

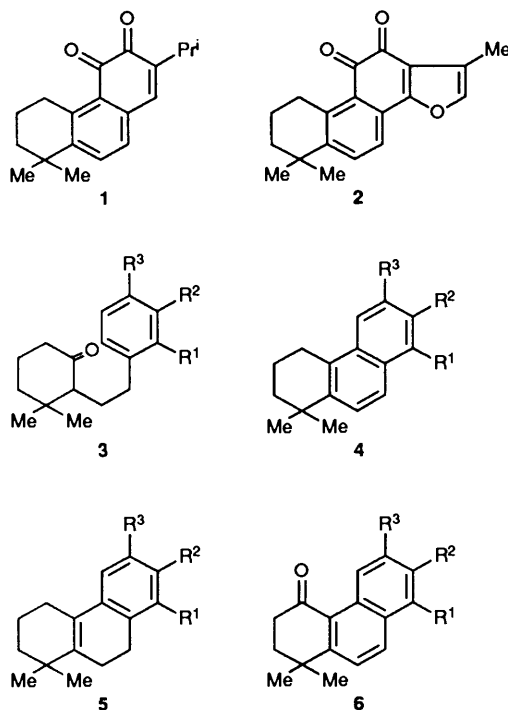
## An Expeditious Synthesis of 1,2,3,4-Tetrahydro-1,1-dimethylphenanthrenes

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A simple convergent and general method has been developed for the synthesis of 1,2,3,4-tetrahydro-1,1-dimethylphenanthrenes **4a-f** and a few 1,2,3,4,9,10-hexahydro-1,1-dimethylphenanthrenes **5c-f** by polyphosphoric acid catalysed reaction of the easily accessible 2-(2-arylethyl)-3,3-dimethylcyclohexanones **3a-f**. The tetrahydrophenanthrenes **4a,c,e,f** have been converted to the respective benzylic ketones **6a,c,e,f** by oxidation with pyridinium chlorochromate and Celite.

The 1,1-dimethyltetrahydrophenanthrenes **4a**<sup>1,2</sup> and **4b**<sup>3</sup> and **4c**,<sup>4</sup> key intermediates used in a number of the total syntheses of miltirone **1**<sup>5</sup> and tanshinone IIA **2**,<sup>6</sup> respectively, two important members of a large group of highly bio-active abietane diterpenoid quinones<sup>2</sup> isolated from the roots of *Salvia miltiorrhiza* Bunge (Danshen), have been prepared by a lengthy sequence of reactions from substituted benzene and naphthalene derivatives. We describe now a simple convergent and a highly efficient general synthetic route to **4a-c**, simonellite **4d**<sup>7</sup> and the related tetrahydrophenanthrenes **4e,f** through the easily accessible cyclohexanone derivatives **3a-f**, used in our recent synthesis<sup>8-12</sup> of some diterpenoids.



- 3a, 4a, 6a;** R<sup>1</sup> = H, R<sup>2</sup> = Pr<sup>i</sup>, R<sup>3</sup> = OMe  
**3b, 4b;** R<sup>1</sup> = R<sup>3</sup> = OMe, R<sup>2</sup> = H  
**3c, 4c, 5c, 6c;** R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = OMe  
**3d, 4d, 5d;** R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = Pr<sup>i</sup>  
**3e, 4e, 5e, 6e;** R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = OMe  
**3f, 4f, 5f, 6f;** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H

Polyphosphoric acid induced reactions of **3a**<sup>8</sup> and **3b**<sup>12</sup> in boiling toluene directly afforded **4a**<sup>1,2</sup> and **4b**,<sup>3</sup> in 75 and 79% yields respectively, as the only isolable products by concomitant cyclodehydration and aromatisation.<sup>13</sup> Under the similar conditions, however, the ketones **3c**,<sup>9</sup> **3d**,<sup>11</sup> **3e**<sup>10</sup> and **3f**<sup>9</sup> gave the respective tetrahydrophenanthrenes **4c**,<sup>3</sup> **4d**,<sup>7</sup> **4e**<sup>14</sup> and **4f** in high yields† along with minor amounts of the corresponding hexahydrophenanthrenes **5c-f**, separated by column chromatography. Each of these mixtures on dehydrogenation directly with palladium-charcoal in boiling xylene led to the corresponding tetrahydrophenanthrenes in 82–95% yields.

