 66.1; H, 5.1; S, 13.9%. Calcd for $C_{25}H_{24}O_4S_2$: C, 66.38; H, 5.31; S, 14.16%.

The Claisen Rearrangement Reactions of 6a and 6b. **2-(2-Bromo-2-propenyl)-4-methoxy-6-(2-phenylsulfinyl-2-propenyl)phenol (7a).** A solution of **6a** (1.0 g, 2.46 mmol) in mesitylene (15 ml) was rearranged in the previously mentioned manner to yield, after chromatography [ether], **7a** (650 mg, 65%) as dark brown oil; IR (neat) 3240 (OH, broad), 1040 ($>S=O$) cm^{-1} ; 1H NMR δ =3.12 (d, $J=17$ Hz, 1H, $-CH-C(SOPh)$), 3.45 (d, $J=17$ Hz, 1H, $-CH-CSOPh$), 3.6–3.8 (m, 5H, $-CH_2-CBr=C$ and OCH_3), 5.45 (s, 1H, *trans* $-CBr=CH$), 5.52 (s, 1H, *cis* $-CBr=CH$), 5.74 (s, 1H, *trans* $-OSPhC=CH$), 6.02 (s, 1H, *cis* $-OSPhC=CH$), 6.47 (m, 1H, ArH-3), 6.65 (m, 1H, ArH-5), 7.25 (s, 1H, OH), 7.44 (m, 3H, $-SOPh$), 7.55 (m, 2H, *ortho* $-SOPh$). Found: C, 55.7; H, 4.5; S, 7.6%. Calcd for $C_{19}H_{19}O_3SBr$: C, 56.02; H, 4.67; S, 7.86%.

7-(2-Bromo-2-propenyl)-5-methoxy-2-methylbenzofuran (8a). Repeating the above reaction for **6a** (1.0 g) in the presence of SiO_2 (Fluka 60H) (ca. 1 g) in the reaction mixture gave **8a** (476 mg, 69%); IR (neat) 1620 (s), 1595 (m), 1490 (s), 1440 (s), 1225, 1215 (s) cm^{-1} ; 1H NMR δ =2.25 (s, 3H, CH_3), 3.70 (s, 3H, $-OCH_3$), 3.83–4.15 (m, 2H, $-CH_2-CBr=C$), 5.47 (s, 1H, *trans* $-CBr=CH$), 5.54 (s, 1H, *cis* $-CBr=CH$), 6.37 (s, 1H, ArH-3), 6.60–6.93 (m, 2H, ArH-4,6). MS m/z 281 (M^+ , 100%), 200 (8), 185 (13). Found: C, 55.3; H, 4.3%. Calcd for $C_{13}H_{13}O_2Br$: C, 55.5; H, 4.63%.

4-Methoxy-2,6-bis(2-phenylsulfinyl-2-propenyl)phenol (7b). A solution of **6b** (100 mg, 0.22 mmol) in mesitylene (2 ml) was

rearranged as above to give, after chromatography [(a) ether, (b) ether-MeOH (3:1)], **7b** (72 mg, 72%) as a thick dark oil; ^1H NMR $\delta=2.30$ (s, 1H, -OH), 3.15 (d, $J=16$ Hz, 2H, -CH-CSOPh), 3.45 (d, $J=16$ Hz, 2H, -CH-CSOPh), 3.70 (s, 3H, OCH₃), 5.63 (s, 2H, *trans* -SOPhC=CH), 6.08 (s, 2H, *cis* -SOPhC=CH), 6.45 (s, 2H, ArH-3,5), 7.4–7.9 (m, 10H, -SOPh); MS m/z 452 (M^+ , 6%), 327 (M -SOPh, 44), 202 (13), 201 (55), 200 (100), 185 (30). Found m/z (M^+) 452.5852. Calcd for C₂₅H₂₄O₄S₂: M, 452.5822. Rearrangement of **6b** in DCB yielded an oily residue which upon addition of ether partially crystallized to yield an unidentifiable dark brown solid as flakes, mp 170–172 °C (decomp); IR (KBr) 3450, 2925, 1650 (s), 1510 (s), 1490 (s), 1260 (s), 1110 (s), 830 (m), 770 (m) cm⁻¹. The solid was soluble in CHCl₃; ^1H NMR $\delta=1.55$ (s), 3.2–4.0 (broad peak), 7.2–7.5 (broad peak); ^{13}C NMR $\delta=8.58$, 15.24, 28.14, 45.96, 55.63, 55.86, 114.82, 120.8, 124.74, 129.20, 131.08. MS proved difficult to measure.

5-Methoxy-2-methyl-7-(2-phenylsulfinyl-2-propenyl)-benzofuran (8b). Rearrangement of **6b** (100 mg) in mesitylene (2 ml) in the presence of SiO₂ (Fluka 60H) (ca. 50 mg) yielded **8b** (37 mg, 51%) after chromatography [(a) petroleum ether (40:60), (b) ether], as a brown oil; ^1H NMR $\delta=2.50$ (d, $J=2$ Hz, 3H, CH₃-2), 3.10 (d, $J=16$ Hz, 1H, CH-7), 3.45 (d, $J=16$ Hz, 1H, -CH'-7), 3.65 (s, 3H, -OCH₃), 5.65 (s, 1H, *trans* -SOPhC=CH), 6.10 (s, 1H, *cis* -SOPhC=CH), 6.40 (q, $J=2$ Hz, 1H, H-3), 6.75–7.0 (m, 2H, H-4,6), 7.4–7.8 (m, 5H,

-SOPh); MS m/z 326 (M^+ ; 12), 200 (100). Found: m/z 326.4118. Calcd for C₁₉H₁₈O₃S: M, 326.4094.

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