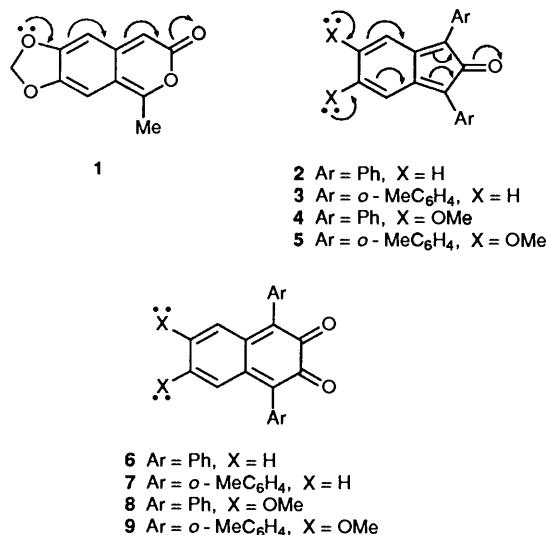


## Stability of Alkoxy-substituted Inden-2-ones and 6,7-Dimethoxy-1,4-diphenyl-2,3-naphthoquinone

David P. Bradshaw, David W. Jones\* and Firstborn Matthew Nongrum  
School of Chemistry, The University, Leeds LS2 9JT, UK

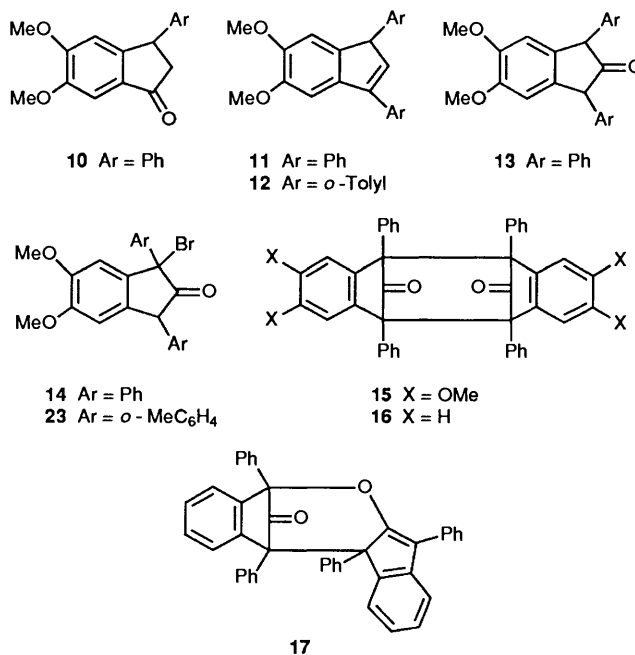
5,6-Dimethoxy-1,3-diphenylinden-2-one **4** and 5,6-dimethoxy-1,3-di-*o*-tolylinden-2-one **5** have been generated by dehydrobromination of 1-bromo-5,6-dimethoxy-1,3-diarylindan-2-ones. They appear more stable than the corresponding inden-2-ones lacking methoxyl substituents. In particular, **5** fails to dimerise at 20 °C whereas other known inden-2-ones dimerise even at low temperature. 6,7-Dimethoxy-1,4-diphenyl-2,3-naphthoquinone **8** generated by lead tetraacetate oxidation of the corresponding dihydroxynaphthalene appears less persistent than the corresponding quinone lacking methoxyl substituents, perhaps because of easier reaction with the lead tetraacetate.

2-Benzopyran-3-ones carrying on alkoxy group at C-6 *e.g.* **1** are much more stable than their counterparts lacking such a substituent. This effect can be associated with the 'push-pull' (vinylogous ester) resonance<sup>1</sup> shown by the arrows in **1**. Inden-2-ones like **2** and **3** dimerise below room temperature.<sup>2,3</sup> It was therefore of interest to see if the introduction of appropriate methoxyl substituents as in the dimethoxy derivatives **4** and **5** would provide inden-2-ones of increased life time. 2,3-



Naphthoquinones are more stable than corresponding inden-2-ones. Thus the green colour associated with the diphenyl derivative **6** persisted for 45 min at -20 °C. The sterically stabilised derivative **7** is on the verge of being isolable in pure form.<sup>3</sup> It was therefore of interest to examine the effect of introducing methoxyl substituents as in the derivatives **8** and **9**.

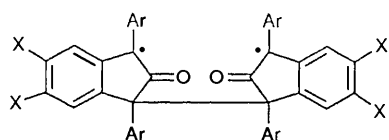
The indanone **10**, readily prepared by reaction of veratrole with cinnamic acid in polyphosphoric acid,<sup>4</sup> was a convenient starting point for the preparation of **4** and **8**. It was readily converted into the known indene **11**<sup>5</sup> (PhMgBr; H<sub>3</sub>O<sup>+</sup> work-up) and hence into the indan-2-one **13** *via* hydroboration-oxidation followed by Pfitzner-Moffatt oxidation. Reaction of **13** with one equivalent of bromine at -14 °C gave the monobromide **14** which, without purification, was reacted with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene. At 20 °C the (4 + 4)  $\pi$ -dimer **15** of the isoindenone **4** formed immediately, providing little evidence for increased stability of **4** over **2**. 1,3-Diphenylisoindenone **2** forms a similar dimer **16** as well as a small amount of the (6 + 4)  $\pi$ -dimer **17**; compound **17** is readily



