Reaction of 2,6-Disubstituted Phenols with Vinyllead Triacetates and Alk-1-ynyllead Triacetates: Synthesis of 6-Vinyl- and 6-Alkynyl-Cyclohexa-2,4-dienones and Crystal Structure of 1,3,5,7-Tetramethyl-3,5-bis(phenylethynyl)-1,3,4,4a,5,8a-hexahydro-1,4-ethenonaphthalene-2,6-dione

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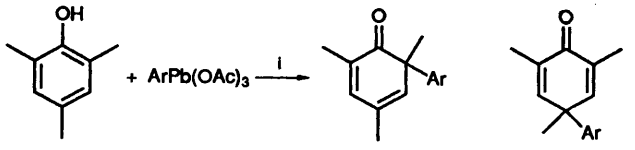
(*E*)-Styryllead triacetate **9**, generated by reaction of lead tetraacetate with trimethyl[(*E*)-styryl]-stannane **7**, has been found to react with 2,4,6-trimethylphenol **1** to give the 6-(*E*)-styrylcyclohexa-2,4-dienone **11** in high yield. This electrophilic vinylation reaction has been investigated for the vinyllead triacetates **9** and **10** and the 2,6-dimethylphenols **1**, **13**, **14** and **15**. An analogous alkynylation reaction occurred when phenylethynyllead triacetate **24** was treated with 2,4,6-trimethylphenol; however, the product in this case, cyclohexadienone **25**, underwent a Diels–Alder dimerisation to give the 1,4-ethenonaphthalene **26**. The product **28** from a reaction of the phenylacetylenelead compound **24** and 2,6-dimethylphenol behaved similarly, and here the 1,4-ethenonaphthalene structure **27** for the dimer was determined by single crystal X-ray analysis.

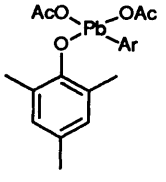
Previous work has shown that aryllead triacetates react with 2,6-disubstituted phenols to give predominantly 6-aryl-2,6-disubstituted cyclohexa-2,4-dienones (as in **2**),[1,2,3] although when a substituent is also present in the 4-position, as in the case of 2,4,6-trimethylphenol **1** (see Scheme 1), some of the 4-arylcyclohexa-2,5-dienone (as in **3**) may also be produced.[1] The



1 **2** **3**

Scheme 1 *Reagents and conditions:* i, $CHCl_3$, py, 40–60 °C

mechanism of this arylation has been investigated by Professor Sir Derek Barton and co-workers[2,4] and by ourselves,[3] and this work points to a ligand coupling pathway involving an intermediate such as that shown in structure **4**. An intermediate

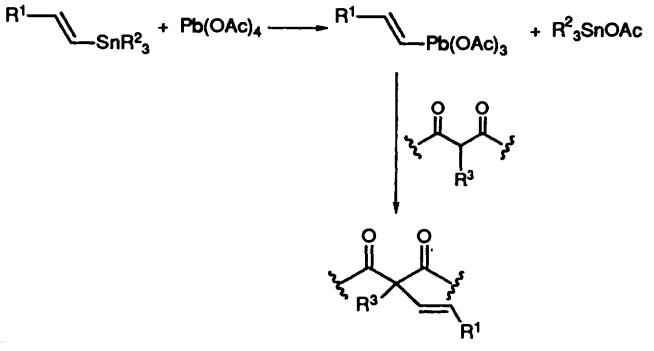


4

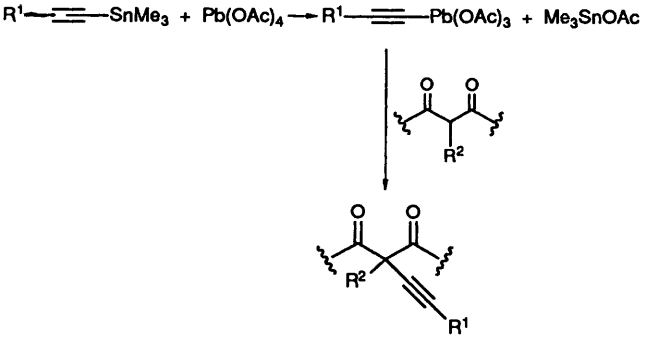
of this type has been established by Barton[5,6] for the closely related phenylation of phenols by certain phenylbismuth(v) reagents; however, attempts to isolate an analogous lead(iv) intermediate have not been successful.[4]

More recently we have developed routes to vinyllead(iv)[7,8] and alk-1-ynyllead(iv)[9] triacetates and shown that they behave as vinyl and alk-1-ynyl cation equivalents respectively, reacting with β-dicarbonyl compounds to give the α-vinyl and α-alkynyl derivatives as outlined in Schemes 2 and 3.

We were interested in extending the vinylation and alkynylation reactions to 2,6-dimethylphenols, since the expected products, **5** and **6** respectively, were potentially useful synthetic intermediates. For example, Barton–Quinkert photochemical ring opening of cyclohexa-2,4-dienones such as **5** and **6**[10] was



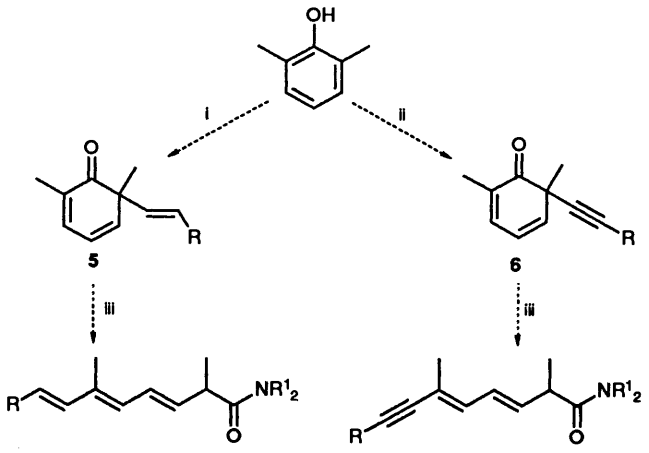
Scheme 2



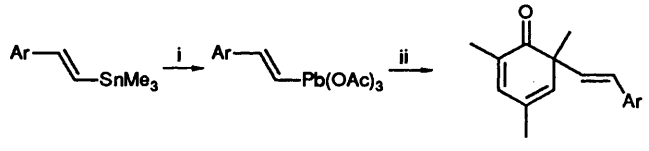
Scheme 3

expected to provide a simple entry into advanced retinoid precursors, as indicated in Scheme 4.

