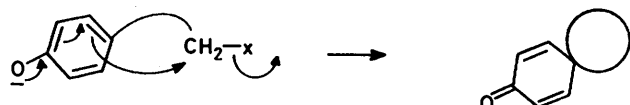


## Adamantanoid Dienones from Intramolecular Ar<sub>1</sub>6-Participation

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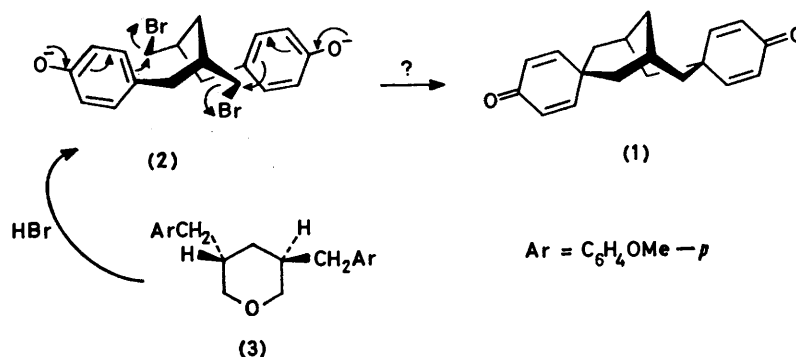
Heating the phenolic iodide (14) with potassium *t*-butoxide and *t*-butyl alcohol in a sealed tube gave the phenolic dienone (6) or the adamantanoid dienone (18a) depending on the quantity of potassium *t*-butoxide used. Treatment of (18a) with DDQ gives the adamantanoid bis-dienone (17), which fails to undergo the dienone-phenol rearrangement in the presence of trifluoroacetic acid.

INTRAMOLECULAR displacement of a leaving group by a nucleophilic aryl ring has been used, in the case of phenolate anions, to prepare a variety of dienones<sup>1</sup> (Scheme 1). Previously, an attempt was made to



SCHEME 1

synthesise the bis-dienone (1) by treatment of the dibromide (2) with 2 mol of potassium *t*-butoxide in *t*-butyl alcohol (a double Ar<sub>1</sub>6-participation<sup>2</sup>).



Using crude dibromide (2) (prepared by opening of the *trans*-3,5-disubstituted tetrahydropyran (3) with concentrated hydrobromic acid) we obtained a product, after attempted conversion to (1), to which structure (4) was assigned on the basis of spectroscopic data.<sup>3</sup> The low yield of (4) (5–10%) fell to zero when we subsequently subjected the crystalline DL-dibromide (2) to the base conditions above. Evidently the progenitor of (4) was an impurity in (2), presumably a by-product in the acid treatment of (crystalline) tetrahydropyran (3).

In this paper we report a more rational synthesis of the dienone (4).<sup>4</sup> This synthetic pathway follows in its final steps, the route by which it is thought dienone (4) was produced initially from the impurity in (2) (Scheme 2).

### RESULTS AND DISCUSSION

Intramolecular displacement of a leaving group X from (5) would produce the phenolic dienone (6), in which an intramolecular Michael addition [arrows in (6)] would generate the adamantane skeleton of (4). Ideally,

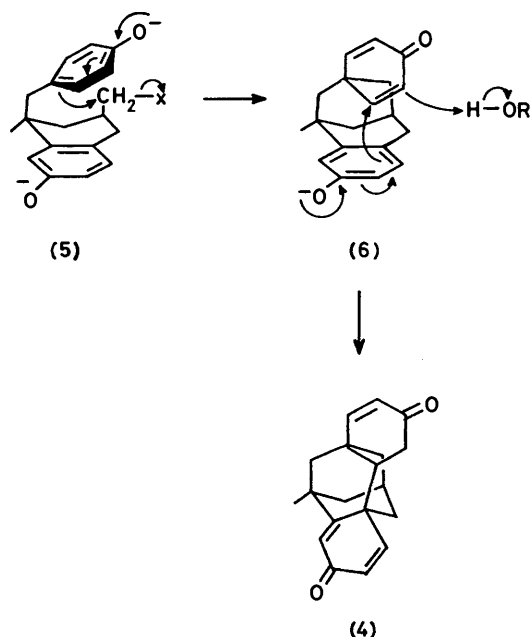
therefore, synthesis of (4) requires a stereospecific synthesis of (5) with *p*-hydroxybenzyl and CH<sub>2</sub>X *cis*, since it is only this stereoisomer which is capable of forming the phenolic dienone (6).