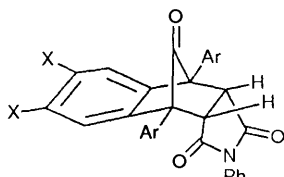
converted into **16** probably *via* the biradical intermediate **18**. The easier dissociation of the dimer **15** than of **16** agrees with increased stability of **4** compared to **2**; *N*-phenylmaleimide and **15** gave the adduct **19** of **4** in 92% yield after 4 h at 20 °C. In contrast <40% of the dimer **16** was consumed after 18 h at 80 °C in the presence of the dienophile. However easier dissociation of **15** than of **16** could also be due to rate-limiting formation of the biradical **20** which should be more stable than **18** by virtue of the methoxy groups *para* to the radical sites. As well as the stabilisation produced by a *p*-methoxy upon a benzhydrylic radical a merostabilisation (capto-dative) effect is also possible here.<sup>6</sup>

In pursuit of a more clear-cut stabilisation of an inden-2-one by alkoxy groups we turned our attention to the 5,6-dimethoxy-1,3-di-*o*-tolyl derivative **5**. Unlike **2** the sterically stabilised derivative **3** forms a (6 + 6)  $\pi$ -dimer **21**.<sup>3</sup> Indeed, in our present experiments we have found in addition to **21** the (4 + 2)  $\pi$ -dimer **22**. The change in dimer type from **16** and **17** to **21** and **22** reflects increased steric hindrance at C-1 and C-3 in the di-*o*-tolyl system **3** compared to the diphenyl system **2**. Electronic stabilisation associated with methoxy substitution and steric protection by the *o*-tolyl groups might make **3** more readily observed.

The required bromo ketone **23** was prepared by a sequence analogous to that used to make **14** but involving the indene **12** (Experimental section). Reaction of **23** with DBU in dichloro-

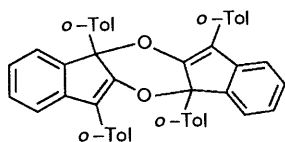


**18** Ar = Ph, X = H  
**20** Ar = Ph, X = OMe

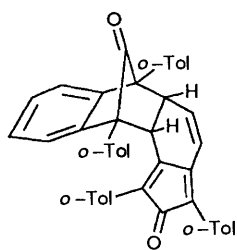


**19** X = OMe, Ar = Ph  
**24** X = OMe, Ar = *o*-MeC<sub>6</sub>H<sub>4</sub>

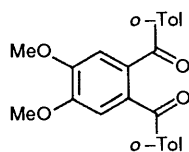
methane at 20 °C produced a strong dark green colour which persisted apparently unchanged over 1 h in the absence of air. The *N*-phenylmaleimide adduct **24** was obtained in *ca.* 50% yield when dehydrobromination was conducted in the presence of *N*-phenylmaleimide. The adduct **24** was obtained in the same yield when addition of the dienophile was delayed for 1 h after the addition of DBU and the reaction worked-up after stirring for one further minute. The deep green colour associated with



**21**



**22**

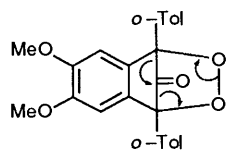


**25**

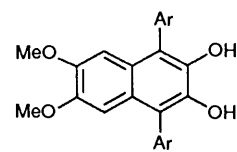
the inden-2-one **5** rapidly disappeared on admitting air to the apparatus and isolation then gave the diketone **25** in 54% yield; compound **25** probably arises *via* the oxygen adduct **26** which could fragment as shown by the arrows. These observations show that **5** is much more stable towards dimerisation than either **2**, **3** or **4**, but that it shows high reactivity towards oxygen which prevents its isolation under normal conditions.

The DBU dehydrobromination proceeds rapidly at low temperature permitting the generation of **2-5** at -50 °C in dichloromethane solution. Measurement of  $\lambda_{\text{max}}$  values and a rough assessment of relative lifetimes under these conditions was therefore possible. Whereas the green colour ( $\lambda_{\text{max}}$  772 nm) due to **5** was indefinitely stable, and **4** ( $\lambda_{\text{max}}$  708 nm) survived for *ca.* 35 min., **2** ( $\lambda_{\text{max}}$  678 nm) was shorter lived (< 5 min) and the green colour due to **3** (tentatively assigned as a very broad band  $\lambda_{\text{max}}$  760–790 nm) was very transient.

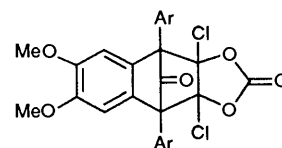
**6,7-Dimethoxy-1,4-diphenyl-2,3-naphthoquinone.**—The diol **27** required to attempt preparation of the 2,3-naphthoquinone **8**