The ketones **6a**<sup>2,15</sup> and **6e**,<sup>16</sup> prepared by a lengthy sequence of reactions, have been transformed recently to some diterpenoids by a reductive angular methylation reaction.<sup>15,16</sup> We have found that the easily accessible tetrahydrophenanthrenes **4a**, **4c**, **4e** and **4f** undergo smooth benzylic oxidation<sup>17</sup> with pyridinium chlorochromate (PCC)-Celite in dichloromethane to afford the respective ketones **6a**, **6c**, **6e** and **6f** in 82–85% yields.

In conclusion, in the present work a simple convergent and general synthetic route has been developed for some key hydrophenanthrene intermediates for the synthesis of diterpenoids.

### Experimental

IR spectra of solids (KBr) and liquids (film) were recorded on a Perkin-Elmer model PE 298 instrument. UV spectra were recorded on a Beckman DU spectrometer for solutions in ethanol (95%). <sup>1</sup>H NMR spectra were recorded at 200 MHz on an XL-200 spectrometer for solutions in CDCl<sub>3</sub> with SiMe<sub>4</sub> as internal standard, *J* values are given in Hz. Analytical GLC was performed on a Shimadzu GC-9A model with a flame-ionisation detector employing a 1.5% OV-17 (6.5 ft. × 0.25 in) column with N<sub>2</sub> as the carrier gas. Column chromatography was performed on neutral alumina (Brockmann Grade 1, of BDH, India) or silica gel [Glaxo Laboratories (India) Ltd.]. Light petroleum refers to the fraction of b.p. 40–60 °C unless otherwise stated. Ether refers to diethyl ether. Elemental analyses were performed by Mr. P. P. Bhattacharya and S. K. Sarkar of this laboratory.

*Cyclisation of 3a to 4a.*—To a well-stirred mixture of polyphosphoric acid (PPA) prepared from orthophosphoric acid (15 cm<sup>3</sup>, 85%) and phosphorus pentoxide (23 g) at 115–120 °C (bath temp.) a solution of ketone **3a**<sup>8</sup> (1 g, 3.30 mmol) in toluene (10 cm<sup>3</sup>) was added, stirring at the same temperature was continued for 10 h. The red mixture was decomposed with crushed ice and the organic matter was extracted with ether. The ethereal extracts were washed thoroughly with water and 3% aqueous Na<sub>2</sub>CO<sub>3</sub> and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent afforded 1,2,3,4-tetrahydro-7-isopropyl-6-methoxy-1,1-

† Since the reaction was carried out under N<sub>2</sub> the dehydrogenation during the cyclisations possibly involved oxygen dissolved in the reaction medium. However, for a given substrate, the yield of the tetrahydro product does not parallel the length of the reaction in PPA.

dimethylphenanthrene **4a** (700 mg, 75%), as a white solid, m.p. 83–84 °C (from methanol) (lit.,<sup>1</sup> m.p. 83–85 °C);  $\nu_{\max}/\text{cm}^{-1}$  1627 and 1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  238 (log  $\epsilon$  4.92);  $\delta$  1.30 (6 H, d, *J* 7, *CHMe*<sub>2</sub>), 1.35 (6 H, s, *CMe*<sub>2</sub>), 1.70–1.79 (2 H, m, 2-*H*<sub>2</sub>), 1.92–2.04 (2 H, m, 3-*H*<sub>2</sub>), 3.07 (2 H, t, *J* 7, 4-*H*<sub>2</sub>), 3.35–3.50 (1 H, m, *CHMe*<sub>2</sub>), 3.98 (3 H, s, *ArOMe*), 7.22 (1 H, s, 5-*ArH*), 7.40 (1 H, d, *J* 8, 10-*ArH*) and 7.66–7.75 (2 H, m, 8-*ArH* and 9-*ArH*) [lit.,<sup>1</sup>  $\delta(\text{CDCl}_3$ ; 60 MHz) 2.5–3.0 (4 H, m, *ArH*), 6.15 (3 H, s, *OMe*), 6.70 (1 H, m, *CHMe*<sub>2</sub>), 7.05 (2 H, t, *J* 6, benzylic *CH*<sub>2</sub>), 8.25 (4 H, m, 2 × *CH*<sub>2</sub>) and 8.7–8.8 (12 H, m, 4 × *Me*)].