Alkylation of dimethyl malonate with *p*-methoxybenzyl chloride gave the monoalkylated product (7) in excellent yield (95%) (Scheme 3). Reduction of the diester (7) with excess of lithium aluminium hydride gave the crystalline diol (8) which, with phosphorus oxychloride and pyridine, gave the dichloride (9) (55%). After some experimentation, conditions were found for direct formation of the diester (10) (35%) from the reaction of malonate (7) with the dichloride (9).

Whether the (unknown) allylic chloride is intermediate in this alkylation, or whether elimination of hydrogen chloride occurs subsequent to the formation of the C–C bond, is not known.

The diester (10), m.p. 50.5–51.5 °C, was identified by its n.m.r. spectrum, and in particular by the olefinic protons ( $\delta$  4.8, br s); it also gave a crystalline diol on reduction with excess of lithium aluminium hydride. Attempted cyclisation of (10) under various acid conditions to give the tetrahydronaphthalene skeleton was unsuccessful; the only product isolated was a compound formulated as the lactone (11), showing  $\nu(\text{CO})$  at 1760 and 1735 cm<sup>-1</sup> in the i.r. and two singlets,  $\delta$  1.65 and 1.10 (ratio 2.7 : 1) in its n.m.r. spectrum, assigned to the methyl groups of two stereoisomers. Attempts to form the tetrahydronaphthalene skeleton from the lactone (11) using polyphosphoric acid (PPA) at 150–200 °C led to increasing yields of polymeric materials and decreasing yields of recovered lactone (11) as the temperature was raised. Mono-demethoxycarbonylation of (10) was therefore carried out using wet DMSO–sodium chloride<sup>5</sup>

giving the monoester (12) (60%), and reduction with lithium aluminium hydride furnished the corresponding alcohol (13), m.p. 59–60 °C (Scheme 4).



SCHEME 2

We anticipated that mild acid conditions would bring about addition of the hydroxy-group to the methylene in (13) with formation of the tetrahydrofuran derivative analogous to (11). Accordingly, cyclisation of (13) was carried out using hydriodic acid under reflux, conditions which, it was assumed, would re-open any tetrahydrofuran ring formed. Spectroscopic evidence supported (14) as the structure of the product from this reaction. That cleavage of the methyl ethers had occurred was

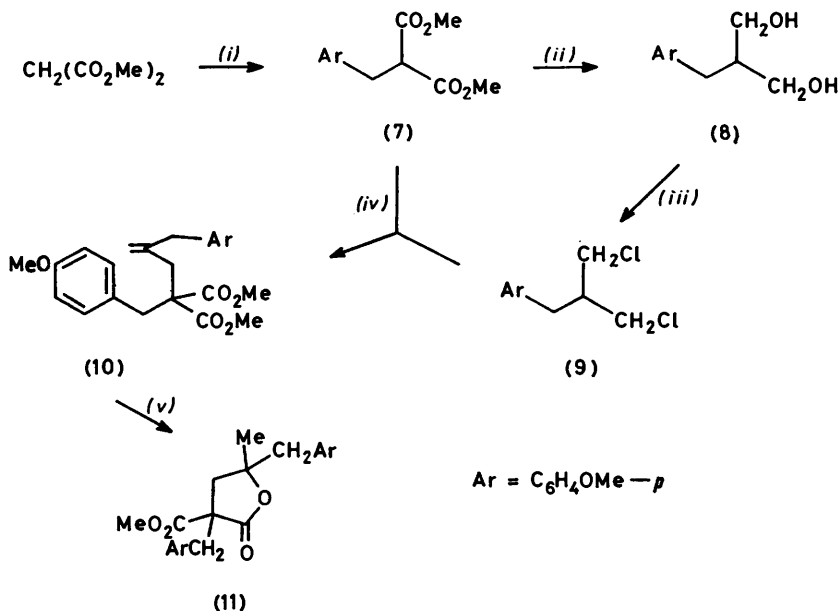
indicated by the two phenolic hydroxy-protons in the n.m.r. at  $\delta$  8.10 (exchangeable in  $D_2O$ ) and in the i.r. at  $3\ 340\text{ cm}^{-1}$ ; the methyl group was present as two overlapping singlets at  $\delta$  1.24 and 1.21, with a ratio of *ca.* 3 : 1 indicating the presence of both stereoisomers. Attempts to separate these stereoisomers of the iodide (14) were frustrated by their instability, particularly towards chlorinated solvents.

