

# Radical $\beta$ -addition to acyclic $\alpha$ -(arylsulfinyl) enones: Pummerer-type rearrangement

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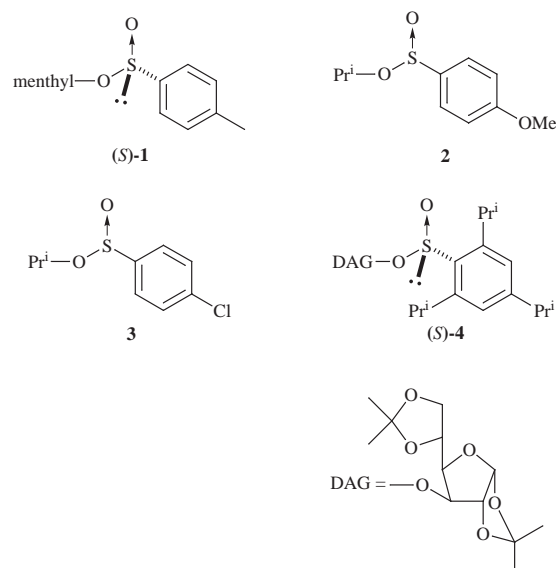
The reaction of (*S,E*)-3-(*p*-tolylsulfinyl)pent-3-en-2-one with an isopropyl radical, generated from isopropyl iodide and triethylborane, gives the non-stereoselective addition product and an unexpected  $\alpha$ -(arylsulfanyl) enone which is formed through a radical addition and subsequent Pummerer-type rearrangement. The formation of the  $\alpha$ -(arylsulfanyl) enone depends upon the additives used as well as the aryl group on the sulfur.

## Introduction

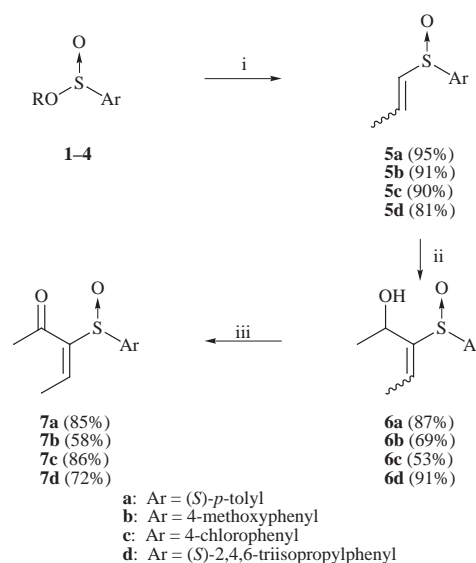
Recently, radical reactions have been recognized as a means for stereoselective carbon–carbon bond formation.<sup>1</sup> There are a number of reports of asymmetric radical reactions using chiral auxiliaries.<sup>2</sup> While the sulfinyl group has been recognized as an attractive chiral auxiliary in radical 1,2-asymmetric induction,<sup>3</sup> there are only a few reports on radical  $\beta$ -addition to chiral vinyl sulfoxides.<sup>4</sup> We have reported a stereoselective intermolecular radical  $\beta$ -addition reaction of 2-(arylsulfinyl)cycloalk-2-enones,<sup>5</sup> in which a chiral sulfinyl group having a sterically bulky aryl group such as a 2,4,6-triisopropylphenyl or 2,4,6-trimethylphenyl group shows extremely high diastereoselectivity in the radical  $\beta$ -addition. We report herein the results of an intermolecular  $\beta$ -addition of alkyl radicals to acyclic  $\alpha$ -(arylsulfinyl) enones.

## Results and discussion

We studied the radical  $\beta$ -addition to acyclic  $\alpha$ -(arylsulfinyl) enones **7a–d** which were prepared from the sulfinates **1–4** in



three steps. The reaction of sulfinates **1–4** with prop-1-enyl-magnesium bromide, which was prepared from magnesium and a mixture of (*E*)- and (*Z*)-1-bromoprop-1-ene, gave a mixture of (*E*)- and (*Z*)-aryl prop-1-enyl sulfoxides **5** in good yields (Scheme 1).<sup>6</sup> A mixture of (*E*)- and (*Z*)-**5** was treated with 2 equiv. of LDA at  $-100^\circ\text{C}$  and subsequently with an excess of acetaldehyde to afford the 3-(arylsulfinyl)pent-3-en-2-ol **6**

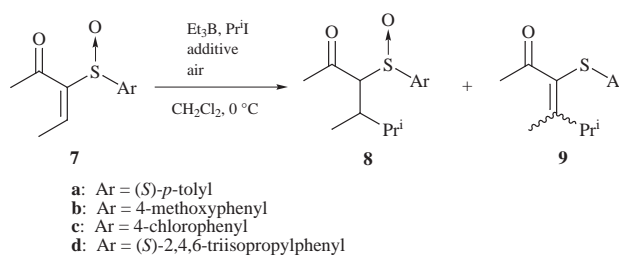


**Scheme 1** Reagents and conditions: i,  $\text{CH}_3\text{CH}=\text{CHMgBr}$ , THF,  $0^\circ\text{C} \rightarrow \text{rt}$ ; ii, LDA,  $\text{CH}_3\text{CHO}$ , THF,  $-100^\circ\text{C}$ ; iii, Jones oxidation or Swern oxidation, and subsequent purification by recrystallization (**7a** and **7d**) or flash column chromatography (**7c**)

which was composed mainly of the (*E*)-isomer due to *cis*–*trans* isomerization during the reaction.<sup>7</sup> Oxidation of **6** was accomplished by Jones oxidation<sup>8</sup> or Swern oxidation<sup>7a</sup> to give the 3-(arylsulfinyl)pent-3-en-2-one **7**. (*E*)-**7a** and (*E*)-**7d** could be isolated by recrystallization from diethyl ether and (*E*)-**7c** by flash column chromatography. A mixture of (*E*)- and (*Z*)-**7b** in an *E*:*Z* ratio of 72:28 was used without separation of the isomers in the following radical reaction.

