***SHORT PAPER***

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# The reactions of DMSO with arylaldehydes in the presence of sodium hydride†

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Dimethyl sulfoxide (DMSO) reacted with arylaldehydes under basic conditions to afford sulfide **1**, β-(benzyloxy)styrene **2** and dialkyl sulfoxide **3**, while the reaction of benzophenone with DMSO gave 1,1-diphenylethylene **4**, 1,1-diphenyl-2-methylthioethylene **5** and sulfoxide **6** at the same time under the same conditions.

**Keywords:** dimethylsulfoxide, arylaldehydes, sodium hydride, disproportionation

## Introduction

Dimethylsulfoxide (DMSO) is a very common solvent used in the preparation of ylides with sodium hydride.[1] But in the preparation of benzylidenecyclopropane derivatives from the reaction of cyclopropylphosphonium salt with arylaldehydes in DMSO using NaH as a base in THF at 66°C, surprisingly we found that the reaction products were 1-chloro-4-(2-methylsulfanylvinyl)benzene **1i**, 2-(4-chlorophenyl)ethenyl 4-chlorobenzyl ether **2i** and 1-chloro-4-(2-methanesulfinylvinyl)benzene **3i** rather than benzylidenecyclopropane (Scheme 1).

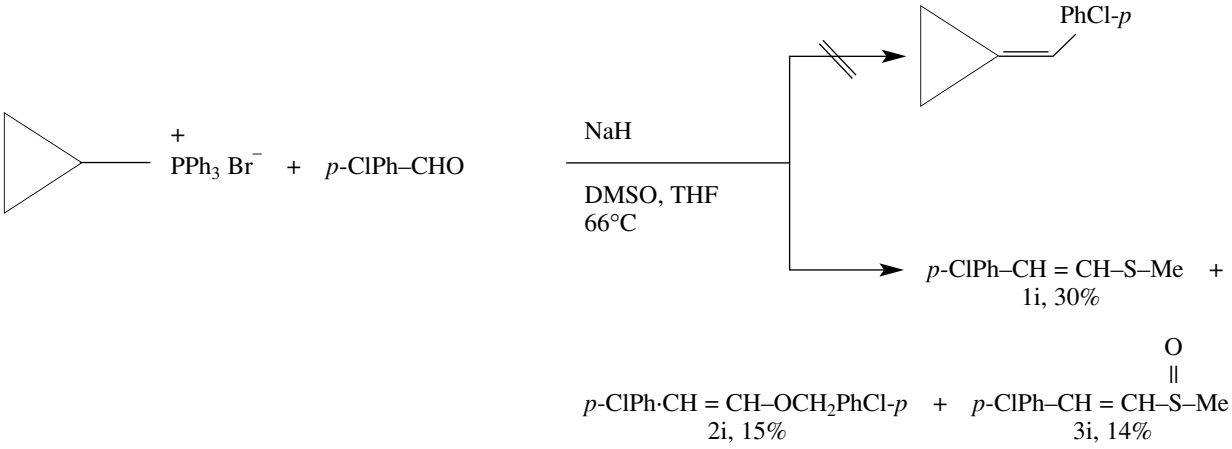
The same products were obtained under the same reaction conditions even without the cyclopropylphosphonium salt. This result prompted us to re-examine the reaction of aldehydes with DMSO in the presence of bases.

It is well known that DMSO reacts with aldehydes under basic conditions to give methyl alkyl sulfoxides.[2,3] Langhals reported that benzylalcohol and benzaldehyde reacted with DMSO in the presence of base to afford β-(benzyloxy)styrene. They also mentioned that aldehyde also could react with DMSO to afford the same product.[4] In addition, Kaiser and Beard found that DMSO reacted with benzophenone to afford the corresponding divinyl sulfoxide.[5] Corey[6a] and Walling[6b] independently reported that, the reaction of DMSO with benzophenone in the presence of base gave some volatile products containing the hydrocarbons such as 1,1-diphenylethylene, diphenylmethane, 1,1-diphenylcyclopropane, diphenylacetaldehyde, and 1,1-dipheny-2-methylthioethylene.

In order to gain more mechanistic insights and disclose the scope and limitations of this unusual phenomenon, we then carefully examined this arylaldehyde, DMSO and sodium hydride promoted reaction. Herein we wish to report the full details of this phenomenon.

## Results and discussion

The reactions of arylaldehydes with DMSO were carried out in THF in the presence of NaH under an argon atmosphere (Scheme 2). We found that, for many arylaldehydes, methyl vinyl sulfide **1**, β-(benzyloxy)styrene **2**, and methyl vinyl sulfoxide **3** were in general formed at the same time in one pot under basic conditions in moderate yields. The results are summarised in Table 1. The structures of **1**, **2** and **3** were determined by spectral data. The substituents on the phenyl ring can affect the distribution of products (Table 1). For arylaldehydes having electron-donating groups, methyl vinyl sulfides **1** were obtained in a *trans*- and *cis*- mixture and the β-(benzyloxy)styrenes **2** were formed in very low yields (Table 1, entry 2–6). We also found that, for the arylaldehydes having phenoxy, *p*-bromo-, or 2,6-dichloro- substituents, the corresponding methyl vinyl sulfoxides **3** were generally




