Pergamon

Tetrahedron 57 (2001) 7965–7978

TETRAHEDRON

Palladium catalysed reaction of allene with phenols. Phenoxymethyl-1,3-dienes and their further reactions

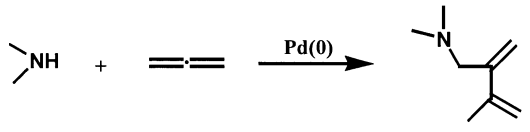
Ronald Grigg,[a,*] Ngampong Kongkathip,[b] Boonsong Kongkathip,[b] Suwaporn Luangkamin[a] and H. Ali Dondas[c]

[a]*Molecular Innovation, Diversity and Automated Synthesis (MIDAS) Centre, School of Chemistry, Leeds University, Leeds LS2 9JT, UK*
[b]*Chemistry Department, Faculty of Science, Kasetsart University, Bangkok, Thailand*
[c]*Chemistry Department, Science and Arts Faculty, Mersin University, Mersin, Turkey*

Received 11 May 2001; revised 25 June 2001; accepted 19 July 2001

Abstract—A 3-step 100% atom economic sequence is reported whereby a variety of phenols react with 2 mol equiv. of allene to give phenoxymethyl-1,3-dienyl ethers. Subsequent thermal Claisen rearrangement to C-1,3-dienes and acid catalysed ring closure furnishes 3:1–6.5:1 mixtures of *exo*-methylene chromans and dihydrobenzofurans with the former predominating.

Palladium catalysed reactions of allenes are proving a remarkably fertile source of new reactions.[1,2] In the majority of cases disclosed to date the reactions involve an aryl/vinyl halide or allylic ester as co-substrate and a Pd(0) catalyst. However there are numerous examples of Pd(II) catalysed nucleophilic attack on allenes.[3] A further less well explored class of reactions involves Pd(0) and substrates with X–H bonds (where X=heteroatom). Thus allene reacts with appropriate NH and OH compounds and carbon monoxide in the presence of a Pd(0) catalyst to give methacrylamides and methacrylate esters.[4] The attraction of this type of process is that it is 100% atom economic. An early pioneering paper by Coulson[5] reported the reaction of allene with primary and secondary amines to give aminomethyl-1,3-dienes (Scheme 1).[6] This earlier report and our continuing interest in the palladium catalysed reactions of allenes encouraged us to explore the Pd(0) catalysed reactions of phenols with allene. Such processes are 100% atom economic and can conceptually be combined with other 100% atom economic processes. Two such processes, Claisen rearrangement of O-dienyl to C-dienyl phenols and subsequent acid catalysed cyclisation of the C-dienyl phenols to annulated dihydrofurans and chromans were deemed worthy of further study. Together they provide a three-step sequence to interesting heterocycles, which are present in many natural products, and require no protecting group strategies. We now report the results of these studies.

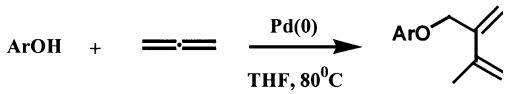


Scheme 1.

1. Phenoxymethyl-1,3-dienes

A range of aryl and heteroaryl phenols were found to react (Scheme 2) with allene (1 bar) in THF over 16 h with an in situ generated Pd(0) catalyst (Table 1) in a Schlenk tube. 5 mol% Palladium acetate and 10 mol% tris-(2-furyl) phosphine proved an effective catalyst system while $Pd(PPh_3)_4$ was less effective. The yields of the derived dienyl ethers **1**–**12** (Scheme 2) varied depending on the substrate structure.

Low yields of dienyl ethers were encountered in the case of 1,3,5-trihydroxybenzene (entry 6), 3-hydroxypyridine (entry 7) and 2-hydroxyisoquinoline (entries 11 and 12). The marked increase in yield when 3,5-dimethoxyphenol was the substrate (entry 5) suggests prototropic processes (keto-enol type) may be responsible for the low yield in the case of the trihydroxybenzene (possibly leading to C-dienyl byproducts). In the case of 3-hydroxypyridine the zwitterionic form **13** may interfere with dienyl ether formation while 3-hydroxyisoquinoline is known to equilibrate with



Scheme 2.