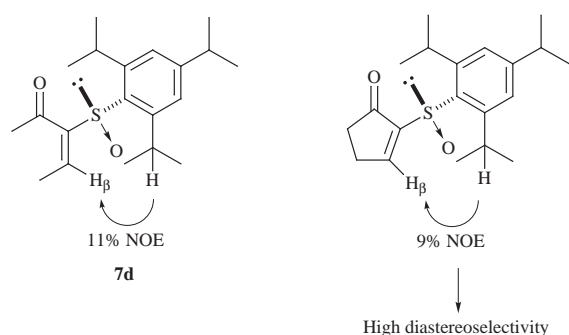
The  $\beta$ -addition of an isopropyl radical to  $\alpha$ -(arylsulfinyl) enones **7a–7d** was carried out as follows. To a degassed solution of the  $\alpha$ -(arylsulfinyl) enone **7** in  $\text{CH}_2\text{Cl}_2$  ( $0.01 \text{ mol dm}^{-3}$ ) was added isopropyl iodide (10 equiv.) and triethylborane (10 equiv.) as a radical initiator<sup>9</sup> at  $0^\circ\text{C}$ , and air was continuously passed through the solution *via* a needle by a microfeeder.<sup>10</sup> The results are shown in Table 1.

The reaction of (*S,E*)-3-(*p*-tolylsulfinyl)pent-3-en-2-one **7a** with an isopropyl radical gave a diastereomeric mixture of the addition products **8a** with low diastereoselectivity (entry 1). The addition product with an ethyl radical generated from triethylborane was not formed.<sup>11</sup> Reactions in the presence of  $\text{TiCl}_2(\text{OPr}^i)_2$ ,<sup>12</sup>  $\text{Ti}(\text{OPr}^i)_4$ ,  $\text{ZnBr}_2$ ,  $\text{BF}_3\cdot\text{OEt}_2$  or  $\text{K}_2\text{CO}_3$  did not alter the stereoselectivity substantially (entries 2–6). We expected a low stereoselectivity, as the *p*-tolyl group is not as effective as the 2,4,6-triisopropylphenyl or 2,4,6-trimethylphenyl group in inducing high stereoselectivity as we observed

**Table 1** Radical  $\beta$ -addition to  $\alpha$ -(arylsulfinyl) enones **7** with isopropyl iodide and triethylborane

Entry	Enone	Additive	<i>t</i> /h	<b>8</b>		<b>9</b>
				Yield (%)	Ratio	Yield (%)
1	<b>7a</b>	none	1	75	21:13:41:19	12
2	<b>7a</b>	TiCl <sub>2</sub> (OP <sup><i>i</i></sup> ) <sub>2</sub>	1	60	13:20:35:32	23
3	<b>7a</b>	Ti(OP <sup><i>i</i></sup> ) <sub>4</sub>	1	80	26:14:48:12	10
4	<b>7a</b>	ZnBr <sub>2</sub>	1	79	39:11:40:10	16
5	<b>7a</b>	BF <sub>3</sub> ·OEt <sub>2</sub>	1	79	45:10:35:10	17
6	<b>7a</b>	K <sub>2</sub> CO <sub>3</sub>	1	80	30:15:42:13	6
7	<b>7a</b>	<i>p</i> -TsOH	1	0	—	57
8	<b>7b<sup>a</sup></b>	none	2	77	17:11:56:16	21
9	<b>7c</b>	none	1	91	21:13:49:17	6
10	<b>7d</b>	none	1.5	0	—	58
11	<b>7d</b>	TiCl <sub>2</sub> (OP <sup><i>i</i></sup> ) <sub>2</sub>	45	0	—	23
12	<b>7d</b>	SiMe <sub>3</sub> Cl	1.5	0	—	33
13	<b>7d</b>	<i>p</i> -TsOH	0.7	0	—	99
14	<b>7d</b>	galvinoxyl	3 days	no reaction	—	—

<sup>a</sup> An *E*:*Z* = 72:28 mixture was used.

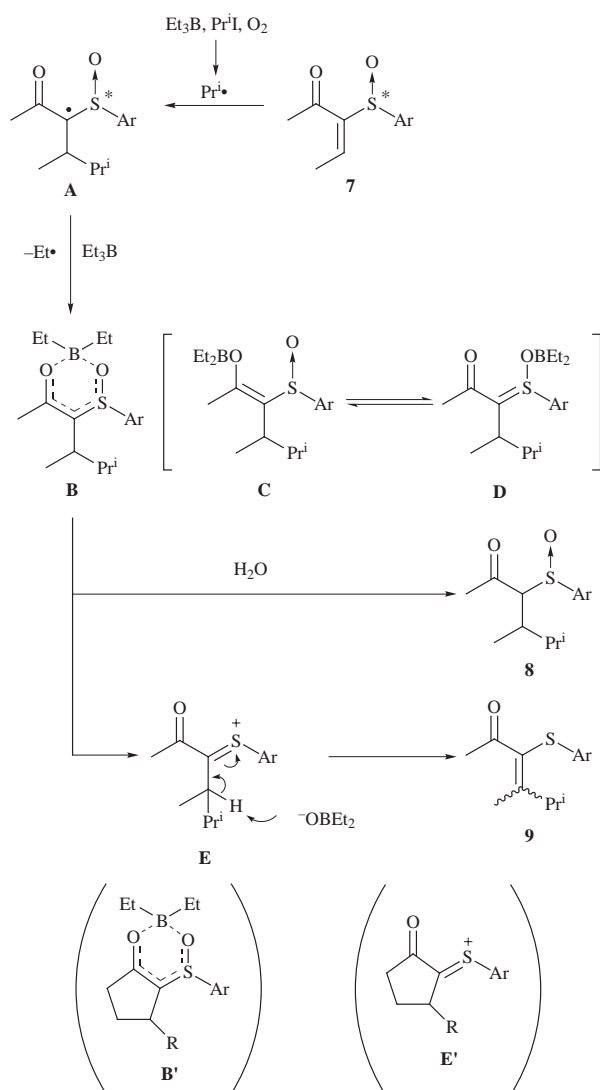
**Fig. 1**

in the reaction of 2-(arylsulfinyl)cyclopent-2-enones.<sup>5</sup> It was, however, surprising that an unexpected product, 4,5-dimethyl-3-(*p*-tolylsulfinyl)hex-3-en-2-one **9a**, was formed besides the addition products **8a**. The yield of the  $\alpha$ -(arylsulfinyl) enone **9a** increased when the reaction was carried out in the presence of *p*-TsOH, where the addition product was not obtained at all (entry 7). The yield of the  $\alpha$ -(arylsulfinyl) enone **9** increased in the reaction of (*E*)-3-(4-methoxyphenylsulfinyl)pent-3-en-2-one **7b** (entry 8) and decreased in the case of 3-(4-chlorophenylsulfinyl)pent-3-en-2-one **7c** (entry 9). Next, we examined the radical  $\beta$ -addition to (*S,E*)-3-(2,4,6-triisopropylphenylsulfinyl)pent-3-en-2-one **7d** which has a significant nuclear Overhauser effect (11%) between the methine proton of the *o*-isopropyl group and the  $\beta$ -vinyl proton in the <sup>1</sup>H NMR spectrum. Since 2-(2,4,6-triisopropylphenylsulfinyl)cyclopent-2-enone, which also has a significant nuclear Overhauser effect between these protons, shows extremely high stereoselection in the radical  $\beta$ -addition,<sup>5</sup> high stereoselectivity was anticipated in the radical  $\beta$ -addition to  $\alpha$ -(arylsulfinyl) enone **7d** (see Fig. 1).