**Scheme 1**

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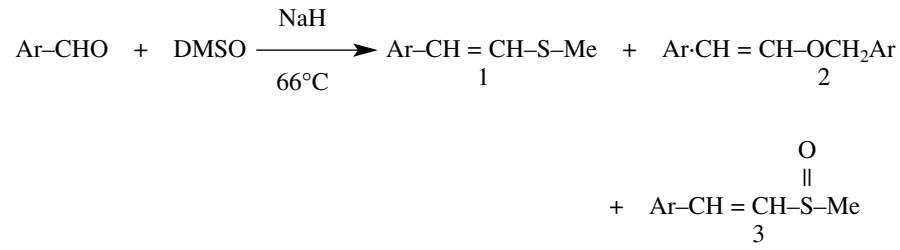
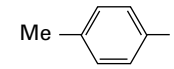
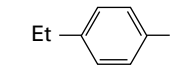
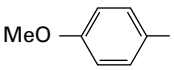
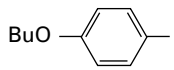
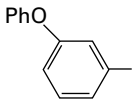
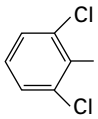
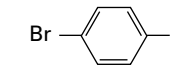
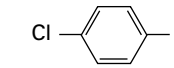
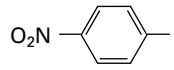
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*




a: Ar = Ph, b: Ar = *p*-MePh; c: Ar = *p*-EtPh; d: Ar = *p*-MeOPh; e: Ar = *p*-BuOPh; f: Ar = *m*-PhOPh; g: Ar = 1,3-di-$Cl_2$Ph; h: Ar = *p*-BrPh; i: Ar = *p*-ClPh; j: Ar = *p*-$NO_2$Ph.

**Scheme 2**

**Table 1** The reactions of arylaldehydes with DMSO in the presence of NaH.

| Entry | Ar | Yield/%[a] | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| 1 |  | 26 | 10 | 15 |
| 2 |  | 35[b] | trace | 11 |
| 3 |  | 10[c] | trace | 41 |
| 4 |  | 2[d] | trace | 50 |
| 5 |  | 8[e] | trace | 18 |
| 6 |  | 23 | trace | trace |
| 7 |  | 12 | trace | trace |
| 8 |  | 32 | 20 | trace |
| 9 |  | 30 | 15 | 14 |
| 10 |  | – | – | – |

[a]Isolated yield. [b]*trans:cis* = 15:1, [c]*trans:cis* = 10:1; [d]*trans:cis* = 5:1; [e]*trans:cis* = 5:1.

obtained in low yields (Table 1, entry 6–8). The effects of substituents in the aldehydes on the yields of these products are not very clear at the present stage. In general, very strong electron-withdrawing groups impair this reaction. For example, the reaction of *p*-nitrobenzaldehyde with DMSO in the presence of NaH under the same conditions gave no products (Table 1, entry 10).

Using KOBu$^t$ as a base under the same conditions, similar results were obtained. It should be emphasised here that the reaction temperature plays a crucial role in this novel reaction. If the reaction temperature is too low, the products are formed in very low yields, while if the reaction temperature is too high, the reaction is too complicated for any pure product to be isolated. Thus, utilising THF as a solvent in this reaction keeps the reaction temperature at 66°C under reflux. Perhaps this is the key reason that we can get these three products in this normal reaction system.

On the other hand, in the reaction of benzophenone with DMSO under the same conditions, 1,1-diphenylethene **4**, 1,1-dipheny-2-methythioethene **5** and 1,1-diphenylallyl methyl sulfoxide **6** were obtained in moderate yields (Scheme 3). The formation of 1,1-diphenylallyl methyl sulfoxide **6** is reported in this paper for the first time. The structures of **5** and **6** were clearly established by X-ray analyses (Figs 1 and 2).

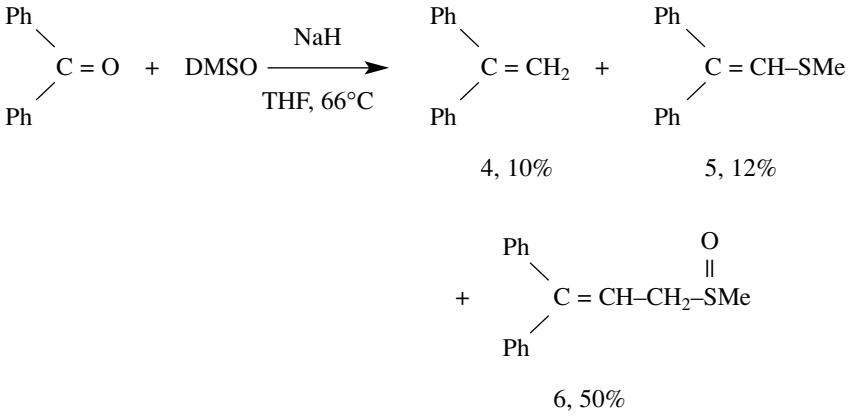
In Scheme 4, we tentatively propose pathways for the formation of **1**, **2** and **3**. The intermediate **A** is first formed under the reaction conditions and undergoes dehydration to give the corresponding methyl vinyl sulfoxides **3**. Product **1** is formed from **3**. The intermediate **A** could also provide an epoxide by an intramolecular $S_N2$ reaction.[4] The nucleophilic attack on the epoxide by the benzyloxy anion derived from benzaldehyde under basic conditions gives the β-(benzyloxy)styrene **2** (Scheme 4). The compound **6** might be formed by nucleophilic attack of DMSO sodium on the corresponding epoxide.

In conclusion, we have found some new results in the reaction of arylaldehydes or ketones with DMSO under basic conditions in THF. This reaction, though not of obvious synthetic utility at the moment, raised a number of questions which warrant additional attention and which might lead to serviceable preparative procedures. Efforts are underway to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

## Experimental

*General:* M.p.s were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Some of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai $GF_{254}$ silica gel coated plates. Flash Column Chromatography was carried out using 200–300 mesh silica gel.