*Cyclisation of 3b to 4b.* The ketone **3b**<sup>12</sup> (1 g, 3.44 mmol) was converted in the same way as described for **4a** into 1,2,3,4-tetrahydro-5,7-dimethoxy-1,1-dimethylphenanthrene **4b** which was obtained as a white solid (735 mg, 79%), m.p. 159–160 °C (light petroleum) (lit.,<sup>3</sup> m.p. 158 °C);  $\nu_{\max}/\text{cm}^{-1}$  1626 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  238 (log  $\epsilon$  4.84) [lit.,<sup>3</sup>  $\lambda_{\max}(\text{EtOH})/\text{nm}$  238, 284, 295, 331];  $\delta$  1.34 (6 H, s, *CMe*<sub>2</sub>), 1.64–1.78 (2 H, m, 2-*H*<sub>2</sub>), 1.90–2.02 (2 H, m, 3-*H*<sub>2</sub>), 3.02 (2 H, t, *J* 7, 4-*H*<sub>2</sub>), 3.94 (3 H, s, *ArOMe*), 3.96 (3 H, s, *ArOMe*), 6.50 (1 H, br s, 5-*ArH*), 6.84 (1 H, br s, 7-*ArH*), 7.38 (1 H, d, *J* 8, 10-*ArH*) and 8.0 (1 H, d, *J* 8, 9-*ArH*).

*Cyclisation of 3c to 4c and 1,2,3,4,9,10-Hexahydro-6-methoxy-1,1-dimethylphenanthrene 5c.*—To a well stirred mixture of polyphosphoric acid (PPA) prepared from orthophosphoric acid (15 cm<sup>3</sup>, 85%) and phosphorus pentoxide (23 g) at 115–120 °C (bath temp.) a solution of ketone **3c**<sup>9</sup> (1 g, 3.84 mmol) in toluene (10 cm<sup>3</sup>) was added, stirring at the same temperature was continued for 10 h. The red mixture was decomposed with crushed ice and the organic matter was extracted with ether. The ethereal extracts were washed thoroughly with water, 3% aqueous Na<sub>2</sub>CO<sub>3</sub> and dried (Na<sub>2</sub>SO<sub>4</sub>). Removal of the solvent afforded a light yellow viscous liquid mixture of **4c** and **5c**, which was chromatographed over neutral alumina (32 g) and eluted with light petroleum (7 × 35 cm<sup>3</sup>) to afford the *title compound 5c* (79 mg, 8.5%), b.p. 150–155 °C (1 mmHg) (Found: C, 83.95; H, 8.85. C<sub>17</sub>H<sub>22</sub>O requires C, 84.24; H, 9.15%);  $\nu_{\max}/\text{cm}^{-1}$  1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  206 (log  $\epsilon$  4.30) and 270 (log  $\epsilon$  4.20);  $\delta$  1.0 (6 H, s, *CMe*<sub>2</sub>), 1.46–1.79 (10 H, m), 3.73 (3 H, s, *ArOMe*) and 6.39–6.87 (3 H, m, *ArH*).