The first reaction examined was the vinylation of 2,4,6-trimethylphenol **1** by *E*-styryllead triacetate **8**, since our previous arylation work indicated that best yields should be obtained with this substrate. The vinyllead reagent **9** was generated from a rapid reaction of the corresponding trimethyl(vinyl)stannane **7** with lead tetraacetate at room temperature, conditions developed in the preceding paper[8] (see Scheme 5), and the mixture was then treated at 0 °C with 2,4,6-trimethylphenol to give the expected cyclohexa-2,4-dienone **11** in excellent yield (entry 1, Table 1). A similar yield of the 2,4-dienone **12** was obtained when 2,4,6-trimethylphenol was treated with (*E*)-*p*-methoxystyryllead triacetate **10** generated



Scheme 4 *Reagents and conditions:* i, $RCH{=}CHPb(OAC)_3$; ii, $RC{\equiv}CPb(OAC)_3$; iii, *hv*, R'_2NH



7 Ar = Ph
8 Ar = *p*-$MeOC_6H_4$
9 Ar = Ph
10 Ar = *p*-$MeOC_6H_4$
11 Ar = Ph
12 Ar = *p*-$MeOC_6H_4$

Scheme 5 *Reagents and conditions:* i, $Pb(OAc)_4$, $CHCl_3$, room temp.; ii, **1**, $CHCl_3$, py, 0 °C

Table 1 Reaction of 2,6-dimethylphenols with vinyllead and alkynyllead triacetates generated *in situ* from the corresponding trimethyl(organo)stannane

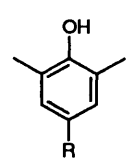
Entry	Phenol	Stannane	Product(s) (% Yield)
1	**1**	**7**	**11** (82)
2	**1**	**8**	**12** (83)
3	**13**	**7**	**16** (40), **21**[a]
4	**13**	**8**	**22** (41), **21**[a]
5	**14**	**7**	**18** (30)
6	**15**	**7**	**19** (67)
7	**15**	**8**	**20** (74)
8	**1**	**23**	**26** (78)
9	**13**	**23**	**27** (12), **21** (14)

[a] Yield not determined.

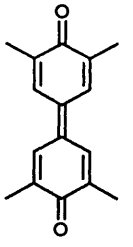
by treating vinylstannane **8** with lead tetraacetate (entry 2, Table 1).

The substrate of particular interest for terpenoid synthesis, 2,6-dimethylphenol **13**, did produce 2,6-dimethyl-6-[(*E*)-styryl]cyclohexa-2,4-dienone **16** when treated with the vinyllead triacetate **9**, generated as in Scheme 5 (entry 3, Table 1); however, the yield was considerably lower than in the above two examples. A second product of this reaction was the diphenoquinone **21**, indicating that vinyllead triacetates were more powerful oxidants than aryllead triacetates, and that the 4-position would require protection in a viable synthetic scheme. Reaction of 2,6-dimethylphenol with the more stable *p*-methoxystyryllead triacetate **10** confirmed this conclusion, producing a mixture of dimers of the analogous cyclohexa-2,4-dienone **17** in a similar modest yield, and accompanied also by the quinone **21** (entry 4, Table 1). The dimers of dienone **17** would appear to be of the form shown in structure **22**, differing only in their configuration at C-3 and C-5 (see below).

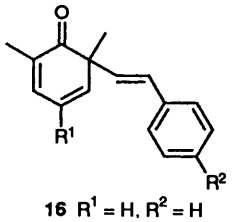
It was evident from the above reactions of 2,6-dimethylphenol that a viable synthesis of retinoid type compounds would require a protecting group in the 4-position. Two such



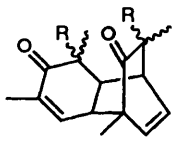
13 R = H
14 R = OMe
15 R = Br



21



16 R^1 = H, R^2 = H
17 R^1 = H, R^2 = OMe
18 R^1 = OMe, R^2 = H
19 R^1 = Br, R^2 = H
20 R^1 = Br, R^2 = OMe

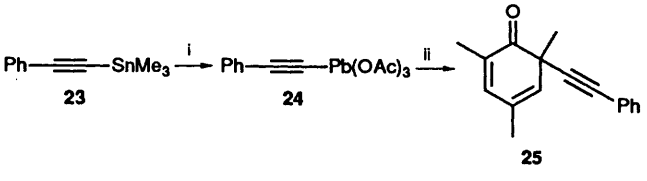


22 R = (*E*)-*p*-methoxystyryl

compounds which were readily available, 4-methoxy-2,6-dimethylphenol **14** and 4-bromo-2,6-dimethylphenol **15**, were examined in the vinylation reaction. The former compound, the 4-methoxyphenol **14**, when treated with the styryllead reagent **9**, generated as in Scheme 5, again gave only a modest yield of the expected cyclohexa-2,4-dienone **18** (entry 5, Table 1); this was accompanied by a number of unidentified products thought to be produced by oxidation.

The second compound, the 4-bromophenol **15**, was less susceptible to oxidation, and afforded the 4-bromo-6-(*E*)-styryldienone **19** in a synthetically useful yield (entry 6, Table 1) when treated with (*E*)-styryllead triacetate in the same way. The potential of the substrate **15** for use in our proposed route to retinoids was further illustrated in its reaction with (*E*)-*p*-methoxystyryllead triacetate **10** to produce the cyclohexa-2,4-dienone **20** in good yield (entry 7, Table 1).

A similar approach to that used above was employed for an examination of the alkynylation of 2,6-dimethylphenols. In an initial experiment 2,4,6-trimethylphenol **1** was treated with the unstable phenylethynyllead triacetate **24**, generated *in situ* by reaction of the trimethylstannylacetylene **23** with lead tetraacetate (Scheme 6). The expected 6-phenylethynylcyclohexa-



23 **24** **25**

Scheme 6 *Reagents and conditions:* i, $Pb(OAc)_4$, cat-$Hg(OAc)_2$, bipy, 0 °C; ii, **1**, 0 °C

2,4-dienone **25** was produced in good yield; however, this material could not be characterised fully since it underwent a [2 + 4]cycloaddition, to give the dimer **26**, which was isolated in 78% yield (entry 8, Table 1). Evidence for the structure assigned to the dimer **26** is presented below.