*General procedure for the reactions of DMSO with arylaldehydes in the presence of NaH in THF*: A suspension of NaH (53 mg, 2.2 mmol) in DMSO (5 ml) was heated at 66°C for 2 h in a 50 ml round bottom flask with a magnetic stir bar under argon atmosphere.




**Scheme 3**

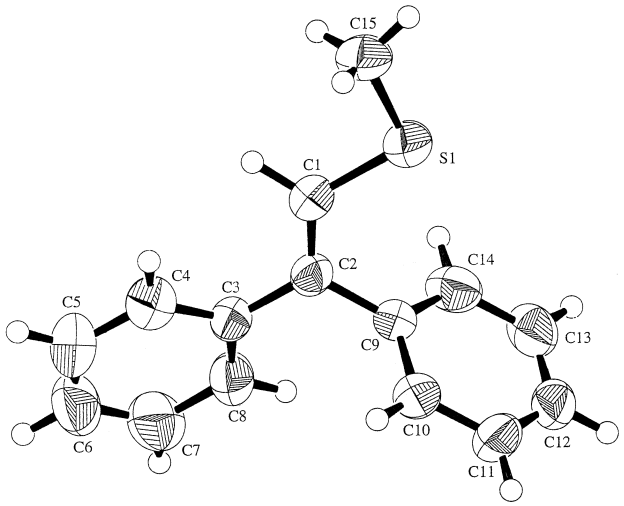



**Fig. 1** The crystal structure of **5**

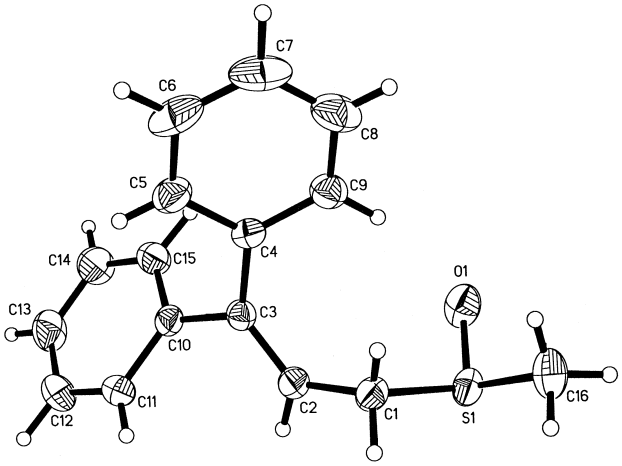



**Fig. 2** The crystal structure of **6**

Then, benzaldehyde (212 mg, 2.0 mmol) in THF (5 ml) was added into the reaction mixture. The reaction mixture was further stirred at 66°C for 2 h. The reaction was quenched by adding water (10 ml) and extracted with ether (20 ml). The organic layer was dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc = 50/1) to give the compound (2-methylsulfanylvinyl)benzene **1a** as a colourless liquid. 78 mg, 26%; IR ($CHCl_3$) $\nu$ 1734, 1668, 1596, 1507, 1434, 1313, 930, 824, 744 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.42 (3H, s, $CH_3$), 6.29 (1H, d, $J$ = 15.7 Hz, CH), 6.78 (1H, d, $J$ = 15.7 Hz, CH), 7.16–7.34 (5H, m, Ar); MS (EI) $m/z$ 150 ($M^+$) [Calc. for $C_8H_7S$: requires (M-15) 135.0268; Found: 135.0275].

*The formation of β-(benzyloxy)styrene* **2a**: A colourless liquid; 42 mg, 10%; IR ($CHCl_3$) $\nu$ 1636, 1599, 1446, 1327, 1145, 1031, 748, $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 4.91 (2H, s, $CH_2$), 5.96 (1H, d, $J$ = 15.2 Hz, CH), 7.11 (1H, d, $J$ = 15.2 Hz, CH), 7.13–7.41 (10H, m, Ar); MS (EI) $m/z$ 210 ($M^+$) [Calc. for $C_{15}H_{14}O$: requires M 210.1045; Found: 210.1034].

*The formation of (2-methanesulfinylvinyl)benzene* **3a**: A colourless liquid. 50 mg, 15%; IR ($CHCl_3$) $\nu$ 1608, 1510, 1265, 1055, 965, 784, 738 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.68 (3H, s, $CH_3$), 6.88 (1H, d, $J$ = 15.5 Hz, CH), 7.23 (1H, d, $J$ = 15.5 Hz, CH), 7.33–7.38 (3H, m, Ar), 7.43–7.47 (2H, m, Ar); MS (EI) $m/z$ 166 $(M)^+$ [Calc. for $C_9H_{10}SO$: requires M 166.0452; Found: 166.0473].