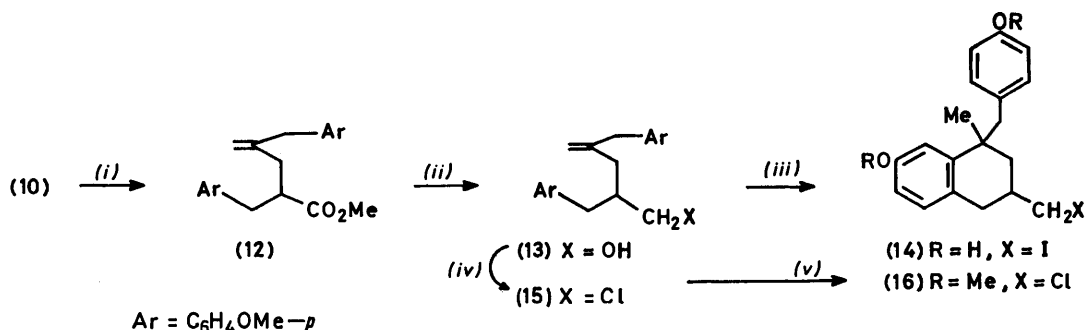
Treatment of the alcohol (13) with phosphorus oxychloride-pyridine gave the chloride (15) (90%) which was successfully cyclised to the tetrahydronaphthalene (16) using PPA. From the two methyl signals in the n.m.r. spectrum of (16), a 2 : 1 ratio of stereoisomers is present.

Heating the mixture of stereoisomeric iodides (14) in dry *t*-butyl alcohol with potassium *t*-butoxide in a sealed Pyrex tube at 170 °C for 3 h gave either the phenolic dienone (6), m.p. 216–219 °C, or the adamantanoid dienone (4), m.p. 237–239 °C, depending on the quantity of *t*-butoxide used (Scheme 5).

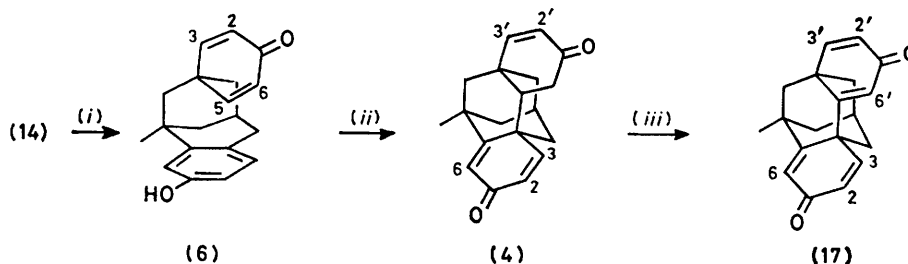
Using 2.5 mol equiv. of base resulted in the formation of (6) (24%) whereas with 1.0 mol equiv., (4) was the predominant or even exclusive product obtained in similar yield. Complete conversion of (6) into (4) took place under the sealed tube conditions above using 0.5 mol equiv. of potassium *t*-butoxide and two drops of water. The structures assigned to both (6) and (4) are consistent with the spectroscopic properties given below but are based essentially on a consideration of their mechanism of formation from the iodide (14). Conversion of the dienone (4) into the bisdienone (17), m.p. 195–202 °C, using DDQ in dioxan, is evidence for a  $\gamma,\gamma$ -disubstituted cyclohexenone ring in the former.

It is possible that the low yield of (4) or (6) in the reaction of the iodide (14) with base is the result of that stereoisomer having *p*-hydroxybenzyl and iodomethyl

SCHEME 3 (i)  $ArCH_2Cl$ , NaH, DMSO; (ii)  $LiAlH_4$ ; (iii)  $POCl_3$ -pyridine; (iv) NaH, DMSO; (v) PPA