The phenol of most interest in this work, 2,6-dimethylphenol **13**, failed to give any of the expected cyclohexa-2,4-dienone **28** (or dimer) when treated with phenylethynyllead triacetate **24** generated under the same conditions as those used in Scheme 6. The major products were compounds **29** and **21** resulting from Wessely acetoxylation[11] and phenol oxidative coupling respectively. This indicated that lead tetraacetate was being

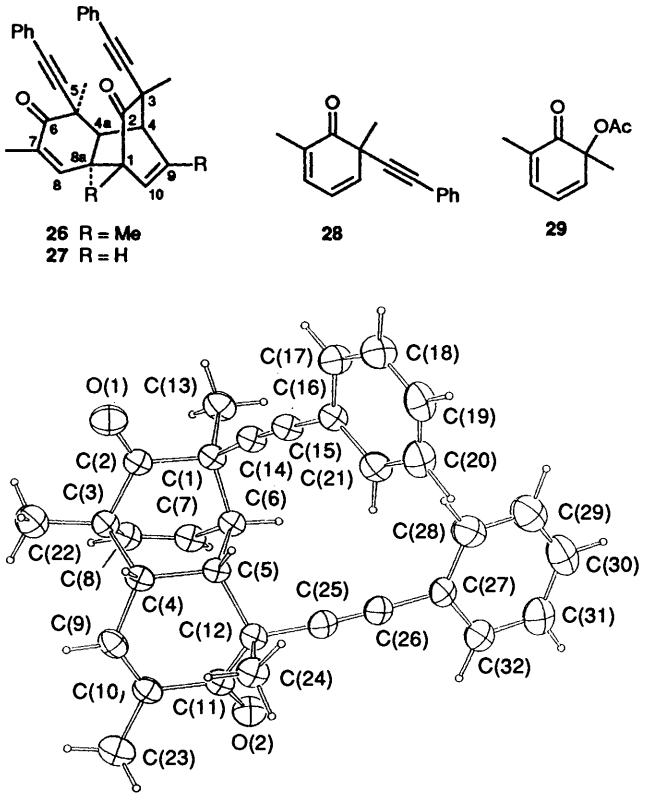


Fig. 1 Compound **27** (with atomic numbering used in crystallographic data)

regenerated in the solution at a faster rate than the alkynylation of the phenol. The regeneration of lead tetraacetate *via* a series of equilibria, resulting eventually in formation of the tetra-alkynyllead compound had been encountered previously,[3,9] and it had been found that this could be retarded by the addition of mercury(II) acetate (0.1 equiv.) When the reaction between the alkynyllead compound **24** and phenol **13** was conducted under these conditions, the dimer **27** of the required product **28** was produced; however, the yield was very low and the major product was the diphenoquinone **21** (entry 9, Table 1). The absence of the acetoxylation product **29** suggested that lead tetraacetate was not present in the reaction mixture, and it would appear, therefore, that phenylethynyllead triacetate is a sufficiently strong oxidant to cause the oxidative coupling of the phenol **13**. Since this approach to potential retinoid precursors was considerably less encouraging than the earlier vinylation results, it was not pursued further.

Structures of the Dimers **22**, **26** *and* **27**.—The dimer formed from reaction of the alkynyllead compound **24** and 2,6-dimethylphenol **13** was obtained as a single diastereoisomer, and it was shown by single crystal X-ray analysis (see Experimental section) to have structure **27**,* for which an ORTEP diagram is given in Fig. 1. A significant feature of compound **27** is the configurations of the stereogenic centres C-3 and C-5, with both phenylethynyl groups orientated towards the centre of the molecule. This is presumably a result of the lower steric demand of the acetylenic sp carbon compared with that of a methyl group in the Diels–Alder reaction.

The dimerisation of dienone **25** also produced a single diastereoisomer, and in analogy with the above compound it has been assigned structure **26**, in which the phenylethynyl groups have the same configurations. Other spectroscopic data (see Experimental section) support the conclusion that the two dimers have the same basic structures.

Unlike the above cases, the Diels–Alder dimerisation of the dienone **17** produced a mixture of diastereoisomers from which a single compound could be isolated. Spectroscopic data for this compound are in accord with structure **22**, in which the configurations at C-3 and C-5 are unknown. Interestingly, the mixture from which dimer **22** was isolated appeared to be composed of four diastereoisomers, differing in their configurations at C-3 and C-5. It would, therefore, appear that, unlike the phenylethynyl group, the steric demands of the styryl and methyl groups were similar in the dimerisation.

* The numbering shown in structures **26** and **27** has also been used for compound **22** in designating NMR signals in the Experimental section.

Table 2 Positional coordinates ($\times 10^4$) for compound **27**

Atom	*x*	*y*	*z*
O(1)	3 329(2)	7 636(2)	10 221(2)
O(2)	1 379(2)	8 691(2)	5 037(2)
C(1)	2 328(3)	6 721(2)	9 032(2)
C(2)	3 123(3)	7 577(2)	9 292(2)
C(3)	3 615(3)	8 336(2)	8 282(2)
C(4)	2 092(3)	9 192(2)	8 138(2)
C(5)	1 094(3)	8 416(2)	8 054(2)
C(6)	2 065(3)	7 069(2)	7 845(2)
C(7)	3 581(3)	6 892(2)	6 920(2)
C(8)	4 376(3)	7 509(3)	7 165(2)
C(9)	2 499(3)	9 910(2)	7 100(3)
C(10)	2 205(3)	9 838(2)	6 103(2)
C(11)	1 314(3)	9 062(2)	5 994(2)
C(12)	238(3)	8 839(2)	7 159(2)
C(13)	3 376(4)	5 415(3)	8 942(3)
C(14)	879(3)	6 868(2)	9 975(2)
C(15)	−339(3)	6 975(2)	10 673(2)
C(16)	−1 862(3)	7 151(2)	11 475(2)
C(17)	−2 143(4)	6 873(3)	12 636(3)
C(18)	−3 609(4)	7 077(3)	13 381(3)
C(19)	−4 802(4)	7 565(3)	12 983(4)
C(20)	−4 540(4)	7 824(3)	11 826(4)
C(21)	−3 076(4)	7 630(3)	11 074(3)
C(22)	4 597(4)	9 009(3)	8 531(3)
C(23)	2 758(5)	10 506(3)	5 045(3)
C(24)	−1 047(3)	10 041(3)	7 667(3)
C(25)	−441(3)	7 930(3)	6 979(2)
C(26)	−969(3)	7 166(3)	6 885(2)
C(27)	−1 503(3)	6 185(2)	6 736(2)
C(28)	−1 769(4)	5 416(3)	7 621(3)
C(29)	−2 188(4)	4 438(4)	7 447(4)
C(30)	−2 326(4)	4 206(3)	6 380(4)
C(31)	−2 098(4)	4 968(3)	5 497(4)
C(32)	−1 691(3)	5 958(3)	5 672(3)