**26**

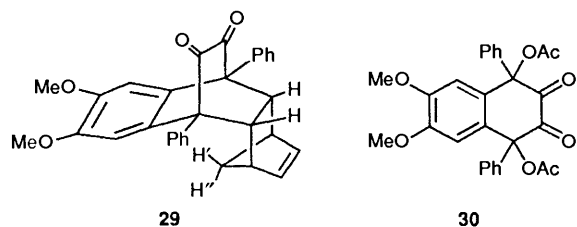


**27** Ar = Ph  
**32** Ar = *o*-MeC<sub>6</sub>H<sub>4</sub>

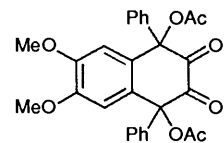


**28** Ar = Ph

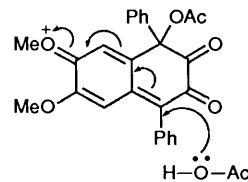
was prepared from the inden-2-one dimer **15**. Dissociation of **15** in the presence of dichlorovinylene carbonate gave the adduct **28** in good yield. Zinc dust dechlorination of **28** was accompanied by decarbonylation and gave the carbonate of **27**; acid hydrolysis then gave **27** in 50% overall yield based on the dimer **15**. Oxidation of **27** with lead tetraacetate (two equiv. at -40 °C in the presence of norbornadiene gave the adduct **29** of the unstable quinone in 43% yield. Whilst the green colour from 1,4-diphenyl-naphthalene-2,3-diol and lead tetraacetate and associated with the quinone **6** persisted for 45 min at -20 °C, the similar green colour from **27** persisted for 50 min only at -78 °C. The surprising apparently reduced stability of **8** in comparison with **6** is associated with easier subsequent acetoxylation of the more electron-rich quinone **8** by the excess lead tetraacetate employed in these oxidations. Indeed the diacetoxy compound **30** was obtained in 90% yield when three equivalents of lead tetraacetate was used. Acetoxylation of **8** would give **31** which would proceed to **30** by addition of acetic acid (see arrows on structure **31**). In earlier experiments **6** gave products related to **30** only slowly and in poor yield. We are currently seeking a



**29**



**30**



**31**

non-oxidative route to **8** to more adequately assess its stability compared to **6**.

The stability of the isoindenone **5**, in particular its failure to dimerise, frustrated attempts to make the quinone **9**. Thus dichlorovinylene carbonate failed to react with dichloromethane solutions of **5** even at the b.p. of the solvent. A route to **32** analogous to that used for the conversion of **28** into **27** could not therefore be followed.

## Experimental

For general details see the preceding paper.<sup>1</sup> All experiments

were conducted under Ar or N<sub>2</sub>. In the NMR data, values of the coupling constants *J* are given in Hz.

**2-Hydroxy-5,6-dimethoxy-1,3-diphenylindane.**—To 5,6-dimethoxy-1,3-diphenylindene (11.58 g; 0.035 mol) in sodium-dried benzene (35 cm<sup>3</sup>) in an ice-bath was added, with stirring, borane–dimethyl sulphide in dichloromethane (38.8 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> solution) over 30 min (beware frothing). To this solution was added 3 mol dm<sup>-3</sup> aqueous sodium hydroxide solution (11.6 cm<sup>3</sup>) dropwise and then 30% hydrogen peroxide (8.80 cm<sup>3</sup>) also dropwise. The ice-bath was then removed and the mixture allowed to warm to 20 °C. The mixture was then boiled under reflux (1 h), poured into ice-water (100 cm<sup>3</sup>) and extracted with ether (3 × 200 cm<sup>3</sup>). The combined organic extracts were washed with saturated brine (3 × 200 cm<sup>3</sup>), dried (K<sub>2</sub>CO<sub>3</sub>) and evaporated to give a solid which was essentially pure product (11.98 g). The *title compound* m.p. 138–142 °C formed colourless prisms from benzene. (Found: C, 79.7; H, 6.4. C<sub>23</sub>H<sub>22</sub>O<sub>3</sub> requires C, 79.9; H, 6.4%;  $\nu_{\max}/\text{cm}^{-1}$  3670–3130br;  $\delta_{\text{H}}(90 \text{ MHz})$  7.46–7.18 (10 H, m), 6.44 (2 H, s), 4.14 (3 H, apparent s, methine H's) and 3.71 (6 H, s); *m/z* (M<sup>+</sup>) 346, 255, 227, 179, 165, 105, 91 and 77 (100.00, 44.9, 31.3, 19.7, 21.8, 22.1, 32.9 and 15.7% respectively).

**5,6-Dimethoxy-1,3-diphenylindan-2-one 13.**—To the foregoing alcohol (7.74 g; 0.022 mol) in sodium-dried benzene (230 cm<sup>3</sup>) was added dry dimethyl sulphoxide (46 cm<sup>3</sup>) and with stirring dicyclohexylcarbodiimide (13.82 g; 3 equiv.) and freshly prepared pyridinium trifluoroacetate (2.16 g; 0.5 equiv.). The mixture was stirred at 20 °C (3 h) then diluted with ether (500 cm<sup>3</sup>) and oxalic acid added until effervescence ceased. The product was shaken with water (300 cm<sup>3</sup>), and the complete mixture filtered. The organic phase was washed with water (3 × 250 cm<sup>3</sup>) and 5% aqueous hydrochloric acid (2 × 250 cm<sup>3</sup>), then dried (MgSO<sub>4</sub>) and evaporated. The crude product was chromatographed on silica (300 g); elution with ether–benzene (1:9) gave the *title compound* (5.36 g, 70%) m.p. 159–161 °C (from benzene) (Found: C, 80.1; H, 6.0. C<sub>23</sub>H<sub>20</sub>O<sub>3</sub> requires C, 80.2; H, 5.9%;  $\nu_{\max}/\text{cm}^{-1}$  1750;  $\delta_{\text{H}}(90 \text{ MHz})$  7.45–7.06 (10 H, m), 6.25 (2 H, s), 4.73 (2 H, s) and 3.83 (6 H, s); *m/z* (M<sup>+</sup>) 344, 316, 285, 239, 165, 115, 78 and 51 (44.1, 38.0, 31.2, 33.4, 8.5, 6.9, 100.0 and 16.0% respectively).