However, formation of the  $\alpha$ -(arylsulfinyl) enone **9d** was observed in the reaction of  $\alpha$ -(arylsulfinyl) enone **7d**, with no addition product **8d** being formed (entries 10–12). The  $\alpha$ -(arylsulfinyl) enone **9d** was even obtained almost quantitatively when *p*-TsOH was added to the reaction mixture (entry 13). Both reactions to form the addition product **8d** and the

$\alpha$ -(arylsulfinyl) enone **9d** seemed to proceed *via* a radical pathway at least in the first step of the alkyl radical addition, because both reactions were completely suppressed by a radical scavenger (entry 14). The presumed reaction mechanism is shown in Scheme 2.

It is well recognized that enones react with alkyl radicals generated from trialkylborane to form a boron enolate *via* a carbon radical  $\alpha$  to the carbonyl group.<sup>9,13</sup> Thus, an isopropyl radical generated from isopropyl iodide by the action of triethylborane with oxygen, attacks the olefinic carbon  $\beta$  to the carbonyl to form a carbon radical  $\alpha$  to the carbonyl (**A**), which then reacts with triethylborane to form the cyclic intermediate **B** or the rapidly equilibrated boron enolates **C** and **D**. Hydrolysis of the intermediate gives the addition product **8**. However, the Pummerer-type products **9** are formed in the present reaction of  $\alpha$ -(arylsulfinyl) enones probably because of the easy formation of the thionium intermediate **E** from the intermediate **B**. On the other hand, the radical reaction of the 2-(arylsulfinyl)cycloalk-2-enones produced no such Pummerer-type products and induced no racemization of the substrate (see below), due to the difficult formation of the corresponding intermediate **B'** and the subsequent intermediate **E'**, shown in Scheme 2.<sup>5</sup> The S–O bond fission in **B** forms **E** and the subsequent proton abstraction from the  $\beta$ -carbon gives the  $\alpha$ -(arylsulfinyl) enone **9** as a mixture of (*E*)- and (*Z*)-isomers. Since the S–O bond fission is the rate-determining step in the Pummerer reaction of sulfoxides having an electron-withdrawing group at the  $\alpha$ -position,<sup>14</sup> the electronic nature of the substituent on the sulfur should have an influence on this step. In the reaction of the  $\alpha$ -(arylsulfinyl) enone **7b** having an electron-donating 4-methoxyphenyl group, the formation of  $\alpha$ -(arylsulfinyl) enone **9b** increases due to its thionium-stabilizing effect (Table 1, entry 8), whereas the reaction of the  $\alpha$ -(arylsulfinyl) enone **7c** having an electron-withdrawing 4-chlorophenyl group decreases the stability of intermediate **E** and hence the yield of  $\alpha$ -(arylsulfinyl) enone **9c** (Table 1, entry 9). *p*-TsOH would accelerate the S–O bond fission to form the thionium ion intermediate **E**, thus leading to the  $\alpha$ -(arylsulfinyl) enone **9** exclusively (Table 1, entries 7 and 13). This assumption is quite reasonable, since acids are known to



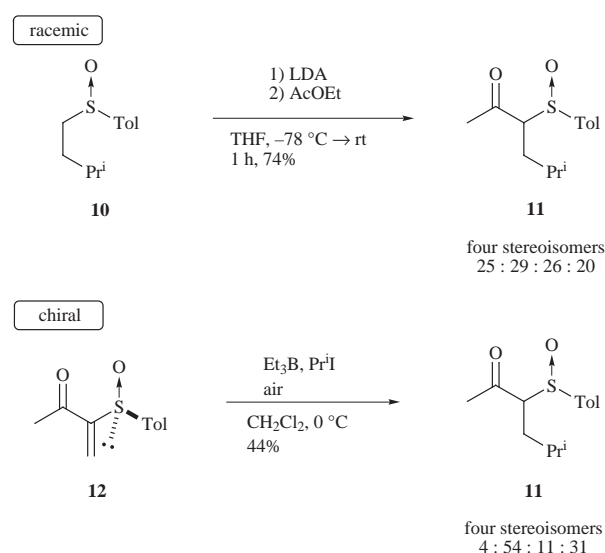
catalyze Pummerer-type reactions from sulfoxides to  $\alpha$ -(aryl-sulfinyl) enones.<sup>15</sup> If this mechanistic pathway is correct then the sulfoxide should racemize during the formation of the cyclic boron enolate **B**. To verify this the following experiment was carried out.

(*S*)-3-(*p*-Tolylsulfinyl)but-3-en-2-one **12**, prepared according to the literature,<sup>8,16</sup> was treated with isopropyl iodide and triethylborane as described above to give the addition product **11** in 44% yield and the ethyl adduct (38% yield) (Scheme 3). HPLC analysis (CHIRALCEL OB-H) of the addition product **11** showed four stereoisomers in a ratio of 4:54:11:31 in order of elution. The retention times for these four stereoisomers were in accord with those for the products obtained on treatment of the racemic isopentyl *p*-tolyl sulfoxide **10** with lithium diisopropylamide and subsequently with ethyl acetate. These results show that the radical addition gives the racemized sulfoxide **11**, supporting the formation of the cyclic boron enolate intermediate **B**.

