Thermal Decomposition of some Allyl Methoxyarenesulphinates

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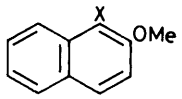
The thermal decomposition of some allyl methoxyarenesulphinates in boiling acetic acid has been studied. The principal products are the diaryl sulphides together with small amounts of the aryl arenethiosulphonates, diaryl sulphoxides, diaryl sulphones, aromatic hydrocarbons, and, in one case, some of the allyl aryl sulphone.

The thermal rearrangement of alkyl (usually allyl) arenesulphinates to alkyl aryl sulphones has been the subject of numerous mechanistic studies[1] but has also found application in synthesis.[2] These studies have used arenesulphinates substituted on the benzene ring with electron-withdrawing or weakly electron-donating groups. The presence of a strongly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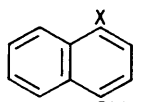
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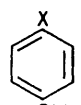
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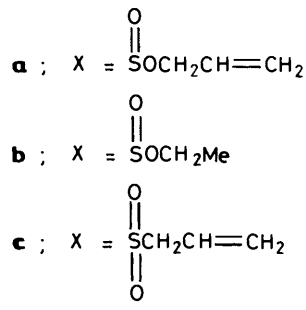

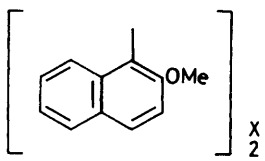
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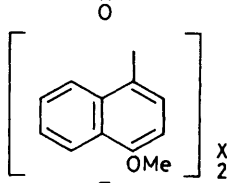
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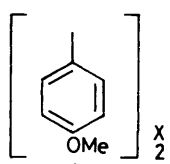
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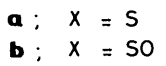

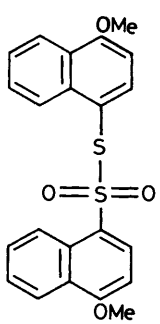
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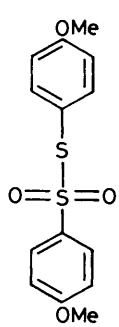
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electron-donating group (*e.g.*, methoxy) on the ring might be expected to alter the course of the reaction by facilitating S–O bond cleavage at the expense of the usual O–alkyl bond cleavage.

The recent discovery[3] of the direct chlorosulphination of certain aromatic methyl ethers to the methoxyarenesulphinyl chlorides has made the corresponding allyl esters readily accessible. Thus, it was of interest to study the thermal behaviour of some of these allyl methoxyarenesulphinates.

Results and Discussion

The allyl ester (**1a**) underwent smooth decomposition in refluxing acetic acid with evolution of sulphur dioxide in less than 25 min to yield a mixture of products, readily separated by column chromatography. The major component (64%) was identified as the diaryl sulphide (**4a**). The presence of one sulphur atom was indicated by the isotopic clusters of the molecular ion at *m/z* 346 and confirmed by microanalysis. The symmetrical nature of the compound was evident from the ^1H and ^{13}C (11 lines) n.m.r. spectra. The minor components were shown to be 2-methoxynaphthalene (18%), the diaryl sulphoxide (**4b**) (3%), and the diaryl sulphone (**4c**) (8%).

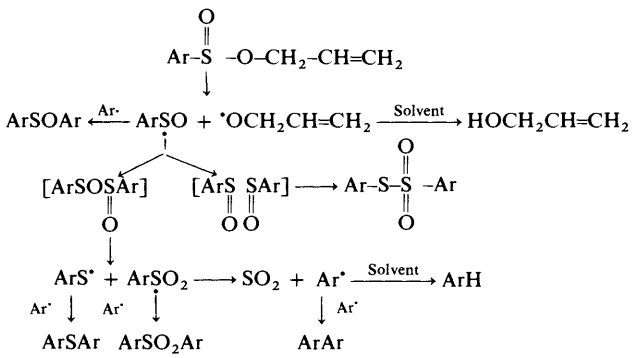
The structures of the latter two components were confirmed by synthesis. Thus, treatment of the Grignard reagent from 1-bromo-2-methoxynaphthalene with bis(imidazol-1-yl) sulphoxide[4] gave the sulphoxide (**4b**) which on oxidation with hydrogen peroxide in acetic acid[5] gave the sulphone (**4c**). Variation of the reaction solvent to toluene or *N,N*-dimethylformamide or use of the ethyl ester (**1b**) gave a t.l.c. profile similar to the original reaction in acetic acid. In the latter reaction none of the ethyl aryl sulphone (**1d**), independently prepared from the corresponding sulphinic acid, was detected.