Keywords: chromans; dihydrobenzofurans; atom economy; Claisen rearrangement; cyclisation.
* Corresponding author. E-mail: r.grigg@chem.leeds.ac.uk

0040–4020/01/$ - see front matter
PII: S0040-4020(01)00771-2

Table 1. Dienyl ether synthesis from aryl/heteroaryl phenols and allene

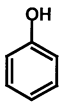
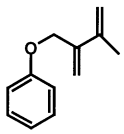
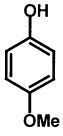
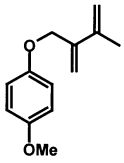
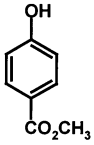
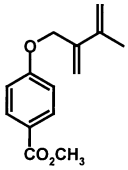
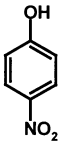
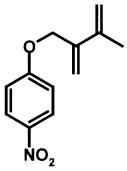
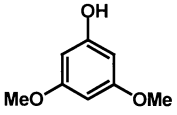
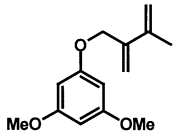
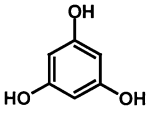
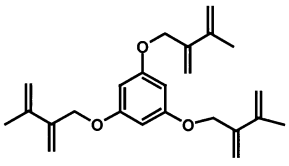
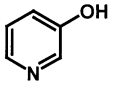
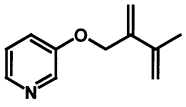
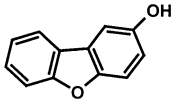
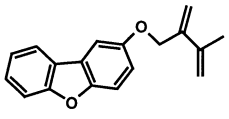
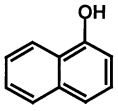
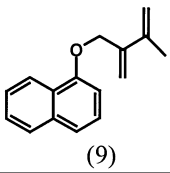
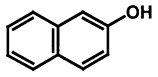
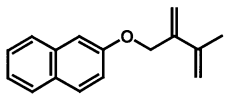
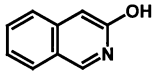
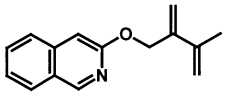
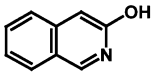
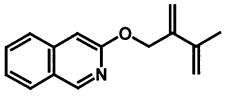
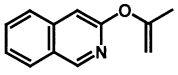
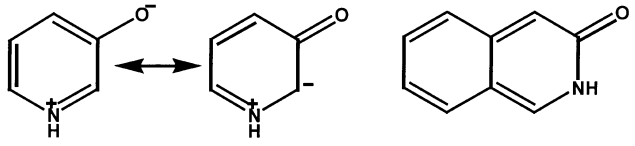
Entry	Phenol	Product	Yield (%)[a]
1		 (1)	67
2		 (2)	69
3		 (3)	56
4		 (4)	64
5		 (5)	66
6		 (6)	33[b]
7		 (7)	34
8		 (8)	60
9		 (9)	78

Table 1. (*continued*)

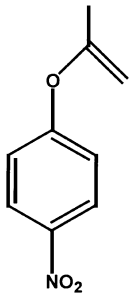
Entry	Phenol	Product	Yield (%)[a]
10		 (10)	79[c]
11		 (11)	30
12		 (11)	12[d]
		 (12)	19[d]

All reactions were carried out in THF in a Schlenk tube for 16 h at 80°C with 1 bar of allene.
[a] Isolated yields.
[b] Allene (1.5 bar) was used.
[c] Reaction temperature 60°C.
[d] Reaction temperature 100°C.

its tautomer **14**. The position of this latter equilibrium is sensitive to solvent polarity[7] and may be responsible for the low yield.