## Experimental

### General

Diethyl ether (ether) and THF were distilled before use from a deep blue solution resulting from addition of benzophenone and sodium.  $\text{CH}_2\text{Cl}_2$  was distilled from calcium hydride. All reactions were monitored by thin layer chromatography on 0.25 mm Merck silica gel (60F-254) precoated glass plates. TLC plates were visualized with UV light and 7% phosphomolybdic



acid or *p*-anisaldehyde in ethanol. Column chromatography was carried out on a column packed with Fuji Silysia silica gel BW-200. Melting points were measured on a Yanaco micro-melting point apparatus and are uncorrected.  $^1\text{H}$  NMR (200 MHz) and  $^{13}\text{C}$  NMR (50.3 MHz) spectra for solutions in  $\text{CDCl}_3$  were recorded on a Varian Gemini-200 instrument, chemical shifts ( $\delta$ ) are expressed in ppm downfield from internal tetramethylsilane, and *J* values are given in Hz. Infrared spectra were recorded on a JASCO FTIR-200 spectrometer. Mass spectra (eV) were recorded on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin-Elmer-240 instrument. Optical rotations were measured on a JASCO DIP-4 polarimeter operating at  $\lambda = 589$  nm corresponding to the sodium D line, in the indicated solvent with concentration in grams of solute per 100  $\text{cm}^3$ . HPLC analyses were performed on a JASCO TRI ROTOR IV using  $4.6 \times 150$  mm COSMOSIL and  $4.6 \times 250$  mm CHIRALCEL OB-H packed columns (flow rate,  $0.5 \text{ cm}^3 \text{ min}^{-1}$ ).

### Preparation of the acyclic $\alpha$ -sulfinyl enones

**4-Methoxyphenyl prop-1-enyl sulfoxide 5b.** To a solution of isopropyl 4-methoxybenzenesulfinate<sup>17</sup> **2** (2.28 g, 10.7 mmol) in THF (11  $\text{cm}^3$ ) was added dropwise a solution of prop-1-enylmagnesium bromide, prepared from 1-bromoprop-1-ene (1.46  $\text{cm}^3$ , 17.1 mmol) and magnesium (389 mg, 16 mmol) in THF (26  $\text{cm}^3$ ), at  $0^\circ\text{C}$  over a period of 5 min. After stirring for 10 min at room temperature, the mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (10  $\text{cm}^3$ ) at  $0^\circ\text{C}$  and concentrated under reduced pressure. The aqueous mixture was extracted with  $\text{Et}_2\text{O}$  ( $3 \times 5 \text{ cm}^3$ ). The combined organic extracts were washed with saturated aqueous  $\text{NaHCO}_3$  (5  $\text{cm}^3$ ), brine (5  $\text{cm}^3$ ), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated to give the crude sulfoxide, which was purified by column chromatography (hexane–ethyl acetate, 40:60) to give the sulfoxide **5b** (1.91 g, 91%) in an *E*:*Z* ratio of 73:27. (*E*)-**5b** (Found: C, 61.18; H, 6.31.  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$  requires C, 61.20; H, 6.16%); TLC  $R_f$  0.37 (hexane–ethyl acetate, 40:60);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2950, 1595, 1500, 1440, 1305, 1260 and 1030;  $\delta_{\text{H}}$  1.91 (3 H, dd, *J* 1.6, 6.8,  $\text{CH}_3\text{CH}=\text{CH}$ ), 3.85 (3 H, s,  $\text{OCH}_3$ ), 6.23 (1 H, dq, *J* 1.6, 15.1,  $\text{CH}_3\text{CH}=\text{CH}$ ), 6.58 (1 H, dq, *J* 6.8, 15.1,  $\text{CH}_3\text{CH}=\text{CH}$ ), 6.94–7.08 (2 H, m, ArH) and 7.50–7.62 (2 H, m, ArH);  $\delta_{\text{C}}$  17.4, 55.3, 114.6, 126.3, 135.0, 135.3, 136.1 and 161.6; *m/z* (EI) 196 ( $\text{M}^+$ , 10%), 155 (50) and 148 (100). (*Z*)-**5b**: TLC  $R_f$  0.27 (hexane–ethyl acetate, 40:60);  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  2945, 1590, 1500, 1460, 1305, 1250 and 1035;  $\delta_{\text{H}}$  2.13 (3 H, d, *J* 5.5,  $\text{CH}_3\text{CH}=\text{CH}$ ), 3.85 (3 H, s,  $\text{OCH}_3$ ), 6.12–6.33 (2 H, m,  $\text{CH}=\text{CH}$ ), 6.94–7.08 (2 H, m, ArH) and 7.50–7.62 (2 H, m, ArH);  $\delta_{\text{C}}$  15.0, 55.4, 114.8, 125.8, 135.5, 136.2, 138.0 and 161.7.

**4-Chlorophenyl prop-1-enyl sulfoxide 5c.** The reaction was carried out as described above using isopropyl 4-chlorobenzenesulfinate<sup>17</sup> **3** (2.46 g, 11.3 mmol) to give the sulfoxide **5c** (2.04 g, 90%) in an *E:Z* ratio of 71:29. (*E*)-**5c** (Found: C, 53.66; H, 4.59. C<sub>9</sub>H<sub>9</sub>ClOS requires C, 53.87; H, 4.52%); TLC *R<sub>f</sub>* = 0.54 (hexane–ethyl acetate, 40:60);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3015, 2910, 1630, 1580, 1480, 1445, 1390, 1090 and 1040;  $\delta_{\text{H}}$  1.92 (3 H, dd, *J* 1.5, 6.7, CH<sub>3</sub>), 6.24 (1 H, dq, *J* 1.5, 15.2, CH<sub>3</sub>CH=CH), 6.64 (1 H, dq, *J* 6.7, 15.2, CH<sub>3</sub>CH=CH) and 7.40–7.62 (4 H, m, ArH);  $\delta_{\text{C}}$  17.7, 125.7, 129.4, 136.0, 136.9, 137.2 and 142.7; *m/z* (EI) 200 (M<sup>+</sup>, 21%), 152 (100) and 117 (54). (*Z*)-**5c**: TLC *R<sub>f</sub>* = 0.44 (hexane–ethyl acetate, 40:60);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3015, 2950, 1630, 1480, 1390, 1090 and 1040;  $\delta_{\text{H}}$  2.16 (3 H, dd, *J* 1.2, 6.7, CH<sub>3</sub>), 6.15–6.42 (2 H, m, CH=CH) and 7.40–7.62 (4 H, m, ArH);  $\delta_{\text{C}}$  15.0, 125.2, 129.2, 136.5, 137.1, 137.5 and 142.9.