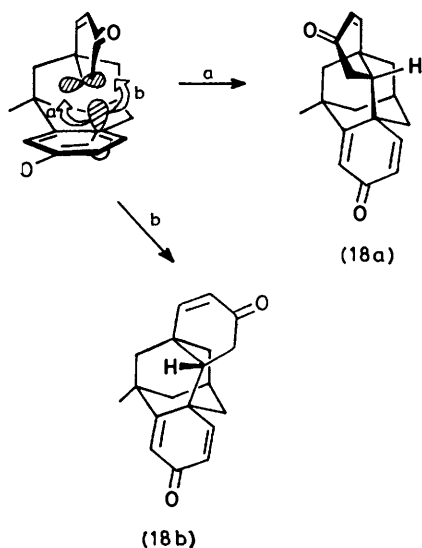
SCHEME 4 (i) DMSO-NaCl; (ii) LiAlH<sub>4</sub>; (iii) HI-P; (iv) POCl<sub>3</sub>-pyridine; (v) PPA



SCHEME 5 (i) Bu<sup>t</sup>OK-Bu<sup>t</sup>OH; (ii) 'KOH'; (iii) DDQ-dioxan

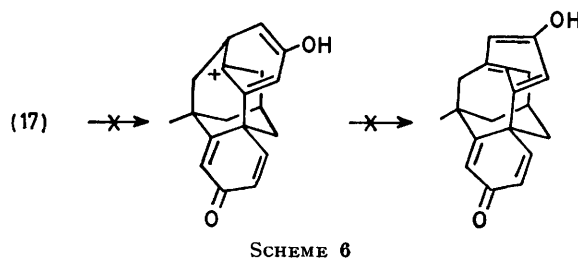
groups *cis* constituting the minor component in the 3 : 1 ratio of stereoisomers observable by n.m.r. However, the other stereoisomer was not recovered after the reaction to test this point.

All three dienones (4), (6), and (17) show typical dienone i.r. stretching frequencies at 1 655 and 1 625—1 610 cm<sup>-1</sup>, with the additional α,β-unsaturated ketone of (6) visible at 1 665 cm<sup>-1</sup>; the phenolic OH of (6) at 3 190 cm<sup>-1</sup> was absent in (4). In the n.m.r. spectrum of the phenolic dienone (6), three of the four dienone protons are clearly separated from those of the aromatic protons. Both H-6 and H-5 lie over the face of the benzene ring in (6) (assuming the conformation drawn) and this accounts for their upfield shift by *ca.* 0.7 p.p.m.



from the normal positions of α- and β-H in dienones.<sup>6</sup> In the n.m.r. spectrum of the bis-dienone (17), all the dienone protons are visible at different chemical shifts.

The spectroscopic data for (4) do not allow a choice between (18a) and (18b), corresponding to Michael addition of the phenolate anion to the two faces of the dienone ring. However, a clear-cut preference for the formation of (18a) can be deduced from an examination of Dreiding models. Deformation of the system to achieve a parallel overlap of the two shaded lobes leading to (18a) is far easier than the alternative leading to (18b).



The bis-dienone (17) remained unchanged after standing in trifluoroacetic acid for one week. Simple dienones undergo the dienone-phenol rearrangement in trifluoroacetic acid within hours at room temperature. Failure of (17) to undergo rearrangement can be ascribed to the strain present in a homoadamantanoid skeleton containing a bent phenyl ring (Scheme 6).

#### EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. The i.r. spectra of crystalline compounds were determined as Nujol mulls, and of other

compounds as thin films using a Perkin-Elmer 237 spectrometer. N.m.r. spectra were recorded on Varian T60 or JEOL JNM PS 100 spectrometers, and mass spectra on A.E.I. MS9 or V.G. Micromass 16B spectrometers. Accurate mass spectra were obtained through the Physico-Chemical Measurements Unit, Harwell. Light petroleum refers to the fraction of b.p. 60–80 °C. Kieselgel refers to Merck Kieselgel 60 PF 254. Basic alumina is Laporte type H (100–200 mesh). Sodium hydride (50% dispersion in oil) was washed with dry light petroleum prior to use and the weights given refer to the dispersion in oil. Distillations of <1 g were carried out using a Kugelrohr oven and bulb-tube with the b.p. quoted as the oven temperature.