**The Dimer of 5,6-Dimethoxy-1,3-diphenylinden-2-one; 15.**—To ketone 13 (500 mg, 1.45 mmol) in dry dichloromethane (7.5 cm<sup>3</sup>) cooled to –14 °C (bath temperature) was added freshly distilled bromine (256 mg; 1.1 equiv.) in dichloromethane (*ca.* 1 cm<sup>3</sup>) and stirring continued (1 h). The reaction mixture was evaporated under reduced pressure in a bath at *ca.* 40 °C. Dry dichloromethane (5 cm<sup>3</sup>) was added and the solution evaporated in the same way. The crude bromo ketone was dissolved in benzene (2 cm<sup>3</sup>) and the solution treated with DBU (0.72 cm<sup>3</sup>) in benzene (2.5 cm<sup>3</sup>) added quickly with stirring at 20 °C. The initial violet colour faded over 20 s with formation of a pale yellow precipitate. Recrystallisation of the filtered solid from chloroform–ethanol with minimal heating gave the *title compound* (450 mg, 90.5%), m.p. 210–214 °C (Found: C, 80.5; H, 5.2. C<sub>46</sub>H<sub>36</sub>O<sub>6</sub> requires C, 80.7; H, 5.3%;  $\nu_{\max}/\text{cm}^{-1}$  1761;  $\delta_{\text{H}}(90 \text{ MHz}, \text{CD}_2\text{Cl}_2)$  7.44–7.16 (20 H, m), 7.10 (4 H, s) and 3.79 (12 H, s); *m/z* (M<sup>+</sup> – 2CO) 628, (M/2) 342, 299, 226, 157, 133 and 44 (4.3, 100.0, 33.2, 18.1, 11.4, 12.3 and 10.4% respectively).

**The N-Phenylmaleimide Adduct of 5,6-Dimethoxy-1,3-diphenylinden-2-one; 19.**—The foregoing dimer 15 (10 mg, 0.014 mmol), dichloromethane (0.8 cm<sup>3</sup>) and N-phenylmaleimide (10 mg, 0.058 mmol) were stirred for 4 h at 20 °C with monitoring by TLC. Evaporation of solvent and trituration with ethanol gave the *title compound* (14 mg, 92%), m.p. 272–274 °C (CO

loss) from dichloromethane–ethanol (Found: C, 76.9; H, 4.8; N, 2.8. C<sub>33</sub>H<sub>25</sub>NO<sub>5</sub> requires C, 76.9; H, 4.9; N, 2.7%;  $\nu_{\max}/\text{cm}^{-1}$  1708 and 1774;  $\delta_{\text{H}}(90 \text{ MHz})$  7.75–7.14 (13 H, m), 6.59–6.46 (2 H, m), 6.42 (2 H, s), 4.29 (2 H, s) and 3.64 (6 H, s).

**The Dichlorovinylene Carbonate Adduct of 5,6-Dimethoxy-1,3-diphenylinden-2-one; 28.**—The dimer 15 (150 mg), dichlorovinylene carbonate (1 g) and sodium-dried benzene (5 cm<sup>3</sup>) were boiled under reflux (3 h). Evaporation of the solvent and removal of excess dienophile at 100 °C in a high vacuum was followed by rapid chromatography on silica in benzene–ether (95:5) to give the *adduct* (164 mg, 75.4%) m.p. 176–178 °C (from ether) (Found: C, 62.1; H, 3.6; Cl, 13.6%; M<sup>+</sup>, 496.047. C<sub>26</sub>H<sub>18</sub><sup>35</sup>Cl<sub>2</sub>O<sub>6</sub> requires C, 62.8; H, 3.6; Cl, 14.3%; M<sup>+</sup>, 496.048;  $\nu_{\max}/\text{cm}^{-1}$  1860 and 1810;  $\delta_{\text{H}}(90 \text{ MHz})$  7.98–7.72 (4 H, m), 7.72–7.41 (6 H, m), 6.38 (2 H, s) and 3.75 (6 H, s); *m/z* (M<sup>+</sup>) 496, 468, 433, 398, 354, 268, 239, 126 and 69 (15.4, 39.5, 54.7, 100, 52.7, 13.9, 44.8, 11.7 and 15.5% respectively).

**The Carbonate of 2,3-Dihydroxy-6,7-dimethoxy-1,4-diphenyl-naphthalene.**—A mixture of the foregoing adduct (300 mg, 0.603 mmol), activated zinc (241 mg, 0.0036 g atom), glacial acetic acid (3.4 cm<sup>3</sup>) and dry tetrahydrofuran (THF) (10 cm<sup>3</sup>) were boiled under reflux (16 h). The solution was cooled, diluted with water and extracted with ether. The ether extracts were washed with saturated aqueous sodium hydrogen carbonate, dried (MgSO<sub>4</sub>), evaporated and the residue chromatographed on silica in benzene–ether (94:6) to give the *title compound* (197 mg, 82%) m.p. 228–230 °C (from dichloromethane–light petroleum) (Found: C, 75.1; H, 4.5. C<sub>25</sub>H<sub>18</sub>O<sub>5</sub> requires C, 75.3; H, 4.5%;  $\nu_{\max}/\text{cm}^{-1}$  1910, 1850 and 1809;  $\delta_{\text{H}}(90 \text{ MHz})$ , 7.45 (10 H, s), 7.25 (2 H, s) and 3.79 (6 H, s); *m/z* (M<sup>+</sup>) 398, 354, 311, 268, 239, 154, 126, 69, 52 and 44 (100, 7.7, 8.6, 6.9, 22.5, 8.3, 15.5, 4.8, 4.9 and 7.7% respectively).