(13) (14)

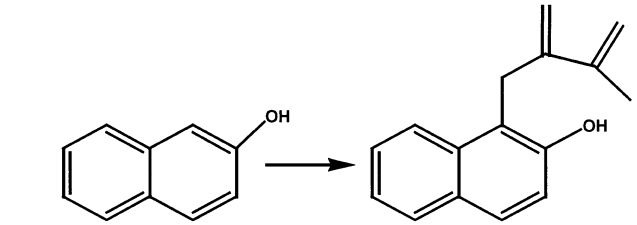


(15)

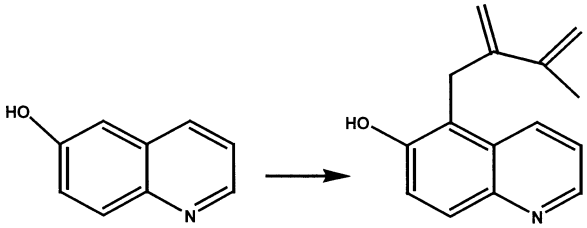
The reaction of 3-hydroxyisoquinoline under more forcing conditions leads to a 1:1.6 mixture of **11** and the 2-propenyl ether **12**. Formation of an analogous 2-propenyl ether **15** (42%) is observed when 4-nitrophenol is reacted (THF, 110°C, 19 h) with allene (1 bar) in the presence of 5 mol% $Pd(PPh_3)_4$. This formal addition of NuH to allene was discussed in a previous paper.[4]

A third type of product, a C-dienyl species, is obtained from both 2-naphthol and 6-hydroxyquinoline which give **16** (50%) and **17** (60%), respectively, using 5 mol% $Pd(PPh_3)_4$ as catalyst (Scheme 3).

In pursuing the O-versus C-diene formation we explored the reaction (THF, 80°C) of 9-phenanthrol with allene (1 bar) using 5 mol% $Pd(PPh_3)_4$ as catalyst. In this case C-dienylation occurred twice, affording **18** in 53% yield (Scheme 4).

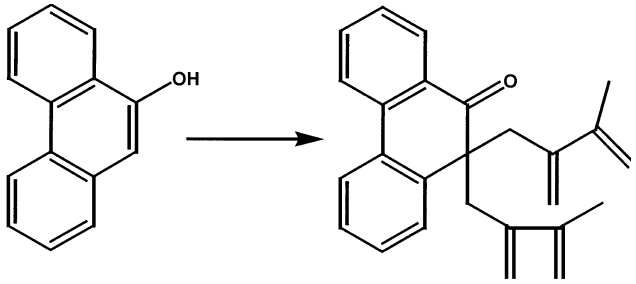


(16)



(17)

Scheme 3.



(18)

Scheme 4.

The C-dienyl species **16**–**18** could arise by direct C-alkylation of the ambident phenolate anions or they could be generated by O-alkylation followed by a Claisen rearrangement. There are comparatively few reports of the related palladium catalysed alkylation of phenols with allyl carbonates, acetates or related π-allylpalladium(II) precursors.[8–10] In these latter studies the products are O-allyl ethers apart from the products from phloroglucinol and β-naphthol, which undergo C-allylation with allyl acetates. Further study of the β-naphthol case showed the O-allyl derivative was the kinetic product (at −20°C) but rearranged to the C-allyl derivative at higher temperatures. Formation of C-alkylation products, which convert to non-identified products could therefore account for the low yields in Table 1 (entries 6, 7 and 11).

Evidence that formation of **16** proceeds via O-dienyl ether **10** was provided by two supplementary experiments. In the first of these the reaction of β-naphthol with allene was carried out in THF at 90°C, as opposed to 60°C in Table 1, for 16 h with the $Pd(OAc)_2$–tris-(2-furyl)phosphine catalyst system. The product (68%) was the C-dienylnaphthalene **16** together with a trace amount of **10**. When O-dienylether **10** was reacted in THF at 60°C for 32 h in the presence of 5 mol% $Pd(PPh_3)_4$ it rearranged to **16** in 54% yield. These results suggest **17** and **18** may also arise via analogous O-alkylation–rearrangement sequences.