*Dimethyl p-Methoxybenzylpropanedioate* (7).—Dimethyl malonate (110 g) was added dropwise over 1 h to a stirred suspension of washed sodium hydride (16 g) in dry DMSO (600 ml) at 25 °C. The mixture was stirred till no more hydrogen was evolved (0.5 h), and then *p*-methoxybenzyl chloride (52 g) added over 0.5 h. After addition, the mixture was heated at 80 °C with stirring for 3 h, then cooled, poured into water (1.4 l), and ether-extracted. The ether extracts were washed with water, dried, and evaporated to yield a brown oil which gave the diester (7) (73 g, 95%) after distillation as a colourless mobile oil, b.p. 140–150 °C at 1.0 mmHg, a single spot on t.l.c.,  $\delta$  (CCl<sub>4</sub>) 6.70 (AA'BB', 4 × Ar-H), 3.59 (s, ArOMe), 3.52 (s, 2 × CO<sub>2</sub>Me), and 3.5–2.8 (m, CH<sub>2</sub>CH);  $\nu_{\max}$  1 730 and 1 610 cm<sup>-1</sup>.

*2-(p-Methoxybenzyl)propane-1,3-diol* (8).—The diester above (22 g) was added dropwise to a stirred suspension of lithium aluminium hydride (6.8 g) in dry ether (350 ml) and the mixture heated under reflux for 2.5 h. After cautious dropwise addition of ethyl acetate to consume unreacted hydride, water was added dropwise and the inorganic salts separated. Evaporation of the organic layer gave the *diol* as a colourless solid (18.5 g, 90%), m.p. 66–67 °C (from ether) (Found: C, 67.4; H, 8.2. C<sub>11</sub>H<sub>16</sub>O<sub>3</sub> requires C, 67.35; H, 8.15%);  $\delta$ (CDCl<sub>3</sub>) 6.70 (AA'BB', 4 × Ar-H), 3.65 (s, OMe), 3.60 (m, 2 × CH<sub>2</sub>OH), 2.50 [m, CH<sub>2</sub>Ar + 2 × OH (exchangeable with D<sub>2</sub>O)], and 1.90 (m, H-2);  $\nu_{\max}$  3 260 cm<sup>-1</sup>.

*2-(p-Methoxybenzyl)-1,3-dichloropropane* (9).—Phosphorus oxychloride (34 g) was added dropwise to a solution of the diol (8) (22 g) in pyridine (250 ml), and the mixture heated at 100 °C for 1 h. After cooling, the solution was poured into ice-cold hydrochloric acid (750 ml, 2M) and the mixture extracted with ether. The ether extract was washed successively with hydrochloric acid, water, and sodium carbonate solution, then dried and the solvent removed to give a viscous brown oil (21 g). Distillation gave the product (9) as a colourless mobile oil (14.1 g, 55%), b.p. 110–115 °C at 0.3 mmHg;  $\delta$ (CCl<sub>4</sub>) 7.17 (AA'BB', 4 × Ar-H), 3.90 (s, OMe), 3.70 (m, 2 × CH<sub>2</sub>Cl), 2.80 (m, CH<sub>2</sub>Ar), and 2.40 (m, H-2);  $\nu_{\max}$  1 610, 1 510, and 1 245 cm<sup>-1</sup>; *m/e* 236, 234, 232 (M<sup>+</sup>), 122, 121, 91, 78, 77, 65, 51, 49, and 39.

*Dimethyl 2-(p-Methoxybenzyl)-2-(2-p-methoxybenzylallyl)-propanedioate* (10).—The propanedioate (7) (7.6 g) was added dropwise to a stirred suspension of sodium hydride (3.6 g) in DMSO (120 ml) at room temperature. The mixture was heated at 60 °C till no more hydrogen was evolved (1 h), cooled, and added over 15 min to (9) (6.9 g) in DMSO (90 ml). After stirring for 2.5 h at 80 °C, the mixture was cooled, poured into cold water (500 ml), and extracted with benzene. The benzene extract was washed with water, dried, and evaporated to give a viscous brown oil (8.3 g).

This was chromatographed on alumina and elution with light petroleum–ethyl acetate (5 : 1) gave the *product* as a white solid (5.5 g), which crystallised from ether (4.5 g, 35%), m.p. 50.5–51.5 °C (Found: C, 69.7; H, 6.8. C<sub>24</sub>H<sub>28</sub>O<sub>6</sub> requires C, 69.9; H, 6.8%);  $\delta$ (CDCl<sub>3</sub>) 6.75 (m, 8 × Ar-H), 4.8 (br s, CH<sub>2</sub>=C), 3.65 (2 × s, 2 × OMe), 3.55 (2 × s, 2 × OMe), 3.2 (br s, 2 × ArCH<sub>2</sub>), and 2.55 (br s, CH<sub>2</sub>=CCH<sub>2</sub>);  $\nu_{\max}$  1 735, 1 612, 1 085, and 900 cm<sup>-1</sup>.