**2,3-Dihydroxy-6,7-dimethoxy-1,4-diphenyl-naphthalene 27.**—The foregoing carbonate (197 mg), concentrated hydrochloric acid (3.5 cm<sup>3</sup>) and glacial acetic acid (14.3 cm<sup>3</sup>) were boiled under reflux (1 h). On cooling, the crystalline precipitate was filtered (122 mg, 66.3%). The filtrate afforded a further 26 mg (14%) of this product after neutralisation (NaHCO<sub>3</sub>), extraction into ethyl acetate, drying the extract (MgSO<sub>4</sub>), evaporation and chromatography on silica in benzene–ether (94:6); *title compound* m.p. 243–246 °C from dichloromethane–light petroleum (Found: C, 77.1; H, 5.3. C<sub>24</sub>H<sub>20</sub>O<sub>4</sub> requires C, 77.4; H, 5.3%;  $\nu_{\max}/\text{cm}^{-1}$  3500;  $\delta_{\text{H}}(90 \text{ MHz})$  7.62–7.35 (10 H, m), 6.73 (2 H, s), 5.41 (2 H, s, *exch.* D<sub>2</sub>O) and 3.65 (6 H, s); *m/z* (M<sup>+</sup>) 372, 342, 325, 297, 235, 186, 162 and 134 (100, 7.4, 8.0, 4.3, 12.2, 3.5, 3.7 and 5.8% respectively).

**Trapping 6,7-Dimethoxy-1,4-diphenyl-2,3-naphthoquinone with Norbornadiene.**—To a stirred solution of lead tetraacetate (25 mg, 2 equiv.) and norbornadiene (1 cm<sup>3</sup>) in dry dichloromethane (1 cm<sup>3</sup>) at –40 °C was added the foregoing dihydroxy-naphthalene (11 mg), in small portions, over 30 min. After stirring at –40 °C (30 min) the mixture was allowed to attain room temperature. Two drops of ethylene glycol were added and the mixture diluted with ether, and washed with water and saturated aqueous sodium hydrogen carbonate, dried (MgSO<sub>4</sub>), evaporated and chromatographed on silica in benzene–ether (20:1) to give the *adduct 29* (5.7 mg; 43%), m.p. 245–249 °C (from chloroform–ethanol) (Found: C, 80.55; H, 5.7. C<sub>31</sub>H<sub>26</sub>O<sub>4</sub> requires C, 80.5; H, 5.6%;  $\nu_{\max}/\text{cm}^{-1}$  1741, 1724, 1601 and 1503;  $\delta_{\text{H}}(90 \text{ MHz})$  –0.2 (1 H, br d, *J* 10), 0.76 (1 H, br d, *J* 10), 2.79 (2 H, br s), 3.22 (2 H, t, *J* 1.6), 3.74 (6 H, s), 6.50 (2 H, t, *J* 1.6), 6.84 (2 H, s) and 7.43–7.68 (10 H, m); *m/z* (M<sup>+</sup>) 462, 340, 310, 281, 252 and 169 (1.1, 100, 5.8, 3.4, 9.1 and 3.2% respectively).

**Lead Tetraacetate Oxidation of 2,3-Dihydroxy-6,7-dimethoxy-1,4-diphenyl-naphthalene in the Absence of a Trap.**—The dihydroxynaphthalene (62 mg) was added in small portions over 0.5 h to lead tetraacetate (221 mg, 3 equivs.) in dichloromethane (3 cm<sup>3</sup>) with stirring at  $-50^{\circ}\text{C}$  (CO<sub>2</sub>–Me<sub>2</sub>CO–MeCN bath). After stirring at  $-50^{\circ}\text{C}$  (1 h) the mixture was allowed to warm to  $20^{\circ}\text{C}$ . Ethylene glycol (5 drops) was added and after 15 min the mixture was poured into water and extracted into ether. The organic layer was washed with saturated aqueous sodium hydrogen carbonate, then water, dried (MgSO<sub>4</sub>), evaporated and the residue chromatographed on silica in dichloromethane as eluent to give 1,4-diacetoxy-6,7-dimethoxy-1,4-diphenyl-naphthalen-2,3-dione **30** (74 mg, 90%), m.p.  $230\text{--}233^{\circ}\text{C}$  (from methanol) (Found: C, 68.9; H, 4.95%; M<sup>+</sup>, 488.148. C<sub>28</sub>H<sub>24</sub>O<sub>8</sub> requires C, 68.8; H, 4.9%; M<sup>+</sup>, 488.147);  $\nu_{\text{max}}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1754 and 1731;  $\delta_{\text{H}}$  (300 MHz) 2.15 (6 H, s), 3.82 (6 H, s), 6.76 (2 H, s) and 7.35 (10 H, s);  $m/z$  (M<sup>+</sup>) 488, 398 and 330 (17.5, 17.8 and 100% respectively). Preliminary experiments using two equivalents of lead tetraacetate at  $-70^{\circ}\text{C}$  established that oxidation was slow, the green colour taking *ca.* 10 min to develop fully; after completion of the addition the green colour remained for *ca.* 50 min and then gradually changed to brown, and the diacetoxyated product was formed in 54% yield.

**5,6-Dimethoxy-3-(*o*-tolyl)indan-1-one.**—Veratrole (0.49 cm<sup>3</sup>, 3.86 mmol), *o*-methylcinnamic acid (660 mg, 4.07 mmol) and polyphosphoric acid (3.2 g) were heated at  $110^{\circ}\text{C}$  (1 h). The product was quenched with ice–water and extracted into dichloromethane (100 cm<sup>3</sup>). The extract was washed with saturated aqueous sodium hydrogen carbonate, then brine, dried (MgSO<sub>4</sub>), evaporated and the residue recrystallised from dichloromethane–ethanol (1:9) to give the *title compound* (74 mg, 64.4%), m.p.  $137\text{--}139^{\circ}\text{C}$  (Found: C, 76.4; H, 6.4. C<sub>18</sub>H<sub>18</sub>O<sub>3</sub> requires C, 76.6; H, 6.4%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 1690;  $\delta_{\text{H}}$  (90 MHz) 2.43 (3 H, s), 2.50 (1 H, dd, *J* 18 and 4), 3.25 (1 H, dd, *J* 18 and 8), 4.75 (1 H, dd, *J* 8 and 4), 3.86 (3 H, s), 3.95 (3 H, s), 6.69 (2 H, s), 6.8 (1 H, br m) and 7.0–7.3 (3 H, m);  $m/z$  282, 267, 251, 191, 165, 152, 115, 91, 77 and 43 (100, 26.5, 22.2, 16.8, 29.9; 18.8, 14.4, 15.7, 11.8 and 8.2% respectively).