Experimental

For general experimental procedures see our earlier paper.[12] Syntheses of the trimethyl(vinyl)stannanes[8] and trimethyl-(phenylethynyl)stannane[9] were reported previously.

Reaction of 2,4,6-*Trimethylphenol* **1** *with* (E)-*Styryllead Triacetate* **9**.—Trimethyl[(*E*)-styryl]stannane **7** (2.47 g, 9.26 mmol) in chloroform (5 cm^3) was added to a solution of lead tetraacetate (4.10 g, 9.26 mmol) in chloroform (30 cm^3), and the mixture was stirred at room temperature for 1 min. The mixture was cooled to 0 °C, and a solution of 2,4,6-trimethylphenol (1.15 g, 8.42 mmol) in chloroform (5 cm^3) and pyridine (1.46 g, 18.5 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1 h and at room temperature for 6 h, and then poured into ether (100 cm^3) and filtered. The filtrate was washed with dilute hydrochloric acid (1.5 mol dm^{-3}; 2 × 100 cm^3), water (2 × 100

Table 3 Bond lengths (Å) and angles (°) for compound **27**

C(2)–O(1)	1.204(4)	C(11)–O(2)	1.213(4)
C(2)–C(1)	1.540(4)	C(6)–C(1)	1.554(4)
C(13)–C(1)	1.549(3)	C(14)–C(1)	1.465(3)
C(3)–C(2)	1.524(4)	C(4)–C(3)	1.594(4)
C(8)–C(3)	1.504(4)	C(22)–C(3)	1.519(6)
C(5)–C(4)	1.555(4)	C(9)–C(4)	1.499(4)
C(6)–C(5)	1.555(3)	C(12)–C(5)	1.559(4)
C(7)–C(6)	1.496(3)	C(8)–C(7)	1.314(5)
C(10)–C(9)	1.331(4)	C(11)–C(10)	1.476(4)
C(23)–C(10)	1.510(4)	C(12)–C(11)	1.524(3)
C(24)–C(12)	1.555(3)	C(25)–C(12)	1.471(4)
C(15)–C(14)	1.187(4)	C(16)–C(15)	1.445(4)
C(17)–C(16)	1.379(4)	C(21)–C(16)	1.394(5)
C(18)–C(17)	1.376(4)	C(19)–C(18)	1.373(6)
C(20)–C(19)	1.371(6)	C(21)–C(20)	1.378(4)
C(26)–C(25)	1.188(5)	C(27)–C(26)	1.438(5)
C(28)–C(27)	1.388(5)	C(32)–C(27)	1.392(5)
C(29)–C(28)	1.372(6)	C(30)–C(29)	1.374(8)
C(31)–C(30)	1.376(6)	C(32)–C(31)	1.379(6)
C(6)–C(1)–C(2)	105.7(2)	C(13)–C(1)–C(2)	108.2(2)
C(13)–C(1)–C(6)	112.4(2)	C(14)–C(1)–C(2)	111.0(2)
C(14)–C(1)–C(6)	110.2(2)	C(14)–C(1)–C(13)	109.3(2)
C(1)–C(2)–O(1)	122.3(2)	C(3)–C(2)–O(1)	123.4(3)
C(3)–C(2)–C(1)	114.3(2)	C(4)–C(3)–C(2)	105.7(2)
C(8)–C(3)–C(2)	107.1(2)	C(8)–C(3)–C(4)	104.6(2)
C(22)–C(3)–C(2)	111.0(3)	C(22)–C(3)–C(4)	113.7(2)
C(22)–C(3)–C(8)	114.1(2)	C(5)–C(4)–C(3)	108.9(2)
C(9)–C(4)–C(3)	108.5(2)	C(9)–C(4)–C(5)	114.8(3)
C(6)–C(5)–C(4)	109.0(2)	C(12)–C(5)–C(4)	113.6(2)
C(12)–C(5)–C(6)	114.5(2)	C(5)–C(6)–C(1)	106.1(2)
C(7)–C(6)–C(1)	107.5(2)	C(7)–C(6)–C(5)	110.9(2)
C(8)–C(7)–C(6)	114.3(2)	C(7)–C(8)–C(3)	116.4(2)
C(10)–C(9)–C(4)	125.6(3)	C(11)–C(10)–C(9)	119.7(2)
C(23)–C(10)–C(9)	123.3(3)	C(23)–C(10)–C(11)	117.0(3)
C(10)–C(11)–O(2)	121.8(2)	C(12)–C(11)–O(2)	122.9(3)
C(12)–C(11)–C(10)	115.2(2)	C(11)–C(12)–C(5)	110.2(2)
C(24)–C(12)–C(5)	109.6(2)	C(24)–C(12)–C(11)	107.7(2)
C(25)–C(12)–C(5)	109.4(2)	C(25)–C(12)–C(11)	111.3(2)
C(25)–C(12)–C(24)	108.6(2)	C(15)–C(14)–C(1)	174.9(4)
C(16)–C(15)–C(14)	176.6(3)	C(17)–C(16)–C(15)	121.6(3)
C(21)–C(16)–C(15)	119.3(3)	C(21)–C(16)–C(17)	119.1(3)
C(18)–C(17)–C(16)	119.9(3)	C(19)–C(18)–C(17)	120.6(3)
C(20)–C(19)–C(18)	120.2(3)	C(21)–C(20)–C(19)	119.7(4)
C(20)–C(21)–C(16)	120.4(3)	C(26)–C(25)–C(12)	176.3(3)
C(27)–C(26)–C(25)	176.0(2)	C(28)–C(27)–C(26)	121.0(3)
C(32)–C(27)–C(26)	120.2(3)	C(32)–C(27)–C(28)	118.8(3)
C(29)–C(28)–C(27)	120.8(4)	C(30)–C(29)–C(28)	119.7(4)
C(31)–C(30)–C(29)	120.7(4)	C(32)–C(31)–C(30)	119.8(4)
C(31)–C(32)–C(27)	120.3(3)		