Reduction of compound (10) with excess of lithium aluminium hydride as described for (8) gave *5-hydroxy-4-hydroxymethyl-2,4-di-(p-methoxybenzyl)pent-1-ene* as colourless crystals (from light petroleum), m.p. 84–85 °C (Found: C, 74.3; H, 8.0. C<sub>22</sub>H<sub>28</sub>O<sub>4</sub> requires C, 74.15; H, 7.85%);  $\delta$ (CCl<sub>4</sub>) 6.8 (m, 8 × Ar-H), 4.9 (br s, CH<sub>2</sub>=C), 3.75 (s, 2 × OMe), 3.5 (br s, 2 × CH<sub>2</sub>OH), 3.3 (br s, CH<sub>2</sub>Ar), 2.6 (br s, CH<sub>2</sub>Ar), and 2.0 [br s, 2 × OH (exchangeable with D<sub>2</sub>O) + 2 × H-3];  $\nu_{\max}$  3 380, 910, and 900 cm<sup>-1</sup>.

*Methyl p-Methoxybenzyl-(2-p-methoxybenzylallyl)acetate* (12).—The diester (10) (5.0 g) was heated in DMSO (60 ml) with sodium chloride (1 g) and water (2 g) at 195 °C for 3 h according to the method of Krapcho.<sup>5</sup> After work-up, the crude product was obtained as a brown oil (5.1 g) which after chromatography over alumina (elution with light petroleum–ethyl acetate) gave the *monoester*, b.p. 200–210 °C at 0.2 mmHg (Kugelrohr), as a colourless oil (2.6 g, 60%) (Found: C, 74.35; H, 7.4. C<sub>22</sub>H<sub>28</sub>O<sub>4</sub> requires C, 74.6; H, 7.35%);  $\delta$ (CCl<sub>4</sub>) 6.8 (m, 8 × Ar-H), 4.75 (br s, CH<sub>2</sub>=C), 3.65 (s, 2 × OMe), 3.5 (s, OMe), 3.2 (br s, ArCH<sub>2</sub>C=), and 2.8–1.9 (m, ArCH<sub>2</sub>CHCH<sub>2</sub>);  $\nu_{\max}$  1 735, 1 611, and 900 cm<sup>-1</sup>.

*5-Hydroxy-2,4-di-(p-methoxybenzyl)pent-1-ene* (13).—The ester (12) was reduced using an excess of lithium aluminium hydride in ether as described for (8), to give the *alcohol* (13) (75%) as colourless crystals (from ether), m.p. 59–60 °C (Found: C, 77.35; H, 8.05. C<sub>21</sub>H<sub>26</sub>O<sub>3</sub> requires C, 77.3; H, 8.0%);  $\delta$ (CDCl<sub>3</sub>) 7.15 (m, 8 × Ar-H), 5.0 (br s, CH<sub>2</sub>=C), 3.90 (s, 2 × OMe), 3.65 (br s, CH<sub>2</sub>OH), 3.55 (br s, CH<sub>2</sub>Ar), 2.6 (br s, CH<sub>2</sub>Ar), 2.1 (m, 2 × H-3, H-4), and 1.40 [s, OH (exchangeable with D<sub>2</sub>O)];  $\nu_{\max}$  3 380 cm<sup>-1</sup>.

*5-Chloro-2,4-di-(p-methoxybenzyl)pent-1-ene* (15).—Phosphorus oxychloride (0.9 g), pyridine (50 ml), and the above alcohol (13) (1.0 g) were heated at 90 °C for 1 h. Work-up as described for (9) gave the chloride (15) as a colourless oil (90%), b.p. 150–160 °C at 0.1 mmHg;  $\delta$ (CDCl<sub>3</sub>) 6.95 (m, 8 × Ar-H), 4.95 (br s, CH<sub>2</sub>=C), 3.90 (s, 2 × OMe), 3.45 (br s, CH<sub>2</sub>Cl), 3.2 (br s, ArCH<sub>2</sub>C=C), 2.6 (br s, ArCH<sub>2</sub>), and 2.1 (br s, 2 × H-3, H-4);  $\nu_{\max}$  900 cm<sup>-1</sup>.