**5,6-Dimethyl-1,3-di(*o*-tolyl)indene 12.**—The foregoing ketone (408 mg, 1.45 mmol) in dry ether (35 cm<sup>3</sup>) was added dropwise with stirring to a solution of *o*-tolyllithium [from *o*-tolyl bromide (2.73 g, 16.2 mmol) and lithium shot (112 mg, 0.016 g atom)] in ether (40 cm<sup>3</sup>). The mixture was then boiled under reflux (14 h), poured into ice–conc. hydrochloric acid (35 cm<sup>3</sup>), shaken vigorously and the organic layer washed with saturated aqueous sodium hydrogen carbonate, then with brine, dried (MgSO<sub>4</sub>) and evaporated first on a rotary evaporator and then under a high vacuum at  $100^{\circ}\text{C}$ . Chromatography of the residue with benzene–light petroleum (9:1) gave the *title compound* (196 mg, 38%) (Found: M<sup>+</sup>, 356.177. C<sub>25</sub>H<sub>24</sub>O<sub>2</sub> requires M, 356.177);  $\nu_{\text{max}}$  (CHCl<sub>3</sub>)/cm<sup>-1</sup> 1600 and 1570;  $\delta_{\text{H}}$  (90 MHz) 2.31 (3 H, s), 2.38 (3 H, s), 3.81 (6 H, apparent s), 4.88 (1 H, m), 6.32 (1 H, m), 6.76 (1 H, s), 6.85 (1 H, s) and 6.90–7.31 (8 H, m);  $m/z$  (M<sup>+</sup>) 356, 371 and 325 (100, 17.5 and 18.1% respectively).

**2-Hydroxy-5,6-dimethoxy-1,3-di(*o*-tolyl)indane.**—To the indene **12** (2.65 g, 7.44 mmol) in dry dichloromethane (10 cm<sup>3</sup>) was added, by syringe and with stirring, borane–dimethyl sulphide complex (14.79 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> solution in dichloromethane). The mixture was boiled under reflux (6 h) and excess reagent quenched with ethanol (7.7 cm<sup>3</sup>) followed by aqueous sodium hydroxide (2.15 cm<sup>3</sup>; 2 mol dm<sup>-3</sup>) and after cooling to  $0\text{--}5^{\circ}\text{C}$ , hydrogen peroxide (1.74 cm<sup>3</sup> of 100 vol.). After stirring (2 h) at  $0\text{--}5^{\circ}\text{C}$  the product was poured into iced water, extracted into ether, the ether extracts dried (K<sub>2</sub>CO<sub>3</sub>), evaporated and the residue chromatographed on silica in

dichloromethane to give the *title compound* (2.51 g, 90%), m.p.  $65\text{--}67^{\circ}\text{C}$  (from benzene) (Found: C, 80.2; H, 6.9%; M<sup>+</sup>, 374.187. C<sub>25</sub>H<sub>26</sub>O<sub>3</sub> requires C, 80.2; H, 6.9%; M<sup>+</sup>, 374.188);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 3600–3160;  $\delta_{\text{H}}$  (90 MHz) 2.12 (1 H, br s, exch. D<sub>2</sub>O), 2.45 (6 H, s), 3.69 (6 H, s), 4.52 (3 H, br, apparent s), 6.37 (2 H, s) and 7.15 (8 H, s);  $m/z$  (M<sup>+</sup>) 374, 269, 253 and 91 (25.4, 17.1, 10.3 and 100% respectively).

**5,6-Dimethoxy-1,3-di(*o*-tolyl)indan-2-one.**—The foregoing alcohol (112 mg, 0.29 mmol), benzene (2 cm<sup>3</sup>), dry dimethyl sulphoxide (0.62 cm<sup>3</sup>), dicyclohexylcarbodiimide (181 mg, 3 equivs.) and pyridinium trifluoroacetate (28 mg, 0.5 equiv.) were stirred at  $20^{\circ}\text{C}$  (12 h). The product was diluted with ether and an aqueous solution of oxalic acid (10%) added until effervescence ceased. The filtered product was transferred to a separating funnel and the organic layer separated and washed with dilute hydrochloric acid, then water, dried (MgSO<sub>4</sub>) and evaporated. Chromatography of the residue on silica in dichloromethane gave the *title compound* as an oil (93 mg, 83%) (Found: M<sup>+</sup>, 372.171. C<sub>25</sub>H<sub>24</sub>O<sub>3</sub> requires M<sup>+</sup>, 372.172);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 1750;  $\delta_{\text{H}}$  (90 MHz) 2.71 (6 H, s), 3.79 (6 H, s), 5.07 (2 H, s), 6.66 (2 H, s) and 6.89–7.21 (8 H, m);  $m/z$  (M<sup>+</sup>) 372, (M<sup>+</sup> – CO) 344, 329, 298 and 253 (54.2, 32.7, 100, 15.7 and 29.9% respectively).