cm^3) and brine (50 cm^3), and then dried (Na_2SO_4) and evaporated. The residue was fractionated by flash chromatography (ethyl acetate–light petroleum, 1:39) to yield 2,4,6-*trimethyl*-6-[(E)-*styryl*]*cyclohexa*-2,4-*dienone* **11** (1.65 g, 82%) as an oil (Found: C, 85.9; H, 7.6. $C_{17}H_{18}O$ requires C, 85.7; H, 7.6%); $\delta_H(CDCl_3)$ 1.39 (3 H, s, 6-Me), 1.87 (3 H, d, *J* 0.9, 4-Me), 1.96 (3 H, d, *J* 1.4, 2-Me), 5.97 (1 H, br s, $W_{h/2}$ 5.5, 5-H), 6.19 (1 H, d, *J* 16.1, C*H*=CH), 6.36 (1 H, d, *J* 16.1, CH=C*H*), 6.68 (1 H, br q, *J* 1.4, 3-H) and 7.12–7.35 (5 H, m, ArH); $\delta_C(CDCl_3)$ 15.4 (6-Me), 21.2 (4-Me), 24.7 (2-Me), 51.8 (C-6), 126.2 (2 C, C-3′ and C-5′), 127.3 (C-4′), 127.7 (C-4), 128.3 (2 C, C-2′ and C-6′), 128.7 (H*C*=CH), 131.9 (C-2), 132.3 (HC=*C*H), 136.7 (C-1′), 137.0 (C-5), 142.0 (C-3) and 202.8 (C-1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 650 and 1 590; λ_{max}(EtOH)/nm 254 (ε 17 300); *m*/*z* 238 (M, 80%), 223 (M − Me, 22), 210 (M − CO, 25) and 195 (223 − CO, 100).

Reaction of 2,4,6-*Trimethylphenol* **1** *with* (E)-p-*Methoxystyryllead Triacetate* **10**.—Trimethyl[(*E*)-*p*-methoxystyryl]stannane **8** (2.31 g, 7.79 mmol) in chloroform (5 cm^3) was added to a solution of lead tetraacetate (3.45 g, 7.79 mmol) in chloroform (25 cm^3), and the mixture was stirred at room temperature for 2 min. The mixture was cooled to 0 °C and a solution of 2,4,6-trimethylphenol (0.96 g, 7.08 mmol) in chloroform (5 cm^3) and pyridine (1.23 g, 15.6 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 2 h and then allowed to warm to room temperature overnight when it was worked up as above. The residue was fractionated by flash chromatography (ethyl acetate–light petroleum, 1:24) to afford 2,4,6-*trimethyl*-6-[(E)-p-*methoxystyryl*]*cyclohexa*-2,4-*dienone* **12** (1.39 g, 83%), m.p. 61.5–63.5 °C (from ethyl acetate–light petroleum) (Found: C, 80.4; H, 7.6. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%); $\delta_H(CDCl_3)$ 1.38 (3 H, s, 6-Me), 1.88 (3 H, d, *J* 0.9 4-Me), 1.97 (3 H, d, *J* 1.4, 2-Me), 5.98 (1 H, m, 5-H), 6.05 (1 H, d, *J* 16.2, C*H*=CH), 6.29 (1 H, d, *J* 16.2, CH=C*H*), 6.69 (1 H, dq, *J* 2.2, 1.4, 3-H) 6.81 and 7.26 (4 H, AA′BB′, 3′-H and 5′-H, 2′-H and 6′-H respectively); $\delta_C(CDCl_3)$ 15.4 (6-Me), 21.2 (4-Me), 24.7 (2-Me), 51.8 (C-6), 55.1 (OMe), 113.7 (2 C, C-3′ and C-5′), 127.4 (2 C, C-2′ and C-6′), 127.6 (C-4), 128.1 (H*C*=CH), 129.6 (C-1′), 130.2 (HC=*C*H), 132.0 (C-2), 137.3 (C-5), 142.0 (C-3), 159.0 (C-4′) and 203.1 (C-1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 650, 1 637 and 1 608; λ_{max}(EtOH)/nm 265 (ε 23 400); *m*/*z* 268 (M, 100%), 253 (M − Me, 31), 238 (M − OCH_2, 10) and 225 (253 − CO, 55).

Reaction of 2,6-*Dimethylphenol* **13** *with* (E)-*Styryllead Triacetate* **9**.—A mixture of the stannane **7** (2.15 g, 8.06 mmol) in chloroform (5 cm^3) and lead tetraacetate (3.57 g, 8.06 mmol) in chloroform (25 cm^3) was treated with the phenol **13** (0.90 g, 7.33 mmol) in chloroform (5 cm^3) and pyridine (1.27 g, 16 mmol) as in the synthesis of the dienone **11** above. The crude product was fractionated by flash chromatography (ethyl acetate–light petroleum, 1:49) to yield 2,6-*dimethyl*-6-[(E)-*styryl*]*cyclohexa*-2,4-*dienone* **16** (0.66 g, 40%) as an oil (Found: M^+, 224.1207. $C_{16}H_{16}O$ requires *M*, 224.1201); $\delta_H(CDCl_3)$ 1.48 (3 H, s, 6-Me), 1.91 (3 H, br s, 2-Me), 6.21 (1 H, d, *J* 16.5, C*H*=CH), 6.23 (1 H, dd, *J* 9.5, 6.6, 4-H), 6.33 (1 H, dd, *J* 9.5, 1.5, 5-H), 6.38 (1 H, d, *J* 16.5, CH=C*H*), 6.85 (1 H, m, 3-H) and 7.16–7.39 (5 H, m, ArH); $\delta_C(CDCl_3)$ 15.7 (6-Me), 24.6 (2-Me), 52.8 (C-6), 120.6 (C-4), 126.4 (2 C, C-3′ and C-5′), 127.6 (C-4′), 128.5 (2 C, C-2′ and C-6′), 129.2 (*C*=C), 131.9 (C=*C*), 132.8 (C-2), 136.8 (C-1′), 137.8 (C-5), 143.0 (C-3) and 203.0 (C-1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 657 and 1 599; λ_{max}(EtOH)/nm 252 (ε 11 320); *m*/*z* 224 (M, 42%), 209 (M − Me, 25), 181 (209 − CO, 35) and 120 (100).