*Cyclisation of Diester (10), Alcohol (13), and Chloride (15)*.—(i) *Diester* (10). The diester (200 mg) was added to polyphosphoric acid (10 ml) and the mixture heated with stirring at 80 °C for 1 h. After cooling, the mixture was poured into water and extracted with ethyl acetate; the ethyl acetate layer was separated, washed with water, dried, and evaporated. Chromatography of the crude product over Kieselgel eluting with light petroleum–ethyl acetate (5 : 1) gave an epimeric mixture of lactones (11) (30%), giving a single spot on t.l.c., as the major product:  $\delta$ (CDCl<sub>3</sub>) 6.95 (m, 8 × ArH), 3.95 (br s, 3 × OMe), 3.6–2.0 (m, 2 × ArCH<sub>2</sub> + CH<sub>2</sub>), and 1.65 and 1.10 [2 × s (ratio 11 : 4 respectively), 2 × Me (2 epimers)];  $\nu_{\max}$  1 760 and 1 735 cm<sup>-1</sup>.

(ii) *Alcohol* (13). Hydriodic acid (55%) was freed from iodine by distillation from red phosphorus at atmospheric pressure. The alcohol (13) (500 mg) was heated under reflux in hydriodic acid (20 ml) with red phosphorus (500

mg) at 130 °C for 0.5 h with vigorous stirring. The same work-up procedure as described for (10) above gave a glassy foam (520 mg), and chromatography over Kieselgel using light petroleum–ethyl acetate (40 : 1→1 : 1) gave the iodide (14) as a foam (275 mg, 45%);  $\delta[(\text{CD}_3)_2\text{CO}]$  8.10 [br s, 2 × OH (exchangeable with  $\text{D}_2\text{O}$ )], 6.85 (m, 7 × Ar-H), 3.28 (m,  $\text{CH}_2\text{I}$ ), 2.8–0.9 (m, 2 ×  $\text{CH}_2\text{Ar}$  +  $\text{CH}_2\text{CHCH}_2\text{I}$ ), and 1.24 and 1.21 [2 × s, 2 × Me, two epimers (ratio 3 : 1 respectively)];  $\nu_{\text{max}}$  3 340  $\text{cm}^{-1}$ ;  $m/e$  408 ( $M^+$ ), 301, 175, 174, 173, 172, 159, 158, 157, 146, 145, 127, and 107. Although pure by t.l.c. the compound decomposed upon attempted distillation.

(iii) *Chloride* (15). The chloride (200 mg) was treated with polyphosphoric acid (10 ml) for 0.5 at 110 °C as described for the diester (10) above. Chromatography of the crude product using Kieselgel (50 : 1—5 : 1, light petroleum–ethyl acetate) gave the tetrahydronaphthalene derivative (16) as a mixture of epimers (single spot on t.l.c.);  $\delta(\text{CDCl}_3)$  6.85 (m, 7 × Ar-H), 3.81, 3.77, 3.73 (3 × s, OMe, 2 epimers), 3.45 (m,  $\text{CH}_2\text{Cl}$ ), 3.1–1.2 (m, 2 ×  $\text{CH}_2\text{Ar}$  +  $\text{CH}_2\text{CH}$ ), and 1.29 and 1.23 (2 × s, Me, 2 epimers);  $m/e$  346, 344 ( $M^+$ ), 226, 225, 224, 223, 222, 187, 159, 147, and 121.