Heating the allyl ester (**2a**) in acetic acid similarly yielded mostly the diaryl sulphide (**5a**) (55%) together with small amounts of 1-methoxynaphthalene (1.5%), the diaryl sulphoxide (**5b**) (5%), the diaryl sulphone (**5c**) (6%), and a new component (25%) identified as the thiosulphonate (**7**). The latter showed two methoxy absorptions in both the ^1H and ^{13}C n.m.r. spectra. Isotopic clusters of the molecular ion at *m/z* 378 showed the presence of two sulphur atoms, verified by microanalysis. I.r. absorptions at 1 320, 1 140, and 1 120 cm^{-1}, typical of this class of compound,[6] confirmed the assigned structure. The structures of the sulphoxide (**5b**) and the sulphone (**5c**) were confirmed by synthesis from 4-bromo-1-methoxynaphthalene as before. Thermal decomposition of the ethyl ester (**2b**) gave the same products. Again no ethyl aryl sulphone (**2d**) was detected.

The allyl *p*-methoxyphenyl derivative (**3a**) showed thermal behaviour intermediate between that of the two previous cases and the more usual course of the reaction. Thus, as well as anisole (9%), the diaryl sulphide (**6a**) (32%), the diaryl sulphoxide (**6b**) (5%), the diaryl sulphone (**6c**) (5%), and the aryl arenethiosulphonate (**8**) (26%), a substantial amount (19%) of the allyl sulphone (**3c**) was isolated. Also detected by g.l.c. were allyl alcohol and traces of allyl acetate and 4,4′-dimethoxybiphenyl.

Apart from the sulphone (**3c**) formed by the usual rearrangement,[1] the other products of the reactions are typically those expected[7] from the intermediacy of sulphinyl radicals as suggested in Scheme 1. The isolated products of these reactions as well as sulphones (**1d**) and (**2d**) were shown in themselves to be thermally stable except the sulphoxide (**4b**) which underwent a slow disproportionation (> 6 h in acetic acid at reflux) to the sulphide (**4a**) and sulphone (**4c**). However, this would be a minor pathway to the latter two compounds as the decomposition of the sulphinate (**1a**) takes place much more rapidly.

The high proportion of sulphides formed in these reactions, especially in the naphthalene cases, shows the ability of the methoxy group to stabilize particularly the arylsulphenyl radical. Similar stabilization of these radicals by electron releasing groups has been demonstrated in other systems.[8]



Scheme 1.

Experimental

^1H (90 MHz) and ^{13}C (22.49 MHz) N.m.r. spectra were recorded on a Jeol FX90Q instrument; ^1H (300 MHz) spectra were measured on a Bruker instrument at the Brisbane N.M.R. Centre; [^2H]chloroform was used as solvent with tetramethylsilane as an internal reference. I.r. spectra were measured with a Hitachi 260-10 instrument; polystyrene lines were used for calibration. Electron-impact mass spectra were measured by Mr. N. G. Keats with an AEI MS 30 instrument. G.l.c. employed a Packard 427 chromatograph with a 1 m 3% OV-1 on Chromosorb W column with a flow rate of 25 ml min^{-1}. Eastman Chromagram silica gel sheets were used for t.l.c. Microanalyses were by the Australian Microanalytical Service and the Australian National University.

