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

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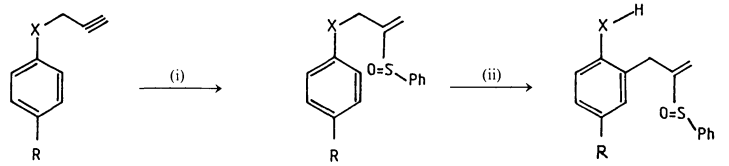
The hitherto unknown Claisen rearrangement of 2-phenylsulfinyl-2-propenyl phenyl ethers to the corresponding 2-(2-phenylsulfinyl-2-propenyl)phenols is reported. The latter compounds underwent Michael reactions with a variety of nucleophiles to provide functionalized phenolic adducts. *O*-Alkylation of 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 rearrangement[1] 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%). ^{1}H 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 (δ=4.1—4.5 in starting materials **2a**—**d**) to high field (δ=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*]thiophens and 2-methylbenzofurans have previously been obtained from the Claisen rearrangement of 2-chloro-2-propenyl



1 (**a**) R=H, X=O
(**b**) R=Cl, X=O
(**c**) R=CH_3, X=O
(**d**) R=OCH_3, X=O
(**e**) R=H, X=S
(**f**) R=H, X=NEt
(**g**) R=CH_3, X=NH

2 (**a**) R=H, X=O
(**b**) R=Cl, X=O
(**c**) R=CH_3, X=O
(**d**) R=OCH_3, X=O
(**e**) R=H, X=S
(**f**) R=H, X=NEt
(**g**) R=CH_3, X=NH

3 (**a**) R=H, X=O
(**b**) R=CH_3, X=O
(**c**) R=OCH_3, X=O
(**d**) R=Cl, X=O

Scheme 1. Reagents: (i) $PhS\overset{O}{\overset{\|}{C}}H_2CH_2CN$, 110 °C, under N_2. (ii) As solutions in mesitylene or 1,2-dichlorobenzene, 180 °C (oil bath), 18—24 h, under N_2.

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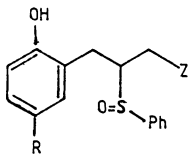

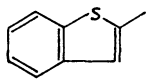

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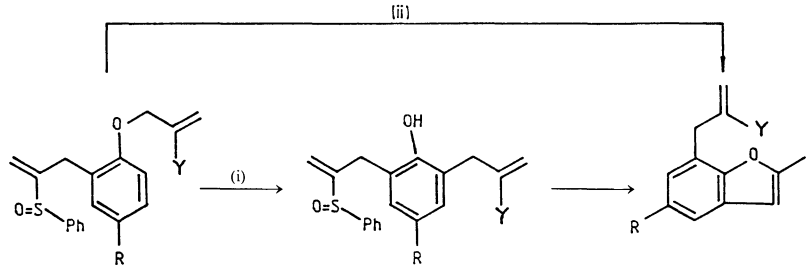
5 (a) R=H, Z=$CH(CO_2Et)_2$
(b) R=H, Z=$NH(CH_2)_2CO_2Et$
(c) R=H, Z=$-SCH_2CO_2Et$
(d) R=OCH_3, Z=OEt



6 (a) R=OCH_3, Y=Br
(b) R=OCH_3, Y=SOPh

7 (a) R=H, Y=Br
(b) R=OCH_3, Y=SOPh

8 (a) R=H, Y=Br
(b) R=OCH_3, Y=SOPh

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-propene[2] 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≡C–), 2115 (–C≡C–) cm^{-1}; ^1H NMR δ=2.50