**(R)-Prop-1-enyl 2,4,6-triisopropylphenyl sulfoxide 5d.** The reaction was carried out as described above using (*S*)-diacetone D-glucosyl 2,4,6-triisopropylbenzenesulfinate<sup>5</sup> (*S*)-**4** (4.94 g, 9.67 mmol) to give the sulfoxide **5d** (2.29 g, 81%). (*E*)-**5d** (Found: C, 73.68; H, 9.51. C<sub>18</sub>H<sub>28</sub>OS requires C, 73.92; H, 9.65%); TLC *R<sub>f</sub>* = 0.26 (hexane–ethyl acetate, 80:20); [ $\alpha$ ]<sub>D</sub><sup>25</sup> –63.1 (*c* 0.482 in CHCl<sub>3</sub>);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2960, 1600, 1470, 1050 and 1030;  $\delta_{\text{H}}$  1.23, 1.25 and 1.32 [18 H, 3 × d, *J* 6.7, 6.8, 6.8, 3 × CH(CH<sub>3</sub>)<sub>2</sub>], 2.10 (3 H, dd, *J* 1.6, 7.1, CH<sub>3</sub>CH=CH), 2.75–3.01 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.85–4.08 [2 H, m, 2 × CH(CH<sub>3</sub>)<sub>2</sub>], 6.27 (1 H, dq, *J* 7.1, 9.9, CH<sub>3</sub>CH=CH), 6.75 (1 H, dq, *J* 1.6, 9.9, CH<sub>3</sub>CH=CH) and 7.08 (2 H, s, ArH);  $\delta_{\text{C}}$  14.7, 24.0, 24.8, 28.8, 34.3, 123.1, 135.3, 135.9, 136.9, 149.8 and 152.4; *m/z* (EI) 292 (M<sup>+</sup>, 19%), 275 (100), 233 (39), 191 (74) and 149 (66). (*Z*)-**5d** (Found: C, 73.62; H, 9.64. C<sub>18</sub>H<sub>28</sub>OS requires C, 73.92; H, 9.65%); TLC *R<sub>f</sub>* = 0.37 (hexane–ethyl acetate, 80:20); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +203 (*c* 0.350 in CHCl<sub>3</sub>);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2960, 1600, 1470 and 1055;  $\delta_{\text{H}}$  1.18–1.39 [18 H, m, 3 × CH(CH<sub>3</sub>)<sub>2</sub>], 1.92 (3 H, d, *J* 5.0, CH<sub>3</sub>CH=CH), 2.75–3.01 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.79–4.05 [2 H, m, 2 × CH(CH<sub>3</sub>)<sub>2</sub>], 6.36–6.51 (2 H, m, CH=CH) and 7.06 (2 H, s, ArH);  $\delta_{\text{C}}$  17.8, 23.7, 24.8, 28.2, 34.3, 123.0, 133.5, 134.0, 134.7, 150.3 and 152.6; *m/z* (EI) 292 (M<sup>+</sup>, 16%), 275 (100), 233 (40), 191 (77) and 149 (69).

**(S<sub>S</sub>)-3-(*p*-Tolylsulfinyl)pent-3-en-2-ol 6a.** To a solution of LDA (13.0 mmol) was added a solution of (*R*)-prop-1-enyl *p*-tolyl sulfoxide **5a**<sup>6</sup> (1.06 g, 5.89 mmol) in THF (6 cm<sup>3</sup>) at –100 °C over a period of 3 min. After the reaction mixture was stirred for 2 min, a solution of acetaldehyde (25.2 cm<sup>3</sup>, 1.17 mol cm<sup>-3</sup> in THF, 29.5 mmol) was added. The reaction mixture was stirred for 15 min, then quenched with saturated aqueous NH<sub>4</sub>Cl (10 cm<sup>3</sup>), and concentrated under reduced pressure. The aqueous mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 cm<sup>3</sup>). The combined organic extracts were washed with brine (10 cm<sup>3</sup>), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give the crude alcohol, which was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>–ethyl acetate, 60:40) to give the alcohol **6a** (1.14 g, 87%) as a mixture of four diastereomers composed mainly of the (*E*)-isomers. (*E*)-**6a** (Found: C, 64.28; H, 7.30. C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>S requires C, 64.25; H, 7.19%); TLC *R<sub>f</sub>* = 0.17 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3370, 2980, 1600, 1495, 1450, 1400, 1380, 1080 and 1030;  $\delta_{\text{H}}$  1.07 and 1.22 [3 H, 2 × d, *J* 6.7 and 6.8, CH(OH)CH<sub>3</sub>], 1.98 (3 H, d, *J* 7.2, CH<sub>3</sub>CH=C), 2.41 (3 H, s, ArCH<sub>3</sub>), 2.70–2.84 (1 H, m, OH), 4.61–4.85 [1 H, m, CH(OH)], 6.43 and 6.53 (1 H, 2 × q, *J* 7.2 and 7.2, CH=C), 7.22–7.37 (2 H, m, ArH) and 7.43–7.59 (2 H, m, ArH); *m/z* (EI) 224 (M<sup>+</sup>, 12%), 206 (6) and 140 (100).

**3-(4-Methoxyphenylsulfinyl)pent-3-en-2-ol 6b.** The reaction was carried out as described above using the sulfoxide **5b** (1.20 g, 6.11 mmol) to give the alcohol **6b** (1.01 g, 69%) as a mixture of four diastereomers; TLC *R<sub>f</sub>* = 0.17 (hexane–ethyl acetate, 30:70);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3370, 2975, 1595, 1500, 1250, 1090 and 1025;  $\delta_{\text{H}}$  1.01–1.46 [3 H, m, CH(OH)CH<sub>3</sub>], 1.89–2.22 (3 H, m, CH<sub>3</sub>CH=C), 2.56–2.92 (1 H, m, OH), 3.85 and 3.86 (3 H, 2 × s, OCH<sub>3</sub>), 4.05–4.85 [1 H, m, CH(OH)], 6.23–6.62 (1 H, m,

CH=C), 6.90–7.12 (2 H, m, ArH) and 7.39–7.67 (2 H, m, ArH); *m/z* (EI) 240 (M<sup>+</sup>, 17%), 192 (9) and 156 (100).