Preparation of the Sulphinate Esters.—2-Methoxynaphthalene-1-sulphinyl chloride[3] (3.00 g, 12.5 mmol) was added to a stirred mixture of allyl alcohol (1.45 g, 25 mmol), pyridine (1.0 ml), and benzene (30 ml) at room temperature. The initial yellow colour was discharged within 5 min and stirring was continued for a further 30 min. The solution was washed with cold portions of water, 1M HCl (10 ml), 0.05M Na_2CO_3 (10 ml), water, and brine, and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure at < 35 °C leaving a colourless oil (3.12 g, 95%) which solidified with time, m.p. 87—91 °C. Recrystallization from light petroleum (b.p. 40—50 °C) gave colourless flakes of *allyl 2-methoxynaphthalene-1-sulphinate* (**1a**), m.p. 94—95 °C (decomp.) (Found: C, 64.0; H, 5.2; S, 12.1. $C_{14}H_{14}O_3S$ requires C, 64.1; H, 5.4; S, 12.1%); $\nu_{max.}$($CHCl_3$) 1 620 (C=C) and 1 128 cm^{-1} (SO); δ_H(300 MHz) 9.10 (1 H, dd, *J* 8.0 and 1.3 Hz, 8-H), 8.01—7.21 (5 H, m, ArH), 6.06—5.19 (3 H, m, CH_2=CH), 4.68 (2 H, d, *J* 7 Hz, CH_2), and 4.01 (3 H, s, OMe).

Similarly prepared from 4-methoxynaphthalene-1-sulphinyl chloride[3] was *allyl 4-methoxynaphthalene-1-sulphinate* (**2a**) (94% yield) as a colourless oil which decomposed on attempted distillation under high vacuum (Found: M^+, 262.0638. $C_{14}H_{14}O_3S$ requires *M*, 262.0664); $\nu_{max.}$($CHCl_3$) 1 630 (C=C) and 1 130 cm^{-1} (SO); δ_H(300 MHz) 8.31 (1 H, dd, *J* 8.0 and 1.3 Hz, 5- or 8-H), 8.20 (1 H, dd, *J* 8.0 and 1.3 Hz, 5- or 8-H), 8.06 (1 H, d, *J* 8 Hz, 2-H), 7.62—7.49 (2 H, m, 6- and 7-H), 6.90 (1 H, d, *J* 8 Hz, 3-H), 5.76 (1 H, m, =CH–), 5.16 (2 H, m, =CH_2), 4.50 and 4.00 (1 H, both dd, CH_2), and 4.06 (3 H, s, OMe).

Ester (**3a**) was prepared in four steps from anisole by first chlorosulphonation[9] to 4-methoxybenzenesulphonyl chloride (62% yield), b.p. 93—95 °C at 0.05 mmHg (lit.,[9] 103—105 °C at 0.25 mmHg). Reduction with aqueous alkaline sodium sulphite[10] gave the sulphinic acid (86%), m.p. 96—98 °C (lit.,[10]

97—98 °C). The sulphinic acid (3.44 g, 0.002 mol) was stirred at room temperature with a solution of thionyl chloride (2.98 g, 0.025 mol) in chloroform (20 ml). Vigorous evolution of SO_2 and HCl ensued and a yellow solution was obtained. This solution of the sulphinyl chloride was cooled in an ice-bath to 5—10 °C and a solution of allyl alcohol (1.74 g, 0.03 mol) and pyridine (2.5 ml) in chloroform (10 ml) was added. The yellow colour was discharged rapidly. Stirring was continued for 1 h then the solution was washed with cold water, ice-cold 3M HCl (30 ml), cold 0.5M Na_2CO_3 (20 ml), water, brine, and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure < 30 °C gave *allyl* 4-*methoxybenzenesulphinate* (**3a**) (3.8 g, 90%) as a colourless oil which could not be distilled without appreciable decomposition (Found: M^+, 212.0480. $C_{10}H_{12}O_3S$ requires M, 212.0507); $\nu_{max.}$(film) 1 630 (C=C) and 1 125 cm^{-1} (SO); δ_H(90 MHz) 7.66, 7.04 (4 H, AA'BB' pattern, J 8 Hz, 2-H, 3-H), 6.10—5.15 (3 H, m, CH=CH_2), 4.18 (2 H, d, J 5 Hz, CH_2), and 3.84 (3 H, s, OMe); δ_C 162.70 (C-4), 132.47, 131.84 (C-1), 127.06, 119.11, 114.38, 64.70 (OCH_2), and 55.53 (OMe).