Pd(II) and Hg(II) salts are known to catalyse both the Cope and hetero-3,3-sigmatropic rearrangements via a cyclisation-induced rearrangement mechanism.[11] These processes are variants of the electrophile-induced additions to alkenes where the metal cation is the electrophile. Pd(II) catalysed rearrangement of allyl vinyl ethers has been reported but there are strict structural requirements for this process.[12] Catalysis of the Claisen rearrangement of O-allylphenolic ethers by Pd(II) salts has not been reported. In the case of the rearrangement of **10**→**16** the catalytically active species appears to be Pd(0). Pd(II) and Pd(0) catalysed rearrangements of allylic thionolesters[13] and allylic imidates[14] have been reported and it appears that different mechanisms operate for the Pd(0) and Pd(II) catalysed processes. In our cases the products can be accounted for by Scheme 5.

The formation of the O-dienylether is fast but reversible whilst formation of the C-dienyl phenol is slow and essentially irreversible under the reaction conditions. The presence of a higher concentration of oxaphilic phosphine when $Pd(PPh_3)_4$ is used as catalyst may assist in shielding the negatively-charged phenolate oxygen and hence promote C-alkylation. In the case of 9-phenanthrol the high degree of olefinic character[15] of the '9,10-double bond' suggest C-alkylation will be especially facile.

2. Mechanism of dienyl ether formation

Coulson showed the reaction of allene with *N*-deuteriomorpholine gave a morpholino-1,3-diene specifically labelled in the methyl group (95±3%) (possibly with a trace amount of deuterium in the adjacent methylene group).[5] The simplest way to account for this labelling pattern as applied to generic nucleophiles, NuH, via the usual Pd(0)/Pd(II) redox shuttle is shown in Scheme 6. In Scheme 6 only the η^1-complexes, and not the η^3-complexes, are shown for brevity.

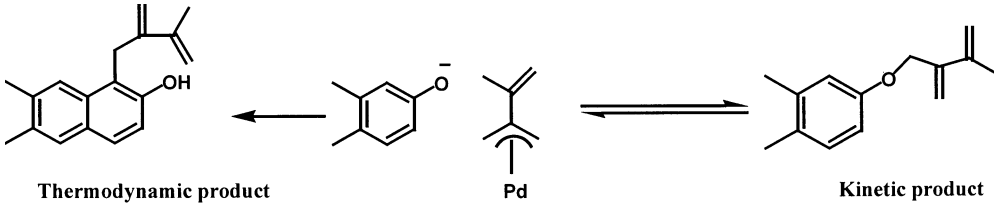
In Scheme 6 intermediate **20** could conceptually revert to the Pd–D species **19** or transform into the Pd–H species **21**. Assuming Scheme 6 is correct the distribution of deuterium shows such reverse reactions to be negligible. An alternative sequence involving a Pd(IV) intermediate is shown in Scheme 7, which is based on Coulson's suggestion[5] that **22** might be a key intermediate. Attack of Nu on the π-allyl species could occur externally or by transfer from Pd(II) depending on the nature of the nucleophile.

Pd(IV) intermediates have been demonstrated or suggested for a range of reactions in recent years.[6]