**3-(4-Chlorophenylsulfinyl)pent-3-en-2-ol 6c.** The reaction was carried out as described above using the sulfoxide **5c** (1.20 g, 5.98 mmol) to give the alcohol **6c** (769 mg, 53%) as a mixture of four diastereomers; TLC *R<sub>f</sub>* = 0.31 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3370, 2980, 1580, 1480, 1395, 1090 and 1030;  $\delta_{\text{H}}$  1.02–1.40 [3 H, m, CH(OH)CH<sub>3</sub>], 1.90–2.24 (3 H, m, CH<sub>3</sub>CH=C), 2.42–2.85 (1 H, m, OH), 4.40–4.92 [1 H, m, CH(OH)], 6.30–6.63 (1 H, m, CH=C) and 7.39–7.67 (4 H, m, ArH); *m/z* (EI) 244 (M<sup>+</sup>, 13%), 226 (16) and 160 (100).

**(S<sub>S</sub>)-3-(2,4,6-Triisopropylphenylsulfinyl)pent-3-en-2-ol 6d.** The reaction was carried out as described above using the sulfoxide **5d** (1.06 g, 3.62 mmol) to give the alcohol **6d** (1.11 g, 91%) as a diastereomeric mixture of (*E*)-isomers in a ratio of 57:43 (Found: C, 71.49; H, 9.71. C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>S requires C, 71.38; H, 9.58%); TLC *R<sub>f</sub>* = 0.26 (hexane–ethyl acetate, 70:30);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 3315, 2970, 1600, 1460, 1370, 1110 and 1020;  $\delta_{\text{H}}$  1.05–1.34 [18 H, m, 3 × CH(CH<sub>3</sub>)<sub>2</sub>], 1.36 and 1.59 [3 H, 2 × d, *J* 6.5 and 6.7, CH(OH)CH<sub>3</sub>], 1.81 and 1.87 [3 H, 2 × d, *J* 7.2 and 7.3, CH<sub>3</sub>CH=C), 2.59 and 3.83 (1 H, 2 × d, *J* 7.1 and 7.8, OH), 2.76–3.03 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.58–4.02 [2 H, m, 2 × CH(CH<sub>3</sub>)<sub>2</sub>], 4.61–5.06 [1 H, m, CH(OH)], 5.51 and 5.77 (1 H, 2 × q, *J* 7.2 and 7.3, CH=C) and 7.07 and 7.10 (2 H, 2 × s, ArH); *m/z* (EI) 336 (M<sup>+</sup>, 3%), 318 (46), 301 (61), 275 (36) and 255 (100).

**(S,E)-3-(*p*-Tolylsulfinyl)pent-3-en-2-one 7a.**—*Method A via the Swern oxidation.*<sup>7a</sup> To a solution of oxalyl chloride (55.5 × 10<sup>-3</sup> cm<sup>3</sup>, 0.636 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 cm<sup>3</sup>) was added dimethyl sulfoxide (60.2 × 10<sup>-3</sup> cm<sup>3</sup>, 0.848 mmol) at –78 °C. After the mixture was stirred for 5 min, a solution of the alcohol **6a** (95.1 mg, 0.424 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.8 cm<sup>3</sup>) was added. The reaction mixture was stirred for an additional 1 h at –78 °C. Then triethylamine (0.12 cm<sup>3</sup>, 0.848 mmol) was added to the reaction mixture, which was stirred for 5 min. The reaction mixture was poured into ice-cooled 1 mol dm<sup>-3</sup> aqueous HCl (10 cm<sup>3</sup>). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 cm<sup>3</sup>). The combined organic extracts were washed with ice–water (10 cm<sup>3</sup>), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give the crude enone, which was purified by column chromatography (hexane–ethyl acetate, 60:40) to give the enone **7a** (64.1 mg, 68%) as a mixture of two diastereomers.

*Method B via the Jones oxidation.*<sup>8</sup> To a solution of the alcohol **6a** (103 mg, 0.458 mmol) in acetone (3 cm<sup>3</sup>) was added at 0 °C the Jones reagent [prepared from chromium(vi) oxide (9.99 g, 100 mmol), 97% sulfuric acid (11.0 cm<sup>3</sup>, 200 mmol) and water (50 cm<sup>3</sup>)], until the starting alcohol disappeared on TLC. The reaction mixture was quenched with water (3 cm<sup>3</sup>) and concentrated under reduced pressure. The aqueous mixture was extracted with Et<sub>2</sub>O. The combined organic extracts were washed with brine (5 cm<sup>3</sup>), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give the crude enone, which was purified by column chromatography (hexane–ethyl acetate, 60:40) to give the enone **7a** (86.5 mg, 85%) as a mixture of two diastereomers. The (*E*)-isomer was further purified by recrystallization from Et<sub>2</sub>O (Found: C, 64.80; H, 6.46. C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>S requires C, 64.84; H, 6.35%); TLC *R<sub>f</sub>* = 0.24 (hexane–ethyl acetate, 60:40); mp 61–62 °C (from Et<sub>2</sub>O); [ $\alpha$ ]<sub>D</sub><sup>25</sup> +255 (*c* 0.434 in CHCl<sub>3</sub>);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2920, 1660, 1625, 1430, 1380, 1220 and 1050;  $\delta_{\text{H}}$  2.22 (3 H, d, *J* 7.4, CH<sub>3</sub>CH), 2.24 (3 H, s, CH<sub>3</sub>CO), 2.38 (3 H, s, ArCH<sub>3</sub>), 7.05 (1 H, q, *J* 7.4, CH=C), 7.25 (2 H, d, *J* 8.3, ArH) and 7.52 (2 H, d, *J* 8.3, ArH);  $\delta_{\text{C}}$  15.7, 21.3, 31.4, 125.6, 129.8, 139.4, 140.1, 141.8, 146.2 and 195.9; *m/z* (EI) 222 (M<sup>+</sup>, 29%), 149 (28), 140 (53) and 139 (100).

**3-(4-Methoxyphenylsulfinyl)pent-3-en-2-one 7b.** The reaction was carried out as described above (Method A) using the alcohol **6b** (700 mg, 2.91 mmol) to give the enone **7b** (399 mg, 58%). An *E:Z* = 72:28 mixture was used for the radical reaction, since attempts to isolate the (*E*)-isomer were unsuccessful (Found: C, 60.31; H, 5.89. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>S requires C, 60.48; H,



5.92%); TLC  $R_f$  = 0.51 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2940, 1655, 1600, 1500, 1255 and 1040;  $\delta_H$  2.22 and 2.24 (3 H, 2 × s, CH<sub>3</sub>CO), 2.24 and 2.38 (3 H, 2 × d, *J* 7.6 and 7.5, CH<sub>3</sub>CH), 3.83 and 3.85 (3 H, 2 × s, OCH<sub>3</sub>), 6.90–7.07 (2 H, m, ArH), 7.05 and 7.32 (3 H, 2 × q, *J* 7.6 and 7.5, CH=C) and 7.48–7.63 (2 H, m, ArH); *m/z* (EI) 238 (M<sup>+</sup>, 51%), 190 (40) and 155 (100).