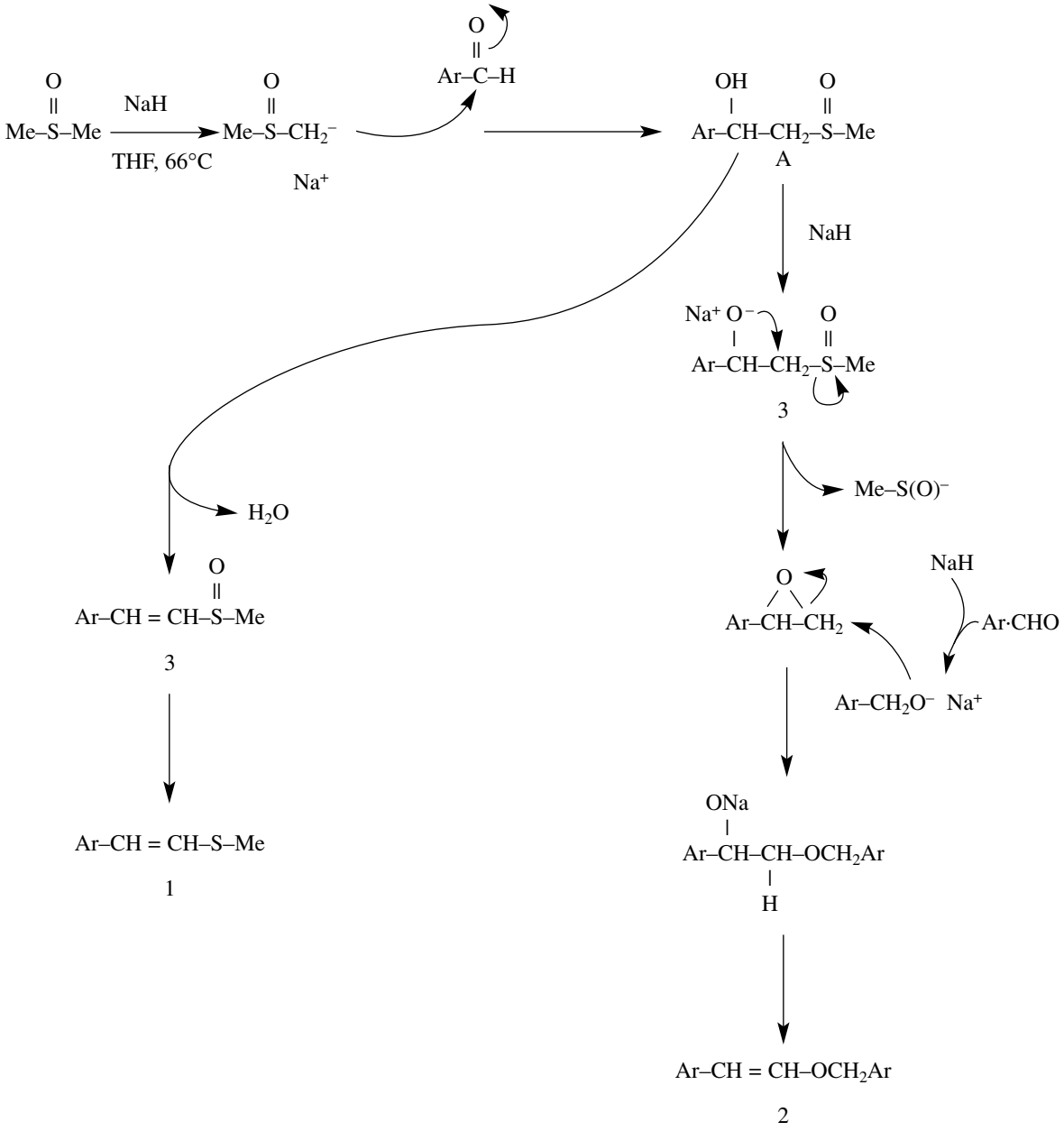
*The formation of 1-methyl-4-(2-methylsulfanylvinyl)benzene* **1b**: A colourless liquid. 115 mg, 35%; *trans*: *cis* = 15:1; IR ($CHCl_3$) $\nu$ 1734, 1668, 1596, 1507, 1434, 1313, 930, 824, 744 $cm^{-1}$; *trans*-**1b**. $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.35 (3H, s, $CH_3$), 2.43 (3H, s, $CH_3$), 6.36 (1H, d, $J$ = 15.4 Hz, CH), 6.73 (1H, d, $J$ = 15.4 Hz, CH), 7.14–7.19 (4H, m, Ar); *cis*-**1b**. $\delta$ 2.36 (3H, s, $CH_3$), 2.45 (3H, s, $CH_3$), 6.21 (1H, d, $J$ = 15.4 Hz, CH), 6.56 (1H, d, $J$ = 15.4 Hz, CH), 7.20–7.26 (4H, m, Ar); MS (EI) $m/z$ 164 ($M^+$) [Calc. for $C_{10}H_{12}S$: requires M 164.0660; Found: 164.0662].

*The formation of 1-(2-methanesulfinylvinyl)benzene* **3b**: A colourless liquid. 40 mg, 11%; IR ($CHCl_3$) $\nu$ 1608, 1510, 1414, 1265, 1055, 965, 784, 738 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.35 (3H, s, $CH_3$), 2.68 (3H, s, $CH_3$), 6.82 (1H, d, $J$ = 15.4 Hz, CH), 7.16–7.18 (2H, m, Ar), 7.23 (1H, d, $J$ = 15.4 Hz, CH), 7.34–7.36 (2H, m, Ar); MS (EI) $m/z$ 180 ($M^+$) [Calc. for $C_{10}H_{12}SO$: requires M 180.0609; Found: 180.0607].