Dilution of the reaction mixture with ether gave a yellow insoluble material which was crystallised from glacial acetic acid to yield the diphenoquinone **21**, m.p. 205 °C (decomp.) (lit.,[13] 207–217 °C).

Reaction of 2,6-*Dimethylphenol* **13** *with* (E)-p-*Methoxystyryllead Triacetate* **10**.—2,6-Dimethylphenol (0.98 g, 8.06 mmol) was treated with a mixture of the stannane **8** (2.63 g, 8.86 mmol) and lead tetraacetate (3.93 g, 8.86 mmol) under the conditions employed above for the preparation of the dienone **12**, and the reaction was worked up in the same way. The crude product crystallised from ethyl acetate–light petroleum to give a mixture of dimers 1,3,5,7-tetramethyl-3,5-bis[(*E*)-*p*-methoxystyryl]1,3,4,4a,5,8a-hexahydro-1,4-ethenonaphthalene-2,6-dione **22** (0.84 g, 41%) which, by fractional crystallisation, gave a *single diastereoisomer*, m.p. 182–185 °C (Found: C, 80.1; H, 7.3. $C_{34}H_{36}O_4$ requires C, 80.3; H, 7.1%); $\delta_H(CDCl_3)$ 1.37, 1.38, 1.41 (9 H, 3 × s, 1-Me, 3-Me, 5-Me), 1.78 (3 H, br s, $W_{h/2}$ 3.2, 7-Me), 2.89 (2 H, m, 4a-H and 8a-H), 2.98 (1 H, br d, *J* 6.4, 4-H), 3.78 (3 H, s, OMe), 3.79 (3 H, s, OMe), 5.52 (1 H, dd, *J* 8.0, 0.9, 9-H), 5.85 (1 H, d, *J* 16.1, C*H*=CH), 6.02 (1 H, d, *J* 16.2, C*H*=CH), 6.25 (1 H, d, *J* 16.1, CH=C*H*), 6.25 (1 H, m, 8-H), 6.27 (1 H, d, *J* 16.2, CH=C*H*) 6.43 (1 H, dd, *J* 6.4, 8.0, 10-H), 6.81 and 7.22 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H, 6′-H respectively) and 6.82 and 7.22 (4 H, AA′BB′, 3′-H, 5′-H and 2′-, 6′-H

respectively); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 717, 1 679 and 1 608; *m/z* 508 (M, 25%), 255 (38) and 254 (M/2, 100).

Reaction of 4-*Methoxy*-2,6-*dimethylphenol* **14** *with* (E)-*Styryllead Triacetate* **9**.—The phenol **14** (0.15 g, 1.0 mmol) was treated with a mixture of stannane **7** (0.32 g, 1.2 mmol) and lead tetraacetate (0.49 g, 1.2 mmol) under the conditions employed above for the synthesis of the dienone **11**, except that the whole reaction was conducted at room temperature. The crude product was fractionated by radial chromatography (ethyl acetate–light petroleum, 1:9) to give 4-*methoxy*-2,6-*dimethyl*-6-[(E)-*styryl*]*cyclohexa*-2,4-*dienone* **18** (0.076 g, 30%) as an oil (Found: M^+, 254.1302. $C_{17}H_{18}O_2$ requires *M*, 254.1307); $\delta_H(CDCl_3)$ 1.43 (3 H, s, 6-Me), 1.86 (3 H, d, ^4J 1.4, 2-Me), 3.67 (3 H, s, OMe), 5.14 (1 H, d, ^4J 3.3, 5-H), 6.19 (1 H, d, ^3J 16.0, vinyl H), 6.45 (1 H, d, ^3J 16.0, vinyl H), 6.68 (1 H, dq, *J* 3.3, 1.4, 3-H) and 7.14–7.35 (5 H, m, Ar-H); $\delta_C(CDCl_3)$ 15.6 (6-Me), 26.2 (2-Me), 51.0 (C-6), 54.9 (OMe), 133.7 (C-2 or C-1′), 136.7 (C-2 or C-1′), 107.4, 126.3, 127.4, 128.4, 128.5, 133.3, 137.7 (7 C, vinylic and aromatic CH), 149.5 (C-4) and 202.3 (C-1); ν_{max}(film)/cm^{-1} 1 666, 1 652, 1 622 and 1 606; λ_{max}(EtOH)/nm 252 (ε 16 100); *m/z* 254 (M, 100%), 239 (M − Me, 30), 226 (M − CO, 60) and 211 (M − C_2H_3O, 82).

Reaction of 4-*Bromo*-2,6-*dimethylphenol* **15** *with* (E)-*Styryllead Triacetate* **9**.—The bromophenol **15** (1.38 g, 6.85 mmol) was treated with a mixture of stannane **7** (2.01 g, 7.54 mmol) and lead tetraacetate (3.34 g, 7.54 mmol) under the conditions used above for the preparation of the dienone **11**. Flash chromatography of the residue in ethyl acetate–light petroleum (1:49) afforded 4-*bromo*-2,6-*dimethyl*-6-[(E)-*styryl*]*cyclohexa*-2,4-*dienone* **19** (1.39 g, 67%) as an oil (Found: M^+, 302.0312. $C_{16}H_{15}BrO$ requires *M*, 302.0312); $\delta_H(CDCl_3)$ 1.45 (3 H, s, 6-Me), 1.90 (3 H, br s, 2-Me), 6.15 (1 H, d, *J* 16.2, vinyl H), 6.39 (1 H, d, *J* 16.2, vinyl H) 6.54, (1 H, d, ^4J 2.5, 5-H), 6.84 (1 H, dq, *J* 2.5, 1.5, 3-H) and 7.16–7.37 (5 H, m, Ar-H); $\delta_C(CDCl_3)$ 15.4 (6-Me), 24.5 (2-Me), 59.5 (C-6), 113.9 (C-4), 126.2 (2 C, C-3′ and C-5′), 127.5 (C-4′), 128.4 (2 C, C-2′ and C-6′), 132.2 (vinyl C), 133.7 (C-2), 136.8 (C-1′), 140.2 (C-5), 141.9 (C-3) and 201.4 (C-1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 609 and 1 513; λ_{max}(EtOH)/nm 253 and 293 (ε 15 200 and 3 430); *m/z* 304 (M, 1.5%), 302 (M, 1.5%), 224 (18), 233 (M − Br, 100), 208 (223 − Me, 20), 195 (223 − CO, 12) and 180 (208 − CO, 23).