(1H, t, J=2 Hz acetylenic proton), 4.60 (2H, d, J=2 Hz, $-OCH_2-$), 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 C_9H_7OCl: 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 (HC≡C–), 2110 (–C≡C–) cm^{-1}; ^{1}H NMR δ=2.23 (3H, s, $-CH_3$), (1H, t, J=2 Hz, acetylenic proton), 4.57 (2H, d, J=2 Hz, $-OCH_2-$), 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 $C_{10}H_{10}O$: 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 (HC≡C–), 2125 (–C≡C–) cm^{-1}; ^{1}H NMR δ=2.45 (1H, t, J=2 Hz, acetylenic proton), 3.63 (3H, s, $-OCH_3$), 4.50 (2H, d, J=2 Hz, $-OCH_2-$), 6.73 (4H, m, ArH). Found: C, 74.0; H, 6.1%. Calcd for $C_{10}H_{10}O_2$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=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 –SOPh), 6.25 (1H, s, olefinic proton *cis* to –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, –SOPh); MS m/z 293 (M$^+$), 277, 167, 126. Found: C, 61.3; H, 4.3%. Calcd for $C_{15}H_{13}O_2SCl$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=2.25 (3H, s, $-CH_3$), 4.30 (1H, d, J=13.5 Hz, diastereotopic allylic proton), 4.68 (1H, d, J=13.5 Hz, diastereiotopic allyl proton), 5.93 (1H, s, olefinic proton *trans* to –SOPh), 6.20 (1H, s, olefinic proton *cis* to –SOPh), 6.63 (2H, d, J=8 Hz, ArH *ortho* to oxygen), 7.0 (2H, d, J=8 Hz, ArH *ortho* CH_3), 7.36—7.75 (5H, m, –SOPhH); MS m/z 272. Found: C, 70.4; H, 5.8%. Calcd for $C_{16}H_{16}O_2S$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=3.70 (3H, s, $-OCH_3$), 4.33 (1H, d, J=14.5 Hz, –OCH–), 4.65 (1H, d, J=14.5 Hz, –OCH–), 5.95 (1H, s, olefinic H *trans* to –SOPh), 6.23 (1H, s, olefinic H *cis* to –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 $C_{16}H_{16}O_3S$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=3.10 (d, J=16 Hz, 1H, diastereotopic allylic –OCH–), 3.50 (d, J=16 Hz, 1H, diastereotopic allylic –OCH–), 5.65 (s, 1H, olefinic H *trans* to –SOPh), 6.00 (s, 1H, olefinic H *cis* to SOPh), 6.6—7.20 (m, 4H, ArH), 7.25—7.90 (m, 3H, –SOPh); MS m/z 258 (M$^+$), 218, 131 (100%). Found: C, 69.6; H, 5.3; S, 12.3%. Calcd for $C_{15}H_{14}O_2S$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=3.05 (d, J=15 Hz, 1H, –OCH–), 3.45 (d, J=15 Hz, 1H, –OCH–), 5.63 (s, 1H, olfefinic 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, –SOPh); MS m/z 292 (M$^+$), 277, 165 (100%), 126. Found: C, 61.4; H, 4.3; S, 11.0%. Calcd for $C_{15}H_{13}O_2SCl$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=2.15 (d, J<2 Hz, 3H, CH_3), 3.12 (d, J=15 Hz, 1H, –OCH–), 3.53 (d, J=15 Hz, 1H, –OCH–), 5.70 (s, 1H, olefinic H *trans* to SOPh), 6.05 (s, 1H, olefinic H *cis* to –SOPh), 6.65—7.05 (m, 3H, ArH), 7.4—7.7 (m, 5H, –SOPh); MS m/z 272 (M$^+$). Found: C, 70.5; H, 5.7; S, 11.6%. Calcd for $C_{16}H_{16}O_2S$: 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 (>S=O) cm^{-1}; ^{1}H NMR δ=3.13 (d, J=16 Hz, 1H, –OCH–), 3.45 (d, J=16 Hz, 1H, –OCH–), 3.67 (s, 3H, $-OCH_3$), 5.67 (s, 1H, olefinic H *trans* to –SOPh), 6.07 (s, 1H, olfefinic H *cis* to –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, –SOPh), 7.55—7.70 (m, 2H, –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 ^{1}H NMR with that reported in the literature. The other product obtained from column chromatography of reaction mixture was *S*-phenyl benzenethiosulfinates (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}; ^{1}H NMR δ=0.9—1.40 (m, 6H, 2×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×-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}; ^{1}H 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}; ^{1}H 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, $ArCH_2$CHSO), 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}; ^{1}H 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}; ^{1}H 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}; ^{1}H 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 Rearragement 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}; ^{1}H NMR δ=3.12 (d, *J*=17 Hz, 1H, -CH-CSOPh), 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}; ^{1}H 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; ^{1}H NMR δ=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, OCH_3), 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 $C_{25}H_{24}O_4S_2$: 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 $CHCl_3$; ^{1}H NMR δ=1.55 (s), 3.2—4.0 (broad peak), 7.2—7.5 (broad peak); ^{13}C NMR δ=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 SiO_2 (Fluka 60H) (ca. 50 mg) yielded **8b** (37 mg, 51%) after chromatography [(a) petroleum ether (40 : 60), (b) ether], as a brown oil; ^{1}H NMR δ=2.50 (d, J=2 Hz, 3H, CH_3-2), 3.10 (d, J=16 Hz, 1H, CH-7), 3.45 (d, J=16 Hz, 1H, -CH'-7), 3.65 (s, 3H, -OCH_3), 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. Cacld for $C_{19}H_{18}O_3S$: M, 326.4094.

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