*The formation of 1-ethyl-4-(2-methylsulfanylvinyl)benzene* **1c**: A colourless liquid. 36 mg, 10%; *trans*: *cis* = 10:1; IR ($CHCl_3$) $\nu$ 1596, 1671, 1507, 1433, 1317, 1060, 930, 838 $cm^{-1}$; *trans*-**1c**. $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.22 (3H, t, $J$ = 7.5 Hz, $CH_3$), 2.37 (3H, s, $CH_3$), 2.61 (2H, q, $J$ = 7.5 Hz, $CH_2$), 6.31 (1H, d, $J$ = 15.5 Hz, CH), 6.73 (1H, d, $J$ = 15.5 Hz, CH), 7.11–7.24 (4H, m, Ar); *cis*-**1c**. $\delta$ 1.22 (3H, t, $J$ = 7.5 Hz, $CH_3$), 2.37 (3H, s, $CH_3$), 2.61 (2H, q, $J$ = 7.5 Hz, $CH_2$), 6.24 (1H, d, $J$ = 15.5 Hz, CH), 6.45 (1H, d, $J$ = 15.5 Hz, CH), 7.26–7.38 (4H, m, Ar); MS (EI) $m/z$ 179 ($MH^+$) [Calc. for $C_{11}H_{14}S$: requires M 178.0816; Found: 178.0815].

*The formation of 1-ethyl-4-(2-methanesulfinylvinyl)benzene* **3c**: A colourless liquid. 159 mg, 41%; IR ($CHCl_3$) $\nu$ 1608, 1563, 1508, 1452, 1414, 1295, 1052, 966, 843, 736, 701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 1.28 (3H, t, $J$ = 7.60 Hz, $CH_3$), 2.69 (2H, q, $J$ = 7.60 Hz, $CH_2$), 2.73 (3H, s, $CH_3$), 6.89 (1H, d, $J$ = 15.4 Hz, CH), 7.24–7.26 (2H, m, Ar), 7.28 (1H, d, $J$ = 15.4 Hz, CH), 7.42–7.45 (2H, m, Ar); MS (EI) $m/z$ 195 ($MH^+$) [Calc. for $C_{11}H_{14}SO$: requires M 194.0765; Found: 194.0724].

*The formation of 1-methoxy-4-(2-methylsulfanylvinyl)benzene* **1d**: A colourless liquid. 8 mg, 2%; *trans*: *cis*= 5:1; IR ($CHCl_3$) $\nu$ 1605, 1506, 1440, 1175, 742 $cm^{-1}$; *trans*-**1d**. $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.37 (3H, s, $CH_3$), 3.79 (3H, s, $OCH_3$), 6.32 (1H, d, $J$ = 15.4 Hz, CH), 6.63 (1H, d, $J$ = 15.4 Hz, CH), 6.64–6.85 (2H, m, Ar), 7.14–7.25 (2H, m, Ar); *cis*-**1d**. $\delta$ 2.41 (3H, s, $CH_3$), 3.81 (3H, s,




**Scheme 4**

$OCH_3$), 6.07 (1H, d, $J$ = 15.4 Hz, CH), 6.61 (1H, d, $J$ = 15.4 Hz, CH), 6.86–6.91 (2H, m, Ar), 7.41–7.44 (2H, m, Ar); MS (EI) $m/z$ 180 ($M^+$) [Calc. for $C_{10}H_{12}SO$: requires M 180.0609, Found: 180.0601].

*The formation of 1-(2-methanesulfinylvinyl)-4-methoxybenzene* **3d**: A white solid. 196 mg, 50%; m.p. 58–61°C; R ($CHCl_3$) $\nu$ 1603, 1570, 1508, 1462, 1305, 1254, 1028, 963 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.69 (3H, s, $CH_3$), 3.82 (3H, s, $OCH_3$), 6.75 (1H, d, $J$ = 15.6 Hz, CH), 6.89–6.92 (2H, m, Ar), 7.18 (1H, d, $J$ = 15.6 Hz, CH), 7.40–7.43 (2H, m, Ar); MS (EI) $m/z$ 196 ($M^+$) [Calc. for $C_{10}H_{12}SO_2$: requires C 61.20, H 6.16; Found: C 61.00, H 6.17].

*The formation of 1-butoxy-4-(2-methylsulfanylvinyl)benzene* **1e**: A colourless liquid. 36 mg, 8%; *trans*: *cis* = 10:1; IR ($CHCl_3$) $\nu$ 1604, 1505, 1465, 1431, 1300, 1250, 1174, 833 $cm^{-1}$; *trans*-**1e**. $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 0.97 (3H, t, $J$ = 7.2 Hz, $CH_3$), 1.23–1.29 (2H, m, $CH_2$), 1.47–1.53 (2H, m, $CH_2$), 2.18 (3H, s, $CH_3$), 3.94 (2H, t, $J$ = 7.2 Hz, $CH_2$), 6.29 (1H, d, $J$ = 15.5 Hz, CH), 6.61 (1H, d, $J$ = 15.5 Hz, CH), 6.82–6.88 (2H, m, Ar), 7.20–7.26 (2H, m, Ar); *cis*-**1e**. $\delta$ 0.97 (3H, t, $J$ = 7.2 Hz, $CH_3$), 1.23–1.29 (2H, m, $CH_2$), 1.47–1.53 (2H, m, $CH_2$), 2.18 (3H, s, $CH_3$), 3.94 (2H, t, $J$ = 7.2 Hz, $CH_2$), 6.06 (1H, d, $J$ = 15.5 Hz, CH), 6.38 (1H, d, $J$ = 15.5 Hz, CH), 6.90–6.98 (2H, m, Ar), 7.39–7.42 (2H, m, Ar); MS (EI) $m/z$ 222 ($M^+$) [Calc. for $C_{13}H_{18}SO$: requires M 222.1078; Found: 222.1104].