Reaction of 4-*Bromo*-2,6-*dimethylphenol* **15** *with* (E)-p-*Methoxystyryllead Triacetate* **10**.—The phenol **15** (1.33 g, 6.62 mmol) was treated with a mixture of the stannane **8** (2.16 g, 7.28 mmol) and lead tetraacetate (3.23 g, 7.28 mmol) as in the preparation of the dienone **12** above. The crude product was fractionated by flash chromatography (ethyl acetate–light petroleum, 1:24) to yield 4-*bromo*-6-[(E)-p-*methoxystyryl*]-2,6-*dimethylcyclohexa*-2,4-*dienone* **20** (1.63 g, 74%), m.p. 126.5–127.5 °C (light petroleum) (Found: M^+, 332.0415. $C_{17}H_{17}BrO_2$ requires *M*, 332.0412); $\delta_H(CDCl_3)$ 1.43 (3 H, s, 6-Me), 1.90 (3 H, q, *J* 0.7, 2-Me), 3.78 (3 H, s, OMe), 5.99 (1 H, d, *J* 16.2, vinyl H), 6.32 (1 H, d, *J* 16.2, vinyl H), 6.53 (1 H, d, *J* 2.5, 5-H), 6.84 (1 H, m, 3-H) and 6.81 and 7.27 (4 H, AA′BB′, 3′-H, 5′-H and 2′-H, 6′-H respectively); $\delta_C(CDCl_3)$ 15.3 (6-Me), 24.4 (2-Me), 55.2 (OMe), 6.03 (C-6), 113.4 (C-4), 113.9 (2 C, C-3′ and C-5′), 127.7 (2 C, C-2′ and C-6′), 128.3 (vinyl C), 129.1 (C-1′), 129.2 (vinyl C), 134.6 (C-2), 141.1 (C-5), 141.5 (C-3), 159.4 (C-4′) and 200.5 (C-1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 607 and 1 512; λ_{max}(EtOH)/nm 217 and 286 (ε 24 800 and 24 100); *m/z* 334 (M, 50%), 332 (M, 52), 253 (M − Br, 19), 239 (18), 238 (253 − Me, 100) and 210 (238 − CO, 17).

Reaction of 2,4,6-*Trimethylphenol* **1** *with Phenylethynyllead Triacetate* **24**.—The stannane **23** (2.06 g, 7.72 mmol) in chloroform (5 cm^3) was added to a solution of lead tetraacetate (3.42 g, 7.72 mmol), mercury(II) acetate (0.25 g, 0.77 mmol) and 2,2′-bipyridyl (1.46 g, 9.26 mmol) in chloroform (20 cm^3) at 0 °C, and the mixture was stirred at 0 °C for 1 min. A solution of 2,4,6-trimethylphenol (0.875 g, 6.44 mmol) in chloroform (5 cm^3) was added and the solution was stirred for 1 h at 0 °C, and then at room temperature for 6 h. The reaction was worked up as in preparation of the dienone **11**, and residue was fractionated by flash chromatography (ethyl acetate–light petroleum, 1:9) to yield the dimer 1,3,5,7,8a,9-*hexamethyl*-3,5-*bis*(*phenylethynyl*)-1,3,4,4a,5,8a-*hexahydro*-1,4-*ethenonaphthalene*-2,6-*dione* **26** (1.18 g, 78%), m.p. 166–167 °C (from ethyl acetate–light petroleum) (Found: C, 86.7; H, 7.1. $C_{34}H_{32}O_2$ requires C, 86.4; H, 6.8%); $\delta_H(CDCl_3)$ 1.23 (3 H, s, 1-Me), 1.42 (3 H, s, 8a-Me), 1.46 (3 H, s, 3-Me), 1.66 (3 H, s, 5-Me), 1.84 [3 H, d, (collapsed to s on irradiation at 6.04) ^4J 1.4, 7-Me], 1.89 [3 H, d (collapsed to s on irradiation at 5.09) ^4J 1.6, 9-Me], 2.98 [1 H, br d (sharpened on irradiation at 6.04 and collapsed to br s $W_{h/2}$ 1.8 on irradiation at 3.41) $J_{4a,4}$ 2.2, 4a-H], 3.41 [1 H, dd (collapsed to d on irradiation at 2.98) $J_{4,4a}$ 2.2, $J_{4,10}$ 2.3, 4-H], 5.09 [1 H, dq (collapsed to q on irradiation at 3.41), $J_{10,4}$ 2.3, $J_{10,9-Me}$ 1.6, 10-H], 6.04 [1 H, dq (collapsed to q on irradiation at 2.98) $J_{8,4a}$ 0.8, $J_{8,7-Me}$ 1.4, 8-H], 7.28–7.36 (6 H, m, ArH), 7.42 (2 H, m, 2 × *ortho*-H), 7.53 (2 H, m, 2 × *ortho*-H), irradiation at 1.89 gave a 1.7% NOE at 5.09 and a 2.1% NOE at 3.41, irradiation at 1.84 gave a 1.5% NOE at 6.04, irradiation at 1.66 gave a 3.0% NOE at 2.98 and a 1.9% NOE at 1.42, irradiation at 1.46 gave a 2.0% NOE at 3.41, irradiation at 1.42 gave a 3.0% NOE at 6.04, a 4.1% NOE at 2.98, a 1.3% NOE at 1.66, and a 2.6% NOE at 1.23, irradiation at 1.23 gave a 3.1% NOE at 6.04, a 3.0% NOE at 5.09 and a 1.2% NOE at 1.42; $\delta_C(CDCl_3)$ 13.4 (1-Me), 16.9 (7-Me), 22.1 (8a-Me), 25.4 (3-Me and 9-Me), 31.7 (5-Me), 43.0 (C-3), 44.9 (C-7), 48.4 (C-8a), 52.5 (C-4 or C-4a), 53.0 (C-4 or C-4a), 58.7 (C-1), 84.4 (acetylenic C), 89.3 (2 × acetylenic C), 90.7 (acetylenic C), 122.9 and 123.3 (2 × Ar C-1), 127.1 (C-10), 128.2 (2 × Ar C-3, C-4 and C-5), 131.6 (2 × Ar C-2 and C-6), 133.2 (C-7), 142.8 (C-8), 144.4 (C-9), 197.1 (C-6) and 209.9 (C-2); ν_{max}(Nujol)/cm^{-1} 1 724 and 1 686; λ_{max}(EtOH)/nm 242 and 253 (ε 42 100 and 37 300); *m/z* 472 (M, 1%), 237 (19), 236 (M/2, 100) and 221 (236 − Me, 34).