*Reaction of Iodide (14) with Potassium *t*-Butoxide*.—Iodide (14) (180 mg) was dissolved in dry *t*-butyl alcohol (60 ml) and a solution of potassium *t*-butoxide (124 mg, 2.5 mol equiv.) in *t*-butyl alcohol (10 ml) added. After flushing the solution with dry nitrogen in a Pyrex-walled tube, the mixture was frozen, evacuated, sealed, and then heated at 170 °C for 3 h. When cool, the tube was opened, ethanoic acid (0.5 ml) added, and the *t*-butyl alcohol removed under reduced pressure. The residue was dissolved in ethyl acetate, washed with sodium thiosulphate and water, dried, and evaporated. Crystallisation of the residue gave the *phenolic dienone* (6), m.p. 216–219 °C (from ethyl acetate–light petroleum). A further quantity (total 30 mg, 24%) of the same material was obtained by chromatography of the filtrate after crystallisation [Kieselgel: light petroleum–ethyl acetate (1 : 1)] (Found: C, 81.2; H, 7.2.  $\text{C}_{19}\text{H}_{20}\text{O}_2$  requires C, 81.4; H, 7.2%);  $\delta[(\text{CD}_3)_2\text{CO}]$  (100 MHz) 8.10 [br s, OH (exchangeable with  $\text{D}_2\text{O}$ )], 7.1–6.6 (m, 3 × Ar-H + H-3), 6.28 (dd,  $J$  12.5 and 2.5 Hz, H-5), 6.00 (dd,  $J$  10 and 2.5 Hz, H-2), 5.60 (dd,  $J$  12.5 and 2.5 Hz, H-6), 3.4–1.4 (m, 4 ×  $\text{CH}_2$  + methine CH), and 1.30 (s, Me);  $\nu_{\text{max}}$  3 190, 1 655, 1 618, 1 608, and 1 580  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (ethanol) 230 ( $\epsilon$  14 000) and 278 nm (2 100);  $m/e$  280 ( $M^+$ ), 173, 172, 171, 160, 159, 158, 145, 144, 131, 122, 107, 91, and 77.

When the above reaction was repeated using 1.0 mol equiv. of potassium *t*-butoxide in *t*-butyl alcohol, the product isolated was the *adamantanoid dienone* (4), m.p. 237–239 °C (from ethanol) in similar yield (Found:  $M^+$ , 280.146 3.  $\text{C}_{19}\text{H}_{20}\text{O}_2$  requires  $M$ , 280.146 3);  $\delta(\text{CDCl}_3)$ ; 100 MHz) 6.72 (d,  $J$  10 Hz, H-3 and H-3'), 6.38 (dd,  $J$  10 and 2 Hz, H-2), 6.32 (s, H-6), 5.94 (d,  $J$  10 Hz, H-2'), 2.6–1.4 (m, 5 ×  $\text{CH}_2$  + 2 × methine-H), and 1.09 (s, Me);  $\nu_{\text{max}}$  1 665, 1 655, 1 622, and 1 602  $\text{cm}^{-1}$ ;  $m/e$  280 ( $M^+$ ), 160, 159, 158, 131, 130, 129, 128, 122, 115, 91, and 77.

*Conversion of (6) into (4)*.—The phenolic dienone (6) (30 mg) was dissolved in *t*-butyl alcohol (30 ml) and potassium *t*-butoxide (8.7 mg, 0.5 mol equiv.) and water (0.2 ml) were added. Heating the mixture in a sealed tube under the conditions described above, with the same work-up procedure, gave a white solid (30 mg), identical with the *adamantanoid dienone* (4).

*Dehydrogenation of dienone (4) with DDQ*.—The dienone (4) (18 mg) was sealed in a bulb with freshly distilled dry dioxan (5 ml) and dichlorodicyanobenzoquinone (110 mg) and heated at 102 °C for 4.5 d. Half the dioxan was removed under reduced pressure and the solid obtained separated. The solution was then evaporated to dryness and chromatographed over alumina using benzene–ethyl acetate (50 : 1→3 : 2) to yield a colourless solid (14 mg). Crystallisation from ethanol gave the *bis-dienone* (17), m.p. 195–202 °C (Found: C, 82.0; H, 6.4.  $\text{C}_{19}\text{H}_{18}\text{O}_2$  requires C, 82.05; H, 6.5%);  $\delta(\text{CDCl}_3)$ ; 100 MHz) 7.09 and 6.97 (2 × d,  $J$  10 Hz, H-3 and H-3'), 6.51 and 6.29 (2 × dd,  $J$  10 and 1.5 Hz, H-2 and H-2'), 6.18 and 6.12 (2 × d,  $J$  1.5 Hz, H-6 and H-6'), 2.6–1.4 (m, 4 ×  $\text{CH}_2$  + methine-H), and 1.24 (s, Me);  $\nu_{\text{max}}$  1 655 and 1 625  $\text{cm}^{-1}$ ;  $m/e$  278 ( $M^+$ ), 263, 195, 194, 167, 166, 165, 152, 130, 121, and 115.

[8/2218 Received, 29th December, 1978]

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