**(E)-3-(4-Chlorophenylsulfinyl)pent-3-en-2-one 7c.** The reaction was carried out as described above (Method A) using the alcohol **6c** (500 mg, 2.04 mmol) to give the enone **7c** (424 mg, 86%) (Found: C, 54.32; H, 4.51. C<sub>11</sub>H<sub>11</sub>ClO<sub>2</sub>S requires C, 54.43; H, 4.57%); TLC  $R_f$  = 0.29 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3080, 2930, 1660, 1620, 1480, 1380, 1210 and 1050;  $\delta_H$  2.26 (3 H, d, *J* 7.6, CH<sub>3</sub>CH), 2.31 (3 H, s, CH<sub>3</sub>CO), 7.11 (1 H, q, *J* 7.6, CH=C) and 7.36–7.65 (4 H, m, ArH);  $\delta_C$  15.8, 31.5, 126.8, 129.3, 137.3, 140.2, 142.2, 146.1 and 195.6; *m/z* (EI) 242 (M<sup>+</sup>, 51%), 183 (25), 144 (46) and 112 (100).

**(S,E)-3-(2,4,6-Triisopropylphenylsulfinyl)pent-3-en-2-one 7d.** The reaction was carried out as described above (Method B) using the alcohol **6d** (338 mg, 1.00 mmol) to give the enone **7d** (242 mg, 72%), which was further purified by recrystallization from Et<sub>2</sub>O (Found: C, 71.65; H, 9.22. C<sub>20</sub>H<sub>30</sub>O<sub>2</sub>S requires C, 71.81; H, 9.04%); TLC  $R_f$  = 0.43 (hexane–ethyl acetate, 70:30); mp 70–71 °C (from Et<sub>2</sub>O);  $[\alpha]_D^{25}$  +286 (*c* 0.402 in CHCl<sub>3</sub>);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 2970, 1675, 1600, 1470, 1375, 1190 and 1050;  $\delta_H$  1.20, 1.22 and 1.27 [18 H, 3 × d, *J* 6.9, 6.9, 6.9, 3 × CH(CH<sub>3</sub>)<sub>2</sub>], 2.17 (3 H, d, *J* 7.6, CH<sub>3</sub>CH), 2.20 (3 H, s, CH<sub>3</sub>CO), 2.73–3.00 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.72–4.00 [2 H, m, 2 × CH(CH<sub>3</sub>)<sub>2</sub>], 6.77 (1 H, q, *J* 7.6, CH=C) and 7.03 (2 H, s, ArH);  $\delta_C$  15.7, 23.7, 25.0, 27.8, 31.3, 34.3, 123.1, 132.1, 135.8, 146.7, 151.3, 153.0 and 197.0; *m/z* (EI) 334 (M<sup>+</sup>, 6%), 317 (4) and 291 (100).

#### General procedure for radical β-addition to α-(arylsulfinyl) enones 7

A solution of the α-(arylsulfinyl) enone **7** in CH<sub>2</sub>Cl<sub>2</sub> (0.01 mol dm<sup>-3</sup>) was degassed under reduced pressure using a sonicator. To this solution was added triethylborane (10 equiv.) and isopropyl iodide (10 equiv.) at 0 °C. In the reaction using an additive, the additive (1.1 equiv.) was added at 0 °C and the mixture was stirred for 1 h before the addition of triethylborane and isopropyl iodide. Then air was passed through the solution by a microfeeder at a rate of 90.0 × 10<sup>-3</sup> cm<sup>3</sup> min<sup>-1</sup> per 1 mmol of triethylborane. The reaction mixture was poured into saturated aqueous NaH<sub>2</sub>PO<sub>4</sub>, and extracted with Et<sub>2</sub>O. The combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated to give the crude product which was purified by column chromatography to give the addition product **8** and the Pummerer-type product **9**.

**4,5-Dimethyl-3-(*p*-tolylsulfinyl)hexan-2-one 8a.** (Found: C, 67.47; H, 8.48. C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>S requires C, 67.63; H, 8.32%); TLC  $R_f$  = 0.51 (hexane–ethyl acetate, 60:40);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2970, 1705, 1360, 1215 and 1060;  $\delta_H$  0.63–1.39 [9 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 1.81, 1.196 and 2.00 (3 H, 3 × s, CH<sub>3</sub>CO), 2.17–2.70 [2 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 2.41 (3 H, s, ArCH<sub>3</sub>), 3.13, 3.23, 3.93 and 3.95 (1 H, 4 × d, *J* 11.7, 11.0, 6.3 and 9.7, COCHSO) and 7.22–7.56 (4 H, m, ArH); *m/z* (EI) 266 (M<sup>+</sup>, 1%), 140 (100) and 127 (70).

**4,5-Dimethyl-3-(4-methoxyphenylsulfinyl)hexan-2-one 8b.** (Found: C, 63.97; H, 7.92. C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>S requires C, 63.80; H, 7.85%); TLC  $R_f$  = 0.53 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2960, 1700, 1600, 1500, 1360, 1090 and 1055;  $\delta_H$  0.65–1.34 [9 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 1.95 and 2.02 (3 H, 2 × s, CH<sub>3</sub>CO), 2.17–2.68 [2 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 3.13 and 3.26 (1 H, 2 × d, *J* 11.8 and 10.8, COCHSO) and 3.73–3.90 (1 H, m, COCHSO), 3.84 and 3.85 (3 H, 2 × s, OCH<sub>3</sub>), 6.96–7.10 (2 H, m, ArH) and 7.37–7.51 (2 H, m, ArH); *m/z* (EI) 282 (M<sup>+</sup>, 20%), 156 (81) and 155 (100).

**4,5-Dimethyl-3-(4-chlorophenylsulfinyl)hexan-2-one 8c.** (Found: C, 58.48; H, 6.56. C<sub>14</sub>H<sub>19</sub>ClO<sub>2</sub>S requires C, 58.63; H,

6.68%); TLC  $R_f$  = 0.65 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2970, 1705, 1480, 1395, 1360, 1280 and 1050;  $\delta_H$  0.72–1.39 [9 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 1.87, 1.96, 1.99 and 2.00 (3 H, 4 × s, CH<sub>3</sub>CO), 1.50–2.70 [2 H, m, CH(CH<sub>3</sub>)<sub>2</sub> and CHCH<sub>3</sub>], 3.13, 3.23, 3.94 and 3.99 (1 H, 4 × d, *J* 12.3, 11.0, 6.5 and 9.5, COCHSO) and 7.37–7.62 (4 H, m, ArH); *m/z* (EI) 286 (M<sup>+</sup>, 3%), 217 (5), 202 (8), 160 (100) and 127 (92).