Preparation of Sulphoxides (**4b**), (**5b**), *and* (**6b**).—The Grignard reagent from 4-bromo-1-methoxynaphthalene[11] (15.8 g, 0.067 mol) and Mg (1.94 g, 0.085 mol) in tetrahydrofuran (120 ml) was prepared. To this stirred solution was added dropwise a solution of bis(imidazol-1-yl) sulphoxide prepared from thionyl chloride (4.0 g, 0.033 mol) and imidazole (9.07 g, 0.13 mol) in tetrahydrofuran[4] (120 ml). The mixture was stirred at room temperature for 3 h then poured into ice-water (400 ml) containing 10M HCl (30 ml). The liberated yellow oil was taken into benzene (200 ml) and the aqueous layer was extracted with additional benzene (100 ml). The combined benzene extracts were washed with 1M NaOH (100 ml) (the solution turns blue), water, and brine, and dried ($MgSO_4$). Evaporation of the solvent left a blue oil which partially solidified with time. Recrystallization from benzene–light petroleum gave colourless needles of *bis*(4-*methoxy*-1-*naphthyl*) *sulphoxide* (**5b**) (13.9 g, 58%), m.p. 156—157 °C (Found: C, 72.7; H, 4.9; S, 8.9. $C_{22}H_{18}O_3S$ requires C, 72.9; H, 5.0; S, 8.9%); $\nu_{max.}$(Nujol) 1 080 and 1 040 cm^{-1} (SO); δ_H(300 MHz) 8.30—8.22 (2 H, complex m, ArH), 7.90 (1 H, d, J 8 Hz, 2-H), 7.51—7.47 (2 H, complex m, ArH), 6.84 (1 H, d, J 8 Hz, 3-H), and 3.99 (3 H, s, OMe); δ_C 158.17 (C-4), 131.01, 130.72, 127.94, 126.87, 125.89, 125.65, 122.96, 122.43, 103.51, and 55.73 (OMe); m/z 346 (100%, M − O), 331 (16, M − OMe), 218 (30), 205 (15, $MeOC_{10}H_6SO$), 189 (37, $MeOC_{10}H_6S$), 158 (22), 114 (35), and 83 (57).

Similarly, from 1-bromo-2-methoxynaphthalene was obtained *bis*(2-*methoxy*-1-*naphthyl*) *sulphoxide* (**4b**) (64%), m.p. 144—145 °C (from $MeCO_2H$) (Found: C, 72.7; H, 5.0; S, 9.2. $C_{22}H_{18}O_3S$ requires C, 72.9; H, 5.0; S, 8.9%); $\nu_{max.}$(Nujol) 1 040 cm^{-1} (S=O); δ_H(300 MHz) 9.34 (1 H, dd, J 8.5 and 1.5 Hz, 8-H), 7.85 (1 H, d, J 9 Hz, 4-H), 7.76 (1 H, dd, J 8.5 and 1.5 Hz, 5-H), 7.59, 7.40 (2 H, both split t, J 8 Hz and 1.5 Hz, 6- and 7-H), 7.09 (1 H, d, J 9 Hz, 3-H), and 3.49 (3 H, s, OMe); δ_C 155.10 (C-2), 133.05, 131.20, 128.07, 127.09, 125.41, 123.95, 112.95, and 56.12 (OMe); m/z 346 (35%, M − O), 300 (10), 157 (100, $MeOC_{10}H_6$), and 115 (65).

Bis(4-methoxyphenyl) sulphoxide (**6b**) was obtained in 59% yield as described,[4] m.p. 92—93 °C (from acetone) (lit.,[4] 97—98.5 °C and lit.,[12] 93—94 °C); δ_H (300 MHz) 7.54, 6.95 (4 H, AA'BB', J 9 Hz and 2 Hz, 2-H, 3-H), and 3.81 (3 H, s, OMe); δ_C 161.78 (C-4), 137.01 (C-1), 126.87 (C-2), 114.68 (C-3), and 55.48 (OMe).