Further elution with light petroleum (60–80 °C) (7 × 30 cm<sup>3</sup>) furnished 1,2,3,4-tetrahydro-6-methoxy-1,1-dimethylphenanthrene **4c** (803 mg, 87%) as a colourless oil which solidified on standing, m.p. 119–120 °C (from light petroleum) (lit.,<sup>4</sup> m.p. 117–118.5 °C);  $\nu_{\max}/\text{cm}^{-1}$  1625 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  236 (log  $\epsilon$  4.54), 280 (log  $\epsilon$  3.64), 315 (log  $\epsilon$  3.08) and 330 (log  $\epsilon$  3.19) [lit.,<sup>4</sup>  $\lambda_{\max}(\text{EtOH})/\text{nm}$  237, 270sh, 279, 289sh, 316 and 331 (log  $\epsilon$  4.87, 3.68, 3.73, 3.64, 3.18 and 3.31)];  $\delta$  1.37 (6 H, s, *CMe*<sub>2</sub>), 1.71–1.80 (2 H, m, 2-*H*<sub>2</sub>), 1.92–2.03 (2 H, m, 3-*H*<sub>2</sub>), 3.08 (2 H, t, *J* 8, 4-*H*<sub>2</sub>), 3.96 (3 H, s, *ArOMe*), 7.14 (1 H, dd, *J* 8 and 1, 7-*ArH*), 7.28 (1 H, br s, 5-*ArH*), 7.41 (1 H, d, *J* 8, 10-*ArH*), 7.64 (1 H, d, *J* 8, 8-*ArH*) and 7.73 (1 H, d, *J* 8, 9-*ArH*).

*Conversion of 3c to 4c.* The crude mixture of **4c** and **5c** prepared by cyclisation of the cyclohexanone **3c** (250 mg, 0.96 mmol) with PPA following the same procedure as described above, was dissolved in xylene (12 cm<sup>3</sup>) and mixed with Pd–C (10%) (125 mg). The magnetically stirred mixture was refluxed for 7 h. The reaction mixture was cooled, filtered and the residue was rinsed with ether (25 cm<sup>3</sup>). The ether washings and the filtrate were combined and the solvent was evaporated under reduced pressure. The resulting product was purified by chromatography on neutral alumina (10 g) using light petroleum as eluent to afford **4c** (217 mg, 95%); identical (m.p., mixed m.p., IR and <sup>1</sup>H NMR spectra and GLC) with the sample described above.

*Cyclisation of 3d to 4d and 1,2,3,4,9,10-Hexahydro-7-isopropyl-1,1-dimethylphenanthrene 5d.*—The ketone **3d**<sup>11</sup> (1 g, 3.67 mmol) was converted in the same way as described for **4a**

into the mixture of **4d** and **5d**. The mixture was chromatographed over neutral alumina (32 g) and elution with light petroleum (7 × 30 cm<sup>3</sup>) afforded the *title compound 5d* (299 mg, 32%), b.p. 150–155 °C (1 mmHg) (Found: C, 89.85; H, 9.95. C<sub>19</sub>H<sub>26</sub> requires C, 89.70; H, 10.30%);  $\nu_{\max}/\text{cm}^{-1}$  1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  214 (log  $\epsilon$  4.37), 221 (log  $\epsilon$  4.35) and 271 (log  $\epsilon$  4.21);  $\delta$  1.08 (6 H, s, *CMe*<sub>2</sub>), 1.24 (6 H, d, *J* 6, *CHMe*<sub>2</sub>), 1.50–1.59 (2 H, m, 2-*H*<sub>2</sub>), 1.70–1.84 (2 H, m, 3-*H*<sub>2</sub>), 2.15–2.28 (2 H, m, 10-*H*<sub>2</sub>), 2.32–2.44 (2 H, m, 4-*H*<sub>2</sub>), 2.69 (2 H, t, *J* 7, 9-*H*<sub>2</sub>), 2.80–2.94 (1 H, m, *CHMe*<sub>2</sub>), 7.02 (1 H, br s, 8-*ArH*), 7.09 (1 H, br d, 6-*ArH*) and 7.19 (1 H, d, *J* 8, 5-*ArH*).

Further elution with light petroleum (60–80 °C) (7 × 35 cm<sup>3</sup>) furnished 1,2,3,4-tetrahydro-7-isopropyl-1,1-dimethylphenanthrene **4d** (537 mg, 58%) as a colourless oil which solidified on standing, m.p. 59 °C (from ethanol) (lit.,<sup>7</sup> m.p. 58–59 °C);  $\nu_{\max}/\text{cm}^{-1}$  1627 and 1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  231 (log  $\epsilon$  4.91) and 279 (log  $\epsilon$  3.79) [lit.,<sup>7</sup>  $\lambda_{\max}$  233, 271sh, 278, 291sh, 310, 317 and 324 ( $\epsilon$  24 300, 6400, 3800, 750, 250 and 880)];  $\delta$  1.34 (6 H, d, *J* 6, *CHMe*<sub>2</sub>), 1.37 (6 H, s, *CMe*<sub>2</sub>), 1.70–1.80 (2 H, m, 2-*H*<sub>2</sub>), 1.90–2.02 (2 H, m, 3-*H*<sub>2</sub>), 3.03–3.16 (3 H, m, *CHMe*<sub>2</sub> and 4-*H*<sub>2</sub>), 7.40–7.52 (2 H, m, 6- and 8-*ArH*), 7.60–7.67 (2 H, m, 5- and 9-*ArH*) and 7.94 (1 H, d, *J* 9, 10-*ArH*).