Reaction of 2,6-*Dimethylphenol with Phenylethynyllead Triacetate* **24**.—A mixture of the stannane **23** (1.00 g, 3.78 mmol), lead tetraacetate (1.67 g, 3.78 mmol), mercury(II) acetate (0.06 g, 0.19 mmol) and 2,2-bipyridyl (0.65 g, 4.15 mmol) was treated with 2,6-dimethylphenol (0.384 g, 3.15 mmol) under the same conditions used for the synthesis of the dimer **26**. The crude material was separated by flash chromatography (ethyl acetate–light petroleum, 1:9) into two fractions. The less polar fraction afforded *the dimer* **27** (79 mg, 12%), m.p. 152.5–154 °C (ethyl acetate–light petroleum) (Found: C, 86.1; H, 6.2. $C_{32}H_{28}O_2$ requires C, 86.4; H, 6.3%); $\delta_H(CDCl_3)$ 1.23 (3 H, s, 3-Me or 5-Me), 1.32 (3 H, s, 3-Me or 5-Me), 1.62 (3 H, s, 1-Me), 1.87 (3 H, br s, $W_{h/2}$ 4.0, 7-Me), 2.96 (1 H, m, 8a-H), 3.42 (1 H, dd, $J_{4a,8a}$ 8.5, $J_{4a,4}$ 0.9, 4a-H), 3.51 (1 H, br d, $J_{4,11}$ 7.5, 4-H), 5.60 (1 H, d, $J_{9,10}$ 8.0, 10-H), 6.33 (1 H, br d, $J_{8,8a}$ 4.2, 8-H), 6.42 (1 H, dd, $J_{10,9}$ 8.0, $J_{9,1}$ 7.5, 9-H) and 7.25–7.55 (10 H, m, ArH); $\delta_C(CDCl_3)$ 16.3 (3-Me or 5-Me), 17.2 (3-Me or 5-Me), 26.5 (1-Me), 30.9 (C-7), 40.4 (C-8a), 45.4 (C-3 or C-5), 46.9 (C-4 or C-4a), 47.8 (C-3 or C-5), 48.0 (C-4 or C-4a), 54.4 (C-1), 88.1 (acetylenic C), 89.0 (2 × acetylenic C), 91.3 (acetylenic C), 122.5 (Ar C-1), 122.6 (Ar C-1), 128.1 (2 × Ar C-4), 128.3 (2 × Ar C-3 and C-5), 131.8 (2 × Ar C-2 and C-6), 132.9 (C-9), 134.9 (C-10), 135.9 (C-7), 137.3 (C-8), 197.7 (C-6) and 209.5 (C-2); $\nu_{max}(CHCl_3)/cm^{-1}$ 1 727, 1 688 and 1 599; λ_{max}(EtOH)/nm 240 and 251 (ε 44 200 and 39 400); *m/z* 444 (M, 0.4%), 222 (M/2, 56), 221 (32), 207 (222-Me, 50), 193 (222 − CHO, 50), 179 (207 −

CO, 76) and 178 (100); the crystal structure analysis is given below.

The more polar fraction yielded the diphenoquinone **21**, (108 mg, 28%) m.p. 210–212 °C (decomp.) (identical with material obtained above).

Crystal Structure Analysis of the Dimer 1,3,5,7-*Tetramethyl*-3,5-*bis*(*phenylethynyl*)-1,3,4,4a,5,8a-*hexahydro*-1,4-*ethenonaphthalene*-2,6-*dione* **27**.—*Crystal data.* $C_{32}H_{28}O_2$, M = 444.58, triclinic, space group $P\bar{1}$, a = 9.850(4), b = 11.725(3), c = 12.008(2) Å, α = 88.66(2), β = 70.76(2), γ = 72.41(3), U = 1 243.7 Å^3, D_c (Z = 2) = 1.187 g cm^{-3}. F(000) = 472, μ = 0.39 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å, Specimen: colourless needles, 0.10 × 0.34 × 0.10 mm, N = 3433, N_o = 1901, ($I > 2.5\sigma'I'$) *hkl* −10 to 10, −12 to 12, 0 to 12, R = 0.034, R' = 0.037, $w = 1.48/[\sigma^2(F_o) + 0.000\,22F_o^2]$. Residual extrema, 0.1 and −0.1 e Å^{-3}. Data collection and processing: Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf–Nonius CAD4 diffractometer, within the limit $1.0 \leqslant \theta \leqslant 25°$, with Mo-K$\alpha$ radiation, graphite monochromator and operating in the $\omega - \theta$ mode. Lorentz and polarization effects corrected for using the Enraf–Nonius SDP system.[14] Structure analysis and refinement: the structure was solved by direct methods using SHELXS–86.[15] Refinement was by blocked-matrix least-squares using SHELX-76.[16] Scattering factors used were those supplied in SHELX-76. An ORTEP[17] plot of the molecule is shown in Fig. 1. Additional material, which is available from the Cambridge Crystallographic Data Centre, comprises structure factors, thermal parameters, hydrogen atom coordinates, torsion angles, bond angles and bond lengths.*

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