*The formation of 1-butoxy-4-(2-methanesulfinylvinyl)benzene* **3e**: A waxy solid. 86 mg, 18%; IR ($CHCl_3$) $\nu$ 1604, 1507, 1304, 1254, 1174, 1053, 967, 732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 0.95 (3H, t, $J$ = 7.3 Hz, $CH_3$), 1.43–1.50 (2H, m, $CH_2$), 1.70–1.77 (2H, m, $CH_2$), 2.65 (3H, s, $CH_3$), 3.95 (2H, t, $J$ = 6.5 Hz, $CH_2$), 6.72 (1H, d, $J$ = 15.6 Hz, CH), 6.85–6.89 (2H, m, Ar), 7.15 (1H, d, $J$ = 15.6 Hz, CH), 7.35–7.39 (2H, m, Ar); MS (EI) $m/z$ 240 ($M^+$) [Calc. for $C_{13}H_{18}SO_2$: requires M 240.1028; Found: 240.1022 ].

*The formation of 1-(2-methylsulfanylvinyl)-3-phenoxybenzene* **1f**: A colourless liquid. 111 mg, 23%; IR ($CHCl_3$) $\nu$ 1590, 1569, 1484, 1432, 1262, 1226, 933, 764, 690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.37 (3H, s, $CH_3$), 6.25 (1H, d, $J$ = 15.5 Hz, CH), 6.79 (1H, d, J = 15.5 Hz, CH), 6.82-7.37 (9H, m, Ar); MS (EI) $m/z$ 242 ($M^+$) [Calc. for $C_{15}H_{14}SO$: requires M 242.0765; Found: 242.0756].

*The formation of 1,3-dichloro-2-(2-methylsulfanylvinyl)benzene* **1g**: A colourless liquid. 22 mg, 5%; IR ($CHCl_3$) $\nu$ 1592, 1550, 1433, 1424, 1178, 935 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.42 (3H, s, $CH_3$), 6.29 (1H, d, $J$ = 15.7 Hz, CH), 7.04 (1H, d, $J$ = 15.7 Hz, CH),

**Table 2** Selected bond lengths of **5** (Å)

| | | | | | |
|---|---|---|---|---|---|
| S(1) | C(1) | 1.755(5) | C(12) | C(13) | 1.37(1) |
| S(1) | C(15) | 1.790(6) | C(13) | C(14) | 1.380(9) |
| S(2) | C(16) | 1.762(5) | C(16) | C(17) | 1.347(8) |
| S(2) | C(30) | 1.803(6) | C(17) | C(18) | 1.485(7) |
| C(1) | C(2) | 1.328(8) | C(17) | C(24) | 1.488(7) |
| C(2) | C(3) | 1.489(7) | C(18) | C(19) | 1.374(7) |
| C(2) | C(9) | 1.491(7) | C(18) | C(23) | 1.357(8) |
| C(3) | C(4) | 1.403(7) | C(19) | C(20) | 1.367(9) |
| C(3) | C(8) | 1.366(8) | C(20) | C(21) | 1.34(1) |
| C(4) | C(5) | 1.406(9) | C(21) | C(22) | 1.36(1) |
| C(5) | C(6) | 1.37(1) | C(22) | C(23) | 1.395(8) |
| C(6) | C(7) | 1.397(9) | C(24) | C(25) | 1.402(8) |

**Table 3** Selected bond angles of **5** (°)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| S(1) | C(1) | H(1) | 115.59 | H(12) | C(15) | H(14) | 111.23 |
| C(2) | C(1) | H(1) | 121.16 | H(13) | C(15) | H(14) | 108.71 |
| C(3) | C(4) | H(2) | 118.93 | S(2) | C(16) | H(15) | 114.11 |
| C(4) | C(5) | H(3) | 119.49 | C(18) | C(19) | H(16) | 119.57 |
| C(6) | C(5) | H(3) | 120.79 | C(20) | C(19) | H(16) | 118.35 |
| C(5) | C(6) | H(4) | 119.19 | C(19) | C(20) | H(17) | 121.10 |
| C(7) | C(6) | H(4) | 120.87 | C(21) | C(20) | H(17) | 119.42 |
| C(6) | C(7) | H(5) | 121.03 | C(20) | C(21) | H(18) | 119.59 |
| C(8) | C(7) | H(5) | 119.69 | C(22) | C(21) | H(18) | 119.49 |
| C(3) | C(8) | H(6) | 118.51 | C(21) | C(22) | H(19) | 120.11 |
| C(7) | C(8) | H(6) | 119.21 | C(23) | C(22) | H(19) | 120.93 |
| C(9) | C(10) | H(7) | 119.64 | C(18) | C(23) | H(20) | 119.46 |
| C(11) | C(10) | H(7) | 120.32 | C(22) | C(23) | H(20) | 119.55 |
| C(10) | C(11) | H(8) | 119.07 | C(24) | C(25) | H(21) | 119.39 |
| C(12) | C(11) | H(8) | 120.59 | C(26) | C(25) | H(21) | 119.94 |
| C(11) | C(12) | H(9) | 120.69 | C(25) | C(26) | H(22) | 121.09 |
| C(13) | C(12) | H(9) | 119.03 | C(27) | C(26) | H(22) | 119.46 |
| C(12) | C(13) | H(10) | 120.37 | C(26) | C(27) | H(23) | 119.07 |
| S(1) | C(15) | H(12) | 109.88 | C(24) | C(29) | H(25) | 119.66 |
| S(1) | C(15) | H(13) | 108.34 | C(28) | C(29) | H(25) | 119.56 |
| S(1) | C(15) | H(14) | 110.27 | S(2) | C(30) | H(26) | 109.29 |
| H(12) | C(15) | H(13) | 108.34 | S(2) | C(30) | H(27) | 111.77 |