*Conversion of 3d to 4d.* The crude mixture of **4d** and **5d** obtained from the cyclisation of **3d** (250 mg, 0.91 mmol) as described above was converted in the same way as described for **3c** into **4d** (190 mg, 82%), identical (m.p., mixed m.p., IR and <sup>1</sup>H NMR spectra and GLC) with the sample described above.

*Cyclisation of 3e to 4e and 1,2,3,4,9,10-Hexahydro-7-methoxy-1,1-dimethylphenanthrene 5e.*—The ketone **3e**<sup>10</sup> (1 g, 3.84 mmol) was converted in the same way as described for **3a** into the mixture of **4e** and **5e**. The mixture was chromatographed over neutral alumina (32 g) and elution with light petroleum (6 × 35 ml) afforded **5e** (232 mg, 25%) as a colourless oil which solidified on standing, m.p. 49–50 °C (from methanol) (Found: C, 83.95; H, 9.35. C<sub>17</sub>H<sub>22</sub>O requires C, 84.24; H, 9.15%);  $\nu_{\max}/\text{cm}^{-1}$  1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  206 (log  $\epsilon$  4.30) and 272 (log  $\epsilon$  4.20);  $\delta$  1.07 (6 H, s, *CMe*<sub>2</sub>), 1.37–2.67 (10 H, m), 3.70 (3 H, s, *ArOMe*) and 6.40–7.0 (3 H, m, *ArH*).

Further elution with light petroleum (60–80 °C) (7 × 30 cm<sup>3</sup>) furnished **4e** (572 mg, 62%) as a colourless solid, m.p. 56–57 °C (from methanol) (lit.,<sup>14</sup> m.p. 55.5–56 °C);  $\nu_{\max}/\text{cm}^{-1}$  1628 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  228 (log  $\epsilon$  4.87);  $\delta$  1.35 (6 H, s, *CMe*<sub>2</sub>), 1.68–1.78 (2 H, m, 2-*H*<sub>2</sub>), 1.88–2.02 (2 H, m, 3-*H*<sub>2</sub>), 3.11 (2 H, t, *J* 8, 4-*H*<sub>2</sub>), 3.93 (3 H, s, *ArOMe*), 7.12–7.26 (2 H, m, 6- and 8-*ArH*), 7.50 (1 H, d, *J* 8, 9-*ArH*), 7.62 (1 H, d, *J* 8, 5-*ArH*) and 7.94 (1 H, d, *J* 8, 10-*ArH*).

*Conversion of 3e into 4e.* The crude mixture of **4e** and **5e** obtained from the cyclisation of **3e** (250 mg, 0.96 mmol) was converted in the same way as described for **4c** into **4e** (196 mg, 85%), identical (m.p., mixed m.p., IR and <sup>1</sup>H NMR spectra and GLC) with the sample described above.