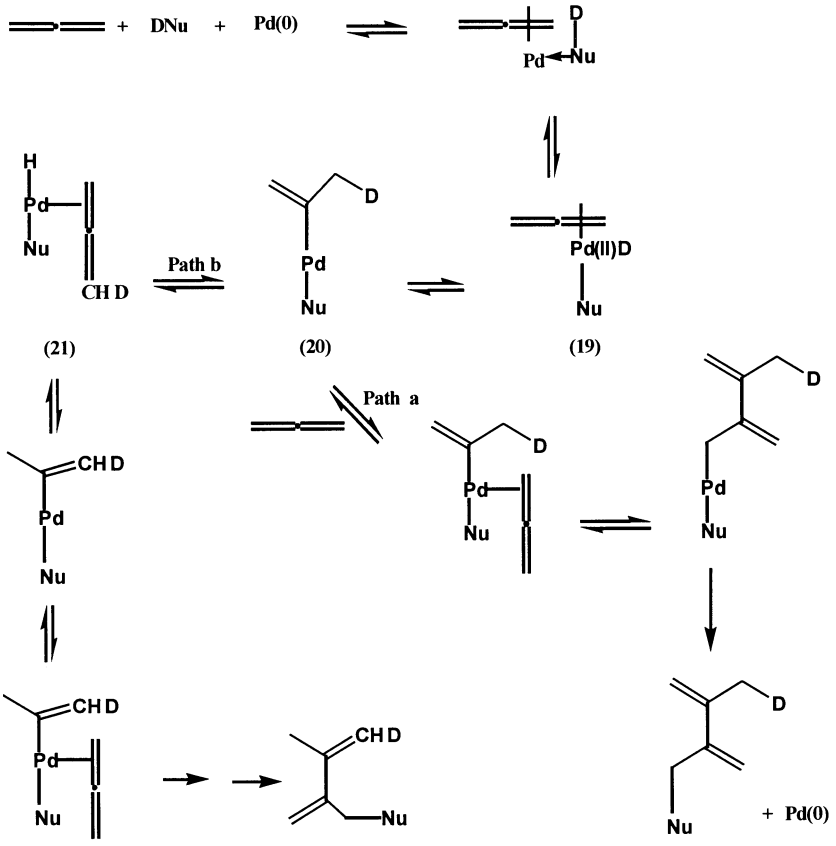
3. Claisen rearrangement of O-dienylethers

The Claisen rearrangement of dienyl ethers **1**, **2**, **5**, **8** and **9** was studied in DMF at 205°C (oil bath temperature) in a Schlenk tube. The expected rearrangement (Scheme 8) occurred furnishing the C-dienes **22**–**27** in 20–63% yield (Table 2).

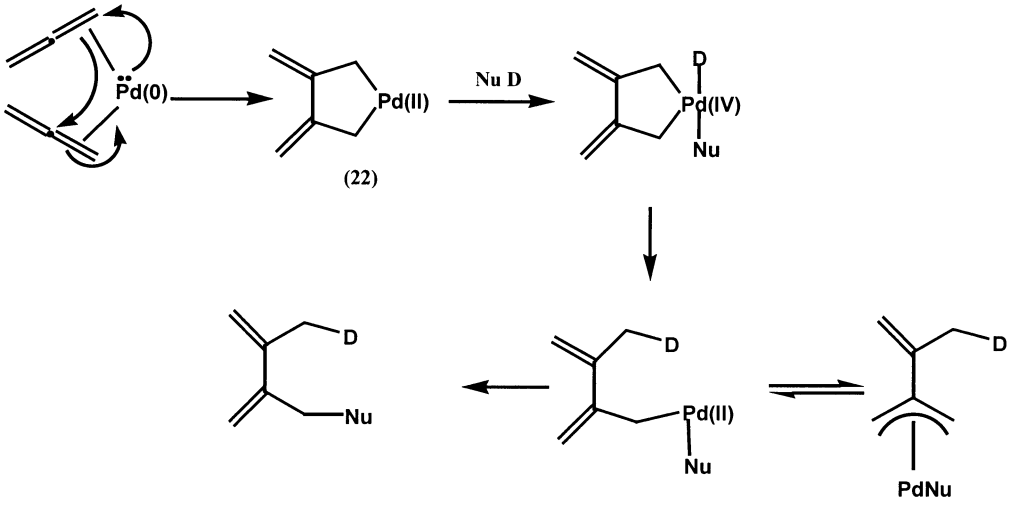
The two low yielding reactions (Table 2, entries 1 and 2) were due to incomplete reaction with the mass balance



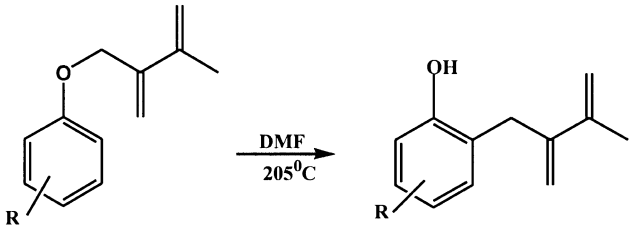
Scheme 5.