Preparation of Sulphones (**4c**), (**5c**), *and* (**6c**).—The sulphoxide (**4b**) (1.1 g) was dissolved in glacial acetic acid (60 ml) by warming on a hot-plate. 30% Hydrogen peroxide (5 ml) was added and the mixture was heated at the boil for 10 min. Additional peroxide (5 ml) was added and the boiling was continued for a further 10 min. The mixture was diluted with water (30 ml), cooled, and colourless crystals were deposited. These were filtered off, washed with water, and dried. Recrystallization from chloroform gave colourless needles of *bis*(2-*methoxy*-1-*naphthyl*) *sulphone* (**4c**) (1.01 g, 88%), m.p. 184—188 °C (decomp.) (Found: C, 69.5; H, 4.7; S, 8.7. $C_{22}H_{18}O_4S$ requires C, 69.8; H, 4.8; S, 8.5%); $\nu_{max.}$($CHCl_3$) 1 348 and 1 155 cm^{-1} (SO_2); δ_H(300 MHz) 9.85 (1 H, dd, J 8.5 and 1.0 Hz, 8-H), 8.15 (1 H, d, J 9 Hz, 4-H), 8.00 (1 H, dd, J 8 and 1.5 Hz, 5-H), 7.87, 7.65 (2 H, both m, 6-H, 7-H), 7.32 (1 H, d, J 9 Hz, 3-H), and 3.61 (3 H, s, OMe); δ_C 157.73 (C-2), 135.40, 131.50, 128.86, 128.38, 124.28, 113.75, and 56.90 (OMe); m/z 380 (M + 2, M + 2/M, 7.9. $C_{22}H_{18}O_4S$ requires M + 2/M, 8.0%), 378 (M, 40%), 314 (72, M − SO_2), 313 (100), 282 (90), 205 (5, $MeOC_{10}H_6SO$), 189 (10, $MeOC_{10}H_6S$), 157 (25, $MeOC_{10}H_6$), 142 (50), and 127 (80).

Similarly obtained was *bis*(4-*methoxy*-1-*naphthyl*) *sulphone* (**5c**) (82%), m.p. 230—231 °C (from chloroform–light petroleum) (Found: C, 69.7; H, 5.1; S, 8.5. $C_{22}H_{18}O_4S$ requires C, 69.8; H, 4.8; S, 8.5%); $\nu_{max.}$($CHCl_3$) 1 332 and 1 155 cm^{-1} (SO_2); δ_H(300 MHz) 8.54 (1 H, d, J 8 Hz, 2-H), 8.48 (1 H, dd, J 8.5, 1.5 Hz, 5-H or 8-H), 8.23 (1 H, dd, J 8.5 and 1.5 Hz, 5- or 8-H), 7.52—7.39 (2 H, complex m, 6-H, 7-H), 6.87 (1 H, d, J 8 Hz, 3-H), and 4.02 (3 H, s, OMe); δ_C 160.07 (C-4), 131.60, 129.69, 128.43, 126.04, 125.94, 124.18, 122.92, 102.00, and 55.97 (OMe); m/z 380 (M + 2, M + 2/M, 7.8. $C_{22}H_{18}O_4S$ requires M + 2/M, 8.0%), 378 (M, 10%), 314 (5, M − SO_2), 283 (8), 157 (35), 114 (20), and 86 (100).

Bis(4-methoxyphenyl) sulphone was obtained in 96% yield in a similar manner, m.p. 128—129 °C (lit.,[13] 130 °C) (from benzene–light petroleum); $\nu_{max.}$(Nujol) 1 335, 1 320, and 1 145 cm^{-1} (SO_2); δ_H(89.55 MHz) 7.84, 6.94 (4 H, AA'BB', J 9 and 2 Hz, 2-H, 3-H), and 3.82 (3 H, s, OMe); δ_C 163.09 (C-4), 133.93 (C-1), 129.45 (C-2), 114.43 (C-3), and 55.63 (OMe); m/z 278 (M, 36%), 171 (5, $MeOC_6H_4SO_2$), 155 (100, $MeOC_6H_4SO$), 139 (5, $MeOC_6H_4S$), 123 (95, $MeOC_6H_4O$), 107 (20, $MeOC_6H_4$), 92 (32), and 77 (35).