1,2,3,4-Tetrahydro-1,1-dimethylphenanthrene **4f** and 1,2,3,4,9,10-Hexahydro-1,1-dimethylphenanthrene **5f.**—The ketone **3f**<sup>10</sup> (1 g, 4.34 mmol) was converted in the same way as described for **4a** into the mixture of **4f** and **5f**. The mixture was chromatographed over neutral alumina (36 g) and elution with light petroleum (10 × 30 cm<sup>3</sup>) afforded the pure **5f** (64 mg, 7%), b.p. 140–145 °C (1 mmHg) (Found: C, 90.3; H, 9.65. C<sub>16</sub>H<sub>20</sub> requires C, 90.50; H, 9.50%);  $\nu_{\max}/\text{cm}^{-1}$  1605;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  207 (log  $\epsilon$  4.04), 213 (log  $\epsilon$  4.04), 220 (log  $\epsilon$  4.04) and 268 (log  $\epsilon$  3.80);  $\delta$  1.08 (6 H, s, *CMe*<sub>2</sub>), 1.50–1.60 (2 H, m, 2-*H*<sub>2</sub>), 1.70–1.84 (2 H, m, 3-*H*<sub>2</sub>), 2.12–2.26 (2 H, m, 10-*H*<sub>2</sub>), 2.44 (2 H, m, 4-*H*<sub>2</sub>), 2.67 (2 H, t, *J* 8, 9-*H*<sub>2</sub>) and 7.10–7.28 (4 H, m, *ArH*).

Further elution with light petroleum (60–80 °C) (7 × 35 cm<sup>3</sup>) afforded **4f** (819 mg, 88%) as a colourless oil, b.p. 165–170 °C (1 mmHg) (Found: C, 91.1; H, 8.4. C<sub>16</sub>H<sub>18</sub> requires C, 91.37; H,

8.63%);  $\nu_{\max}/\text{cm}^{-1}$  1627 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  229 (log  $\epsilon$  4.48) and 281 (log  $\epsilon$  3.72);  $\delta$  1.37 (6 H, s,  $\text{CMe}_2$ ), 1.72–1.80 (2 H, m, 2- $\text{H}_2$ ), 1.92–2.01 (2 H, m, 3- $\text{H}_2$ ), 3.14 (2 H, t, J 7, 4- $\text{H}_2$ ), 7.47–7.70 (4 H, m, ArH), 7.81 (1 H, d, J 8, 10-ArH) and 8.03 (1 H, d, J 8, 9-ArH).

**Conversion of 3f to 4f.** The crude mixture of 4f and 5f obtained from the cyclisation of 3f (250 mg, 1.08 mmol) as described above, was converted in the same way as described for 4c into 4f (217 mg, 95%), identical (IR, GLC and  $^1\text{H}$  NMR spectra) with the sample described above.

**Oxidation of 4a to 6a.**—To a solution of the phenanthrene 4a (300 mg, 1.06 mmol) in dichloromethane (10 ml), was added a finely powdered and homogenised mixture of PCC (1.1 g, 5.10 mmol) and Celite (1.1 g).<sup>17a</sup> The reaction mixture was stirred for 25 h at room temperature and then diluted with ether (10  $\text{cm}^3$ ) and filtered through a short pad of Celite and anhydrous magnesium sulphate. The filter cake was washed with two portions of ether (10  $\text{cm}^3 \times 2$ ) and the combined filtrate was evaporated under reduced pressure to afford 6a (258 mg, 82%), as a colourless solid, m.p. 88–89 °C (from methanol) (lit.,<sup>2</sup> m.p. 89–91 °C);  $\nu_{\max}/\text{cm}^{-1}$  1672, 1625 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  225 (log  $\epsilon$  4.50);  $\delta$  1.30 (6 H, d, J 7,  $\text{CHMe}_2$ ), 1.46 (6 H, s,  $\text{CMe}_2$ ), 2.10 (2 H, t, J 8, 2- $\text{H}_2$ ), 2.88 (2 H, t, J 8, 3- $\text{H}_2$ ), 3.39–3.49 (1 H, m,  $\text{CHMe}_2$ ), 4.04 (3 H, s, ArOMe), 7.45 (1 H, d, J 8, 10-ArH), 7.62 (1 H, s, 8-ArH), 7.96 (1 H, d, J 8, 9-ArH) and 8.94 (1 H, s, 5-ArH) [lit.,<sup>2</sup>  $^1\text{H}$  NMR:  $\delta$  1.29 (d, J 7, 6 H), 1.45 (s, 6 H), 2.07 (t, J 7, 2 H), 2.84 (t, J 7, 2 H), 3.40 (septet, J 7, 1 H), 4.00 (s, 3 H), 7.38, 7.80 (AB<sub>q</sub>, J 9, 2 H), 7.55 (s, 1 H) and 8.78 (s, 1 H)].