**4,5-Dimethyl-3-(*p*-tolylsulfinyl)hex-3-en-2-one 9a.** (Found: C, 72.55; H, 8.17. C<sub>15</sub>H<sub>20</sub>OS requires C, 72.54; H, 8.12%); TLC  $R_f$  = 0.80 (hexane–ethyl acetate, 60:40);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2970, 1730, 1690, 1490 and 1270;  $\delta_H$  1.06 and 1.08 [6 H, 2 × d, *J* 6.8 and 6.8, CH(CH<sub>3</sub>)<sub>2</sub>], 1.91 and 1.98 (3 H, 2 × s, CH<sub>3</sub>C=), 2.23 and 2.24 (3 H, 2 × s, CH<sub>3</sub>CO), 2.28 (3 H, s, ArCH<sub>3</sub>), 2.92–3.03 and 3.43–3.64 [1 H, 2 × m, CH(CH<sub>3</sub>)<sub>2</sub>] and 7.07 (4 H, s, ArH); *m/z* (EI) 248 (M<sup>+</sup>, 100%), 233 (16) and 137 (33).

**4,5-Dimethyl-3-(4-methoxyphenylsulfinyl)hex-3-en-2-one 9b.** (Found: C, 68.17; H, 7.48. C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>S requires C, 68.15; H, 7.62%); TLC  $R_f$  = 0.88 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2960, 1690, 1600, 1500, 1295 and 1245;  $\delta_H$  1.06 and 1.07 [6 H, 2 × d, *J* 6.9 and 6.8, CH(CH<sub>3</sub>)<sub>2</sub>], 1.87 and 1.98 (3 H, 2 × s, CH<sub>3</sub>C=), 2.22 and 2.23 (3 H, 2 × s, CH<sub>3</sub>CO), 2.85–3.05 and 3.45–3.68 [1 H, 2 × m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.77 (3 H, s, OCH<sub>3</sub>), 6.82–6.90 (2 H, m, ArH) and 7.10–7.22 (2 H, m, ArH); *m/z* (EI) 264 (M<sup>+</sup>, 100%), 250 (10), 151 (28), 140 (50) and 113 (75).

**4,5-Dimethyl-3-(4-chlorophenylsulfinyl)hex-3-en-2-one 9c.** (Found: C, 62.66; H, 6.39. C<sub>14</sub>H<sub>17</sub>ClOS requires C, 62.56; H, 6.37%); TLC  $R_f$  = 0.85 (hexane–ethyl acetate, 50:50);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2970, 1690, 1480, 1350, 1205 and 1100;  $\delta_H$  1.03 and 1.07 [6 H, 2 × d, *J* 6.8 and 6.8, CH(CH<sub>3</sub>)<sub>2</sub>], 1.91 and 1.95 (3 H, 2 × s, CH<sub>3</sub>C=), 2.23 (3 H, s, CH<sub>3</sub>CO), 2.90–3.14 and 3.30–3.57 [1 H, 2 × m, CH(CH<sub>3</sub>)<sub>2</sub>] and 7.00–7.25 (4 H, m, ArH); *m/z* (EI) 268 (M<sup>+</sup>, 100%), 254 (20), 225 (12), 155 (24), 143 (13) and 125 (20).

**4,5-Dimethyl-3-(2,4,6-triisopropylphenylsulfinyl)hex-3-en-2-one 9d.** (Found: C, 76.55; H, 10.20. C<sub>23</sub>H<sub>36</sub>OS requires C, 76.61; H, 10.06%); TLC  $R_f$  = 0.72 (hexane–ethyl acetate, 80:20);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2970, 1700, 1600, 1470, 1370 and 1205;  $\delta_H$  1.02 and 1.09 [6 H, 2 × d, *J* 6.8 and 6.8, CH(CH<sub>3</sub>)<sub>2</sub>], 1.13–1.69 [21 H, m, 3 × CH(CH<sub>3</sub>)<sub>2</sub> and CH<sub>3</sub>C=], 1.91 and 1.97 (3 H, 2 × s, CH<sub>3</sub>CO), 2.50–2.73 and 3.48–3.75 [1 H, 2 × m, CH(CH<sub>3</sub>)<sub>2</sub>], 2.72–2.98 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 3.53–3.82 [2 H, m, 2 × CH(CH<sub>3</sub>)<sub>2</sub>] and 6.96 (2 H, s, ArH); *m/z* (EI) 360 (M<sup>+</sup>, 52%), 317 (7), 204 (100) and 189 (67).

**5-Methyl-3-(*p*-tolylsulfinyl)hexan-2-one 11.** (Found: C, 66.52; H, 7.91. C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>S requires C, 66.63; H, 7.99%); TLC  $R_f$  = 0.17 (hexane–ethyl acetate, 80:20); HPLC  $t_R$  = 29.02, 31.70, 33.18 and 37.44 min (hexane–propan-2-ol, 98:2);  $\nu_{\max}$  (neat)/cm<sup>-1</sup> 2960, 1710, 1680, 1625, 1580, 1355, 1290, 1170 and 1040;  $\delta_H$  0.80–1.00 [6 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 1.15–1.41 (2 H, m, CH<sub>2</sub>), 1.49–1.75 [1 H, m, CH(CH<sub>3</sub>)<sub>2</sub>], 1.90, 2.16 (3 H, 2 × s, CH<sub>3</sub>CO), 2.42 (3 H, s, ArCH<sub>3</sub>), 3.54 and 3.76 (1 H, 2 × dd, *J* 5.4, 9.8 and 4.4, 9.6, COCHSO) and 7.27–7.53 (4 H, m, ArH); *m/z* (EI) 252 (M<sup>+</sup>, 5%), 201 (3), 140 (100) and 139 (89).

#### Acknowledgements

This work was partly supported by the Ministry of Education, Science and Culture of Japan (Grant-in-Aid for Scientific Research No. 06805079).

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Paper 8/00828K

Received 30th January 1998

Accepted 10th March 1998