**Table 4** Selected bond lengths of **6** (Å)

| | |
|---|---|
| S(1)–O(1) | 1.4909(15) |
| S(1)–C(16) | 1.777(2) |
| S(1)–C(1) | 1.8298(19) |
| S(2)–O(2) | 1.4869(15) |
| S(2)–C(32) | 1.779(2) |
| S(2)–C(17) | 1.815(2) |
| C(1)–C(2) | 1.485(3) |
| C(2)–C(3) | 1.338(3) |
| C(3)–C(4) | 1.488(2) |
| C(3)–C(10) | 1.492(2) |
| C(4)–C(9) | 1.388(3) |
| C(4)–C(5) | 1.392(3) |
| C(5)–C(6) | 1.381(3) |
| C(6)–C(7) | 1.376(4) |
| C(7)–C(8) | 1.365(4) |
| C(8)–C(9) | 1.379(3) |
| C(10)–C(15) | 1.388(3) |
| C(10)–C(11) | 1.391(2) |
| C(11)–C(12) | 1.381(3) |
| C(12)–C(13) | 1.366(3) |
| C(13)–C(14) | 1.375(3) |
| C(14)–C(15) | 1.377(3) |
| C(17)–C(18) | 1.481(3) |
| C(18)–C(19) | 1.335(3) |
| C(19)–C(20) | 1.489(3) |
| C(19)–C(26) | 1.499(2) |
| C(20)–C(25) | 1.389(3) |
| C(20)–C(21) | 1.391(3) |
| C(21)–C(22) | 1.384(3) |
| C(22)–C(23) | 1.364(3) |
| C(23)–C(24) | 1.371(3) |

**Table 5** Selected bond angles of 6 (°)

| | |
|---|---|
| O(1)–S(1)–C(16) | 106.71(11) |
| O(1)–S(1)–C(1) | 108.23(9) |
| C(16)–S(1)–C(1) | 97.30(11) |
| O(2)–S(2)–C(32) | 106.97(11) |
| O(2)–S(2)–C(17) | 106.80(10) |
| C(32)–S(2)–C(17) | 96.62(12) |
| C(2)–C(1)–S(1) | 110.95(14) |
| C(3)–C(2)–C(1) | 127.02(17) |
| C(2)–C(3)–C(4) | 123.89(16) |
| C(2)–C(3)–C(10) | 119.36(16) |
| C(4)–C(3)–C(10) | 116.62(15) |
| C(9)–C(4)–C(5) | 117.77(18) |
| C(9)–C(4)–C(3) | 122.95(16) |
| C(5)–C(4)–C(3) | 119.25(16) |
| C(6)–C(5)–C(4) | 120.6(2) |
| C(7)–C(6)–C(5) | 120.5(2) |
| C(8)–C(7)–C(6) | 119.4(2) |
| C(7)–C(8)–C(9) | 120.7(2) |
| C(8)–C(9)–C(4) | 120.9(2) |
| C(15)–C(10)–C(11) | 117.72(17) |
| C(15)–C(10)–C(3) | 120.93(16) |
| C(11)–C(10)–C(3) | 121.35(16) |
| C(12)–C(11)–C(10) | 120.60(19) |
| C(13)–C(12)–C(11) | 120.7(2) |
| C(12)–C(13)–C(14) | 119.5(2) |
| C(13)–C(14)–C(15) | 120.1(2) |
| C(14)–C(15)–C(10) | 121.28(19) |
| C(18)–C(17)–S(2) | 110.07(15) |
| C(19)–C(18)–C(17) | 127.12(19) |
| C(18)–C(19)–C(20) | 120.73(17) |
| C(18)–C(19)–C(26) | 122.36(17) |
| C(20)–C(19)–C(26) | 116.81(15) |
| C(25)–C(20)–C(21) | 117.39(18) |
| C(25)–C(20)–C(19) | 120.99(16) |
| C(21)–C(20)–C(19) | 121.60(17) |

7.05 (1H, t, $J$ = 8.1 Hz, Ar), 7.30 (2H, d, $J$ = 8.1 Hz, Ar); MS (EI) $m/z$ 219 ($M^+$) [Calc. for $C_9H_8SCl_2$: requires M 217.9724; Found: 217.9722].

*The formation of 1-bromo-4-(2-methylsulfanylvinyl)benzene* **1h**: A white solid. 146 mg, 32%; m.p. 71–74°C; IR ($CHCl_3$) $\nu$ 1664, 1596, 1421, 1395, 1327, 1265, 1204, 1073 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.39 (3H, s, $CH_3$), 6.23 (1H, d, $J$ = 15.5 Hz, CH), 6.80 (1H, d, $J$ = 15.5 Hz, CH), 7.15–7.17 (2H, m, Ar), 7.40–7.43 (2H, m, Ar); MS (EI) $m/z$ 228 ($M^+$) [Calc. for $C_9H_9SBr$: requires C 47.18%, H 3.96%, Found: C 47.27 %, H 4.03 %].

*The formation of β-(*p-*bromobenzyloxy)*-p-*bromostyrene* **2h**: A white solid. 147 mg, 20%; m.p. 149–152°C; IR ($CHCl_3$) $\nu$ 1741, 1639, 1462, 1376, 1264, 1242, 1158, 1048, 745 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.39 (3H, s, $CH_3$), 4.85 (2H, s, $CH_2$), 5.88 (1H, d, $J$ = 12.9 Hz, CH), 7.03 (1H, d, $J$ = 12.9 Hz, CH), 7.07–7.53 (8H, m, Ar); MS (EI) $m/z$ 368 ($M^+$) [Calc. for $C_{15}H_{12}OBr_2$: requires 365.9255, Found: 365.9244].