**1,2,3,4-Tetrahydro-6-methoxy-1,1-dimethylphenanthrene-4-one 6c.**—The compound 4c (300 mg, 1.25 mmol) was converted, in the same way as described for 6a into the title compound 6c (266 mg, 84%), b.p. 165–170 °C (0.1 mmHg) (Found: C, 80.5; H, 7.1.  $\text{C}_{17}\text{H}_{18}\text{O}_2$  requires C, 80.28; H, 7.13%);  $\nu_{\max}/\text{cm}^{-1}$  1670, 1626 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  218 (log  $\epsilon$  4.50) and 247 (log  $\epsilon$  4.31);  $\delta$  1.48 (6 H, s,  $\text{CMe}_2$ ), 2.11 (2 H, t, J 8, 2- $\text{H}_2$ ), 2.89 (2 H, t, J 8, 3- $\text{H}_2$ ), 4.01 (3 H, s, ArOMe), 7.21 (1 H, dd, J 8 and 1, 7-ArH), 7.46 (1 H, d, J 8, 10-ArH), 7.75 (1 H, d, J 8, 8-ArH), 7.97 (1 H, d, J 8, 9-ArH) and 8.96 (1 H, d, J 1, 5-ArH).

**Oxidation of 4e to 6e.**—The compound 4e (300 mg, 1.25 mmol) was converted in the same way as described for 6a into 6e (269 mg, 85%), b.p. 160 °C (0.1 mmHg) [lit.,<sup>16</sup> b.p. (bath temp.) 170 °C/0.1 mmHg];  $\nu_{\max}/\text{cm}^{-1}$  1673, 1625 and 1600 [lit.,<sup>16</sup>  $\nu(\text{film})/\text{cm}^{-1}$  1672, 1620 and 1600];  $\lambda_{\max}(\text{EtOH})/\text{nm}$  219 (log  $\epsilon$  4.65), 248 (log  $\epsilon$  4.43) and 313 (log  $\epsilon$  3.84);  $\delta$  1.46 (6 H, s,  $\text{CMe}_2$ ), 2.10 (2 H, t, J 7, 2- $\text{H}_2$ ), 2.80 (2 H, t, J 7, 3- $\text{H}_2$ ), 3.96 (3 H, s, ArOMe), 7.15 (1 H, d, J 1, 8-ArH), 7.32 (1 H, dd, J 8 and 1, 6-ArH), 7.56 (1 H, d, J 8, 9-ArH), 7.94 (1 H, d, J 8, 10-ArH) and 9.26 (1 H, d, J 8, 5-ArH) [lit.,<sup>16</sup>  $\delta(\text{CCl}_4)$  1.4 (s, 6 H), 1.99 (m, 2 H), 2.72 (m, 2 H), 3.83 (s, 3 H), 6.90–7.47 (m, 3 H), 7.73 (d, 1 H, J 8) and 9.10 (d, 1 H, J 10)].

**1,2,3,4-Tetrahydro-1,1-dimethylphenanthrene-4-one 6f.**—The compound 4f (300 mg, 1.42 mmol) was converted in the same way as described for 6a into the title compound 6f (271 mg, 85%), b.p. 150–155 °C (0.1 mmHg) (Found: C, 85.75; H, 7.35.  $\text{C}_{16}\text{H}_{16}\text{O}$  requires C, 85.67; H, 7.19%);  $\nu_{\max}/\text{cm}^{-1}$  1672, 1627 and 1600;  $\lambda_{\max}(\text{EtOH})/\text{nm}$  219 (log  $\epsilon$  4.52), 248 (log  $\epsilon$  4.30) and 315 (log  $\epsilon$  3.86);  $\delta$  1.49 (6 H, s,  $\text{CMe}_2$ ), 2.14 (2 H, t, J 7, 2- $\text{H}_2$ ), 2.90 (2 H, t, J 7, 3- $\text{H}_2$ ), 7.52–7.74 (3 H, m, ArH), 7.87 (1 H, br d, 10-ArH), 8.06 (1 H, d, J 8, 9-ArH) and 9.33 (1 H, d, J 8, 5-ArH).

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