Preparation of Ethyl Sulphones (**1d**)—(**2d**).—2-Methoxynaphthalene-1-sulphinic acid[3] (2.22 g, 0.01 mol) was dissolved in a solution of 1M NaOH (10 ml, 0.01 mol) in ethanol (15 ml) and water (5 ml). Ethyl iodide (1.72 g, 0.011 mol) was added and the mixture was heated on a boiling water-bath for 22 h. An additional portion (0.5 g) of ethyl iodide was added during this time. Most of the ethanol was then distilled off and water (20 ml) was added to the residue giving a colourless oil which solidified on cooling. The solid was collected, washed with water, and dried. Recrystallization from ethyl acetate–light petroleum gave *ethyl* 2-*methoxy*-1-*naphthyl sulphone* (**1d**) (2.24 g, 90%), m.p. 101—102 °C (Found: C, 62.6; H, 5.7; S, 12.7. $C_{13}H_{14}O_3S$ requires C, 62.4; H, 5.6; S, 12.8%); δ_H(89.55 MHz) 9.35 (1 H, dd, J 9 and 1.5 Hz, 8-H), 8.04 (1 H, d, J 9 Hz, 4-H), 7.87—7.41 (3 H, m, ArH), 7.35 (1 H, d, J 9 Hz, 3-H), 4.10 (3 H, s, OMe), 3.52 (2 H, q, J 7.5 Hz, CH_2), and 1.33 (3 H, t, J 7.5 Hz, Me); δ_C 158.36 (C-2), 136.71, 131.94, 129.25, 128.82, 128.62, 124.57, 123.75, 119.21, 113.51, 57.53 (CH_2), 51.15 (OMe), and 7.36 (Me).

Similarly obtained was *ethyl* 4-*methoxy*-1-*naphthyl sulphone* (**2d**) (86%), m.p. 113—114 °C (from ethyl acetate–light petroleum) (Found: C, 62.2; H, 6.0; S, 12.4. $C_{13}H_{14}O_3S$ requires C, 62.4; H, 5.6; S, 12.8%); δ_H(89.55 MHz) 8.75—7.58 (4 H, m, ArH), 8.25 (1 H, d, J 8.5 Hz, 2-H), 6.88 (1 H, d, J 8.5 Hz, 3-H), 4.08 (3 H, s, OMe), 3.29 (2 H, q, J 7.5 Hz, CH_2), and 1.22 (3 H, t, J 7.5 Hz, Me); δ_C 160.36 (C-4), 132.81, 130.18, 128.96, 126.23, 126.09, 124.87, 123.89, 123.26, 102.20, 56.07 (OMe), 50.22 (CH_2), and 7.61 (Me); m/z 250 (M, 48%), 221 (18, M − Et), 205 (8, M − OEt), 189 (5, $MeOC_{10}H_6S$), 173 (75, $MeOC_{10}H_6O$), 157 (100, $MeOC_{10}H_6$), 142 (15), 127 (24), and 114 (58).

Thermal Decomposition of the Sulphinate Esters.—(*a*) Allyl 4-methoxynaphthalene-1-sulphinate (**2a**). A solution of the ester (1.5 g) in glacial acetic acid (20 ml) was placed in an oil-bath at 120—125 °C. Progress of the reaction was monitored by t.l.c. (solvent: benzene) and showed no starting material (R_F, 0.35) after 25 min. Evolution of SO_2 was detected (dichromate paper). The mixture was poured into water (60 ml) and extracted with ether (3 × 30 ml); the combined ethereal extracts were washed with water, 1M Na_2CO_3 (until evolution of CO_2 ceased), and brine, and then dried ($MgSO_4$). Evaporation of the solvent left a yellow oil (1.12 g) which was dissolved in benzene–light petroleum (1:1, 20 ml) and chromatographed under medium pressure over silica gel (Woelm for partition chromatography, 60 g). Elution was effected initially with benzene–light petroleum (1:1, 600 ml) then benzene and monitored by t.l.c. (solvent: benzene); 30 ml fractions were collected.