*The formation of 1-chloro-4-(2-methylsulfanylvinyl)benzene* **1i**: A wax solid. 110 mg, 30%; IR ($CHCl_3$) $\nu$ 1596, 1487, 1264, 1089, 930 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.41 (3H, s, $CH_3$), 6.23 (1H, d, $J$ = 15.5 Hz, CH), 6.77 (1H, d, $J$ = 15.5 Hz, CH), 7.18–7.26 (4H, m, Ar); MS (EI) $m/z$ 184 ($M^+$) [Calc. for $C_9H_9SCl$: requires C 58.53, H 4.91; Found: C 58.47, H 4.93].

*The formation of β-(*p-*chlorobenzyloxy)*-p-*chlorostyrene* **2i**: A wax solid. 83 mg, 15%; IR ($CHCl_3$) $\nu$ 1638, 1490, 1264, 1092 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 4.85 (2H, s, $CH_2$), 5.89 (1H, d, $J$ = 12.9 Hz, CH), 7.02 (1H, d, $J$ = 12.9 Hz, CH), 7.12–7.15 (2 H, m, Ar), 7.15–7.29 (2H, m, Ar), 7.29–7.37 (4H, m, Ar); MS (EI) $m/z$ 278 ($M^+$) [Calc. for $C_{15}H_{12}OCl_2$: requires C 64.54, H 4.33; Found: C 64.14, H 4.38].

*The formation of 1-chloro-4-(2-methanesulfinylvinyl)benzene* **3i**: A wax solid. 56 mg, 14%; IR ($CHCl_3$) $\nu$ 1728, 1589, 1668, 1489, 1402, 1176, 962 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.68 (3H, s, $CH_3$), 6.87 (1H, d, $J$ = 15.5 Hz, CH), 7.18 (1H, d, $J$ = 15.5 Hz, CH), 7.30–7.39 (4H, m, Ar); MS (EI) $m/z$ 200 ($M^+$) [Calc. for $C_9H_9SOCl$: requires M 200.0063; Found: 200.0036].

*The formation of 1,1-diphenylethylene* **4**: A colourless liquid. 36 mg, 10%; IR ($CHCl_3$) $\nu$ 1656, 1598, 1490, 1443, 1276, 1065 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 5.46 (2H, s, $CH_2$), 7.28–7.36

(10H, m, Ar); MS (EI) *m*/*z* 180 ($M^+$) [Calc. for $C_{14}H_{12}$: requires M 180.0939. Found: 180.0943].

*The formation of 1,1-dipheny-2-methylthioethylene* **5**: A white solid. 54 mg, 12%; m.p. 54–56°C; IR ($CHCl_3$) $\nu$ 1583, 1491, 1440, 1265 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.38 (3H, s, $CH_3$), 6.57 (1H, s, CH), 7.22–7.43 (10H, m, Ar); MS (EI) *m*/*z* 226 ($M^+$) [Calc. for $C_{15}H_{14}S$: requires C 79.60 %, H 6.23 %, Found: C 79.79 %, H 6.48%].

*The formation of 1,1-diphenylallyl methyl sulfoxide* **6**: A white solid, 244 mg, 50%; m.p. 105–107°C; IR ($CHCl_3$) $\nu$ 1596, 1490, 1442, 1419, 1043, 768, 702 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, TMS, 300 MHz) $\delta$ 2.52 (3H, s, $CH_3$), 3.56 (1H, d, $J$ = 12.0 Hz, $CH_2$), 3.60 (1H, d, $J$ = 12.0 Hz, $CH_2$), 6.22 (1H, t, $J$ = 8.1 Hz, CH), 7.19–7.42 (10H, m, Ar); MS (EI) *m*/*z* 244 ($M^+$) [Calc. for $C_{17}H_{16}SO$: requires C 75.0 %, H 6.25 %, Found: C 74.74 %, H 6.30 %].

The crystal data of **5**: Empirical formula: $C_{30}H_{28}S_2$; Formula weight: 452.67; Crystal system: monoclinic; Space group: $P2_1$ (#4); Unit cell dimensions: $a$ = 6.006(8) Å, $b$ = 8.318(8) Å, $c$ = 25.302(7) Å, β = 90.0000°, $V$ = 1264(2) $Å^3$; $Z$ = 4; $D_{calc}$ = 1.189 g/$cm^3$; $\mu$(MoKα) = 2.26 $cm^{-1}$; $F_{(000)}$ = 480. Its structure has been deposited at the Cambridge Crystallographic Data Center and has been allocated the deposition number: CCDC 169331.

The crystal data of **6**: Empirical formula: $C_{32}H_{32}O_2S_2$; Formula weight: 512.70; Crystal system: monoclinic; Space group: P2(1)/c; Unit cell dimensions: $a$ = 10.2615(6) Å, $b$ = 14.5130(9) Å, $c$ = 18.8378(12) Å, α = 90°, β = 101.1630(10)°, r = 90°, $V$ = 2752.3(3) $Å^3$; $Z$ = 8, $D_{calc}$ = 1.237 mg/$m^3$; $F_{(000)}$ = 1088. Its structure has been deposited at the Cambridge Crystallographic Data Center and has been allocated the deposition number: CCDC 169332.

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