**Generation of 5,6-Dimethoxy-1,3-di(*o*-tolyl)inden-2-one.**—The foregoing ketone (63.4 mg, 0.17 mmol) in dry dichloromethane (1 cm<sup>3</sup>), at  $-14^{\circ}\text{C}$  was treated with bromine (13.6 mg, 0.17 mmol) in dry dichloromethane (0.5 cm<sup>3</sup>). After 1 h when the bromine was consumed the solvent was evaporated in a water-pump vacuum. Fresh dichloromethane (2 cm<sup>3</sup>) was added and evaporated as before to remove any hydrogen bromide. The crude monobromide was dissolved in dichloromethane (1 cm<sup>3</sup>) and DBU (0.05 cm<sup>3</sup>) in dichloromethane (0.5 cm<sup>3</sup>) was added dropwise at  $20^{\circ}\text{C}$ . The green colour associated with the *title isoindenone* persisted for *ca.* 1 h and disappeared when air was admitted into the apparatus. The product was diluted with ether and the ether layer washed with saturated aqueous sodium hydrogen carbonate, then brine, dried (MgSO<sub>4</sub>), evaporated and the product chromatographed on silica in dichloromethane to give 1,2-di(*o*-toluoyl)-4,5-dimethoxybenzene **25** (35 mg, 54%); m.p.  $142\text{--}144^{\circ}\text{C}$  (from dichloromethane–ethanol) (Found: M<sup>+</sup>, 374.150. C<sub>24</sub>H<sub>22</sub>O<sub>4</sub> requires M, 374.151);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 1655;  $\delta_{\text{H}}$  (90 MHz), 2.14 (6 H, s), 3.93 (6 H, s) and 7.03–7.38 (10 H, m);  $m/z$  (M<sup>+</sup>) 374, (M<sup>+</sup> – OMe) 343, (M<sup>+</sup> – C<sub>7</sub>H<sub>7</sub>) 283, 255, 119 and 91 (29.2, 15.2, 15.0, 67.8, 66 and 100% respectively).

**The N-Phenylmaleimide Adduct of 5,6-Dimethoxy-1,3-di(*o*-tolyl)inden-2-one; 24.**—The ketone (87 mg), in dichloromethane (1 cm<sup>3</sup>) was treated dropwise at  $-14^{\circ}\text{C}$  with stirring with bromine (19 mg) in dichloromethane (0.5 cm<sup>3</sup>). After completion of the addition the mixture was stirred at  $-14^{\circ}\text{C}$  (1 h) before evaporation of the solvent at  $20^{\circ}\text{C}$  in a water-pump vacuum. After addition and evaporation of dichloromethane (2 cm<sup>3</sup>) the crude bromide and *N*-phenylmaleimide (152 mg) in dichloromethane (1 cm<sup>3</sup>) were purged with nitrogen, and DBU (0.10 cm<sup>3</sup>) in dichloromethane (0.5 cm<sup>3</sup>) was added dropwise at  $20^{\circ}\text{C}$ . The purple mixture was stirred (1 h), diluted with ether, and the organic extract washed with dilute hydrochloric acid (2 mol dm<sup>-3</sup>), saturated aqueous sodium hydrogen carbonate and brine, dried (MgSO<sub>4</sub>), evaporated and chromatographed on silica in dichloromethane to give the *title compound* (62 mg, 49%); m.p.  $232\text{--}233^{\circ}\text{C}$  (from dichloromethane) (Found: C, 77.0; H, 5.25; N, 2.5. C<sub>35</sub>H<sub>29</sub>NO<sub>5</sub> requires C, 77.3; H, 5.3; N, 2.5%);  $\nu_{\text{max}}$ /cm<sup>-1</sup> 1721 and 1781;  $\delta_{\text{H}}$  (90 MHz) 1.96 (6 H, s), 3.7 (6 H, s), 3.8 (2 H, s), 6.48 (2 H, s), 6.50–6.63 (2 H, m) and 7.21–7.5 (11 H, m).

In related experiments the same adduct was produced in the

same yield when the *N*-phenylmaleimide was added after the green solution of the isoindenone had been stirred (under  $N_2$ ) for 1 h. The green colour of the isoindenone remained until the *N*-phenylmaleimide was added whereupon the purple colour of the DBN-*N*-phenylmaleimide complex appeared. After addition of the dienophile the same yield of adduct was obtained when the reaction was worked-up immediately or work-up was delayed for 1 h with stirring of the reaction at 20 °C.

*Generation of 1,3-Di(o-tolyl)inden-2-one.*—1,3-Di(o-tolyl)indan-2-one (169 mg, 0.543 mmol) in dichloromethane (1 cm<sup>3</sup>) was added dropwise to a stirred solution of bromine (87 mg, 0.543 mmol) in dichloromethane (0.5 cm<sup>3</sup>) at -14 °C. After stirring at -14 °C (1 h) the product was evaporated at ca. 20 °C using a water-pump vacuum; evaporation was repeated after further addition of dichloromethane (1 cm<sup>3</sup>). The residue was dissolved in dichloromethane (1 cm<sup>3</sup>) and DBU (0.25 cm<sup>3</sup>) in dichloromethane (0.5 cm<sup>3</sup>) added at -70 °C with stirring. A deep green colour developed, persisted for ca. 2 min at -70 °C and then became red-brown. After stirring 30 min at -70 °C the product was diluted with ether and water and the ether layer washed with dilute hydrochloric acid (2 mol dm<sup>-3</sup>), saturated aqueous sodium hydrogen carbonate and water, dried (MgSO<sub>4</sub>), evaporated and the residue chromatographed on silica in benzene-petroleum ether (7:3) to give the dimer **21** (42.5 mg, 25%), m.p. 191–193 °C, showing identical IR and NMR spectra with those reported. Further elution of the column with dichloromethane gave a mixture of two compounds tentatively identified as dimers of the type **22** (40 mg, 23.5%); m.p. 180–181 °C (from ethanol) (Found: C, 88.8; H, 5.95; C<sub>46</sub>H<sub>36</sub>O<sub>2</sub> requires C, 89.0; H, 5.8%;  $\nu_{\max}(\text{CHHCl}_3)/\text{cm}^{-1}$  1778 and 1695;  $\delta_{\text{H}}(400 \text{ MHz})$  1.5–2.4 (12 H, br complex m, Me's), 4.33 (1 H, dd, *J* 8.0 and 4.5), 4.73 (0.3 H, d, *J* 8), 4.96 (0.7 H, d, *J* 8), 6.19 (0.7 H, d, *J* 10.5), 6.25 (0.3 H, d, *J* 10.5), 6.38 (0.7 H, dd, *J* 10.5 and 4.5), 6.43 (0.3 H, dd, *J* 10.5 and 4.5) and 6.5–7.7 (20 H, m); *m/z* ( $M^+$ ) 620; ( $M^+ - \text{CO}$ ) 592, ( $M^+ / 2$ ) 310, 265, ( $M^+ - 2 \times \text{C}_7\text{H}_7$ ) 218, 190, 126, 91 and 44 (2.6, 0.4, 100, 34.1, 94.7, 28.0, 13.1, 18.0 and 16.2% respectively).