Fractions 1 and 2 contained 1-methoxynaphthalene (R_F 0.95; 17 mg, 1.5%). From fractions 3—6 was obtained *bis*(4-*methoxy*-1-*naphthyl*) *sulphide* (**5a**) (R_F 0.82; 0.62 g, 55%), m.p. 129—130 °C (from light petroleum) (Found: C, 76.3; H, 5.1; S, 9.4. $C_{22}H_{18}O_2S$ requires C, 76.3; H, 5.2; S, 9.3%); δ_H(300 MHz) 8.40—8.23 (2 H, m, ArH), 7.54—7.50 (2 H, m, ArH), 7.27 (1 H, d, *J* 8 Hz, 2-H), 6.65 (1 H, d, *J* 8 Hz, 3-H), and 3.95 (3 H, s, OMe); δ_C 155.34 (C-4), 133.40, 130.38, 127.11, 126.28, 125.55, 125.01, 123.60, 122.48, 104.10, and 55.49 (OMe); *m*/*z* 346 (*M*, 100%), 331 (30, *M* − Me), 316 (18, *M* − OCH_2), 300 (23), 288 (12), 270 (25), 259 (12), 189 (5), 158 (11), and 114 (26).

Fractions 11—13 gave S-4′-*methoxy*-1′-*naphthyl* 4-*methoxynaphthalene*-1-*thiosulphonate* (**7**), (R_F 0.55; 0.28 g, 25%), m.p. 112—113 °C (from chloroform–light petroleum) (Found: C, 64.9; H, 4.8; S, 15.6. $C_{22}H_{18}O_4S_2$ requires C, 64.4; H, 4.4; S, 15.6%); $\nu_{max.}$(Nujol) 1 320, 1 140, and 1 120 cm^{-1} (SO_2); δ_H(300 MHz) 8.77 (1 H, m, *J* 8.5, 1.4, and 0.6 Hz, ArH), 8.27 (1 H, m, *J* 8.5, 1.4, and 0.6 Hz, ArH), 8.10 (1 H, m, *J* 8.5, 1.4, and 0.6 Hz, ArH), 7.68 (1 H, td, *J* 7.7 and 1.4 Hz, ArH), 7.57 (1 H, td, *J* 7.7 and 1.4 Hz, ArH), 7.53 (1 H, d, *J* 8.1 Hz, ArH), 7.43 (1 H, m, *J* 8.5, 1.4, and 0.6 Hz, ArH), 7.35 (1 H, d, *J* 8.4 Hz, ArH), 7.27 (1 H, td, *J* 7.6 and 1.2 Hz, ArH), 6.96 (1 H, td, *J* 7.6 and 1.2 Hz, ArH), 6.68 (1 H, d, *J* 8.1 Hz, ArH), 6.24 (1 H, d, *J* 8.4 Hz, ArH), and 3.99 and 3.89 (2 × 3 H, both s, 2 × OMe); δ_C 160.51 (C-4), 158.80 (C-4′), 139.20, 135.20, 132.77, 129.30, 128.91, 127.30, 126.23, 126.04, 125.79, 125.45, 124.92, 124.57, 122.72, 122.04, 117.02, 103.90, 101.22, 55.97 (OMe), and 55.78 (OMe); *m*/*z* 378 (*M*, 8%), 346 (16, *M* − 32), 205 (12, $MeOC_{10}H_6SO$), 189 (100, $MeOC_{10}H_6S$), and 102 (52).

Fractions 17—18 gave bis(4-methoxy-1-naphthyl) sulphone (**5c**) (R_F 0.2; 64 mg, 6%) identical with an authentic sample.

Fractions 22—24 yielded bis(4-methoxy-1-naphthyl) sulphoxide (**5b**) (R_F 0.1; 51 mg, 5%) identical with an authentic sample.

(*b*) Allyl 2-methoxynaphthalene-1-sulphinate (**1a**). Thermal decomposition of this compound in acetic acid as in (*a*) gave a crude product similarly subjected to chromatography over silica gel with elution monitoring by t.l.c. (solvent: benzene). The following compounds were obtained.