*Measurement of the Long Wavelength Absorption Band of 5,6-Dimethoxy-1,3-di(o-tolyl)inden-2-one.*—1-Bromo-1,3-dimethoxy-1,3-di(o-tolyl)indan-2-one (ca. 1 mg) in dry dichloromethane (2.5 cm<sup>3</sup>) was placed in a 0.5 cm Pyrex glass cell with an elongated neck closed by a rubber septum. The cell was flushed with argon *via* a hypodermic needle and DBU (0.1 cm<sup>3</sup> of a 10% solution in dichloromethane) added at 20 °C *via* syringe; the green colour attributed to the title compound appeared rapidly. The cell fitted into the holder of a Pye-Unicam PU 8800 UV-VIS spectrophotometer. The visible absorption band extended between ca. 600 and 900 nm with  $\lambda_{\max}$  772 nm. In a similar experiment conducted in benzene the

band appeared at 760 nm. In both experiments the band rapidly disappeared on passing oxygen through the solution, or upon addition of *N*-phenylmaleimide.

*The Dimers of 1,3-Diphenylinden-2-one.*—2-Chloro-1,3-diphenylindan-2-one<sup>7</sup> (400 mg) was added to sodium methoxide [from sodium (260 mg)] in methanol (40 cm<sup>3</sup>) with stirring at -40 °C. The initial green colour faded over 70 min at this temperature. (In other reactions on a smaller scale the colour faded immediately at ca. -25 °C.) The reaction was allowed to warm to 10 °C over 2 h, diluted with water, acidified with acetic acid, extracted into dichloromethane, dried (MgSO<sub>4</sub>) and evaporated at ca. 40 °C in a water-pump vacuum. The residue was triturated with benzene and the known<sup>2</sup> dimer (235 mg) filtered. The liquor was chromatographed on silica in benzene to give the novel dimer **17** (43 mg) m.p. 245–250 °C (From benzene-light petroleum) (Found: C, 89.5; H, 5.2%; *M*(osmometer) 617. C<sub>42</sub>H<sub>28</sub>O<sub>2</sub> requires C, 89.4; H, 5.0%; *M*, 564);  $\nu_{\max}/\text{cm}^{-1}$  1600, 1635 and 1770;  $\delta_{\text{H}}(90 \text{ MHz})$  6.6–6.9 (2 H, m), 6.9–7.2 (26 H, m);  $\delta_{\text{C}}(23.86 \text{ MHz})$  66.09, 69.78, 87.22, 120.37, 124.38, 124.65, 125.74, 125.85, 126.82, 127.31, 127.47, 127.58, 127.85, 128.01, 128.18, 128.28, 128.50, 129.37, 129.75, 130.40, 131.21, 131.53, 133.00, 134.46, 137.98, 140.43, 142.32, 143.40, 168.52 and 283.21.

A portion of the (6 + 4)  $\pi$ -dimer (7 mg) and toluene (3 cm<sup>3</sup>) were boiled under reflux (15 min). On cooling and filtering the (4 + 4)  $\pi$ -dimer was obtained in quantitative yield. The same conversion appeared to proceed slowly in CDCl<sub>3</sub> at 20 °C. The (4 + 4)  $\pi$ -dimer and *N*-phenylmaleimide (1 equiv.) form the isoindenone-*N*-phenylmaleimide adduct to the extent of ca. 35% after refluxing in benzene (18 h).

## References

- 1 D. Bradshaw, D. W. Jones and J. Tideswell, *J. Chem. Soc., Perkin Trans. 1*, 1991, 169.
- 2 J. M. Holland and D. W. Jones, *J. Chem. Soc., Chem. Commun.*, 1969, 587; *J. Chem. Soc. C*, 1971, 608.
- 3 D. W. Jones and A. Pomfret, *J. Chem. Soc., Chem. Commun.*, 1983, 703.
- 4 F.-H. Marquardt, *Helv. Chim. Acta*, 1965, **48**, 1476.
- 5 G. R. Proctor and L. G. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1527.
- 6 A. De Mesmaeker, L. Vertommen, R. Merényi and H. G. Viehe, *Tetrahedron Lett.*, 1982, **23**, 69, and cited references.
- 7 E. P. Kohler, N. K. Richtmyer and W. F. Hester, *J. Am. Chem. Soc.*, 1931, **53**, 205; E. P. Kohler and R. P. Barnes, 1934, **56**, 434.

Paper 0/03498C

Received 31st July 1990

Accepted 29th August 1990