2-Methoxynaphthalene (R_F 0.9; 18%), m.p. 72—73 °C (lit.,[14] 73—75 °C); *bis*(2-*methoxy*-1-*naphthyl*) *sulphide* (**4a**) (R_F 0.7; 64%), m.p. 182—183 °C (from ethyl acetate) (Found: C, 76.5; H, 5.5; S, 9.6. $C_{22}H_{18}O_2S$ requires C, 76.3; H, 5.2; S, 9.3%); δ_H(300 MHz) 8.51 (1 H, dd, *J* 8.5 and 0.6 Hz, ArH), 7.85 (1 H, d, *J* 9 Hz, 2 H), 7.77 (1 H, dd, *J* 8.5 and 0.6 Hz, ArH), 7.45—7.26 (3 H, m, ArH), and 3.71 (3 H, s, OMe); *m*/*z* 346 (*M*, 100%), 300 (38), 282 (12), 189 (5, $MeOC_{10}H_6S$), and 157 (10, $MeOC_{10}H_6$); bis(2-methoxy-1-naphthyl) sulphone (**4c**) (R_F 0.2; 8%), identical with an authentic sample; and bis(2-methoxy-1-naphthyl) sulphoxide (**4b**) (R_F 0.07; 3%), identical with an authentic sample.

(*c*) Allyl 4-methoxybenzenesulphinate (**3a**). Thermal decomposition of this product in acetic acid was carried out as in the previous cases. G.l.c. (initially 50 °C for 2 min, then 20 °C min^{-1} to 180 °C) of the crude ethereal extract showed the presence of allyl alcohol (R_t 1.2 min), a trace of allyl acetate (R_t 1.6 min), anisole (R_t 4.4 min), the allyl sulphone (**3c**) (R_t 5.2 min), and a trace of 4,4′-dimethoxybiphenyl (R_t 6.0 min) (*m*/*z* 214 M^+). Chromatography over silica gel with t.l.c. monitoring (solvent: benzene) allowed separation of the following: anisole (R_F 0.95; 9%); bis(4-methoxyphenyl) sulphide (**6a**) (R_F 0.77; 32%), identical with an authentic sample; S-4′-*methoxyphenyl* 4-*methoxybenzenethiosulphonate* (**8**) (R_F 0.56; 26%), m.p. 89—90 °C (from light petroleum) (Found: C, 54.3; H, 4.5; S, 20.4. $C_{14}H_{14}O_4S_2$ requires C, 54.2; H, 4.6; S, 20.7%); $\nu_{max.}$(Nujol) 1 330 and 1 142 cm^{-1} (SO_2); δ_H(89.55 MHz) 7.51, 7.28, 6.87, 6.84 (8 H, 2 of AA′B′, *J* 9 and 2 Hz, ArH), 3.87 (3 H, s, OMe), and 3.83 (3 H, s, OMe); δ_C 163.48(C-4), 162.16 (C-4′), 138.37, 134.91, 129.89, 118.92, 114.92 (C-1), 113.80 (C-1′), 55.73 (OMe), and 55.48 (OMe); *m*/*z* 310 (*M*, 18%), 171 (20, $MeOC_6H_4SO_2$), 155 (55, $MeOC_6H_4SO$), and 139 (100, $MeOC_6H_4S$); *Allyl* 4-*methoxyphenyl sulphone* (**3c**) (R_F 0.34; 19%), b.p. (Kugelrohr) 155—160 °C at 0.2 mmHg (Found: C, 56.7; H, 5.6; S, 14.8. $C_{10}H_{12}O_3S$ requires C, 56.6; H, 5.7; S, 15.1%); $\nu_{max.}$(neat) 1 640 (C=C) 1 322, and 1 145 cm^{-1} (SO_2); δ_H(89.55 MHz) 7.78, 6.97 (4 H, AA′BB′, *J* 9 and 2 Hz, 2-H, 3-H), 5.98—5.04 (3 H, m, $CH{=}CH_2$), 3.88 (3 H, s, OMe), and 3.77 (2 H, d, *J* 7 Hz, SO_2CH_2); δ_C 163.73 (C-4), 130.67, 129.89 (C-1), 124.96, 124.04, 114.19, 61.14 (CH_2), and 55.68 (OMe); *m*/*z* 212 (*M*, 3%), 171 (100, $MeOC_6H_4SO_2$), 155 (36, $MeOC_6H_4SO$), 148 (40), 123 (29, $MeOC_6H_4O$), 107 (78, $MeOC_6H_4$), 92 (44), and 77 (69); bis(4-methoxyphenyl) sulphone (**6c**) (R_F 0.23; 5%), identical with an authentic sample; and bis(4-methoxyphenyl) sulphoxide (**6b**) (R_F 0.09; 5%), identical with an authentic sample.

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