Scheme 6.



Scheme 7.



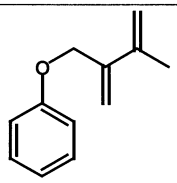
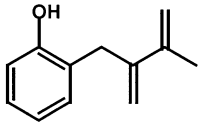
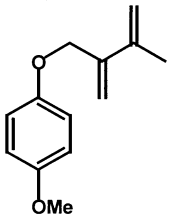
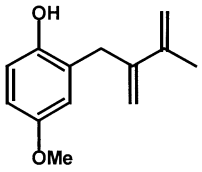
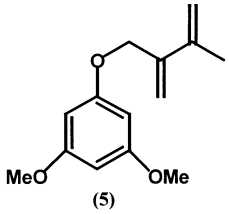
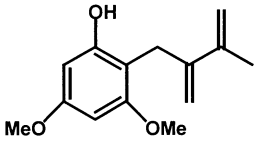
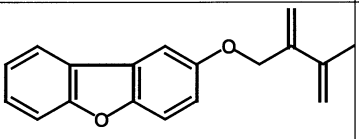
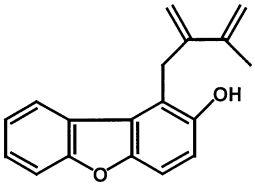
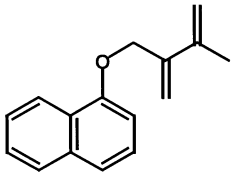
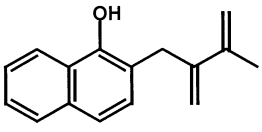
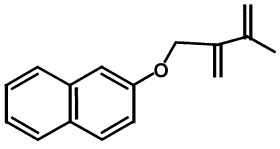
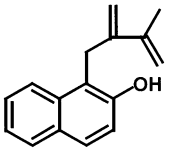
Scheme 8.

consisting largely of unreacted starting material. The more facile rearrangement of the 1-naphthyl O-dienylether compared to the 2-naphthyl O-dienylether (Table 2, entries 5 and 6) is ascribed to steric acceleration due to the buttressing effect of the C(8)-peri-H in the former case.[16]

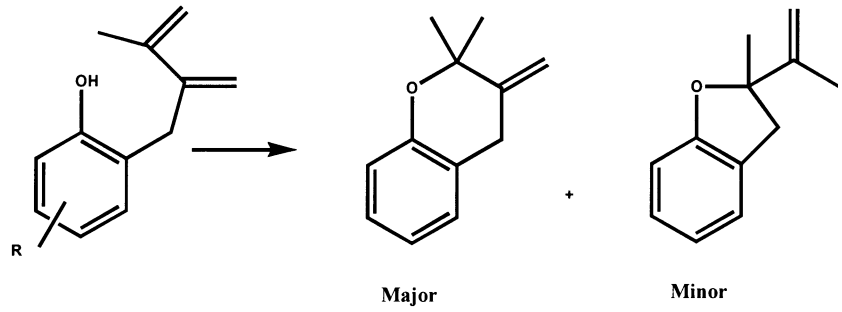
4. Cyclisation of the 2-(1,3-dienylmethyl)-phenols

Cyclisation of the dienylmethyl phenols occurred at room

Table 2. Claisen rearrangement of O-dienyl aryl ethers

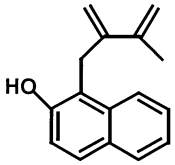
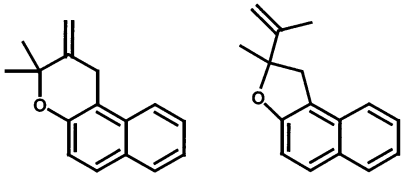
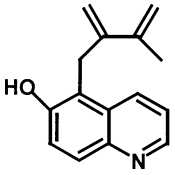
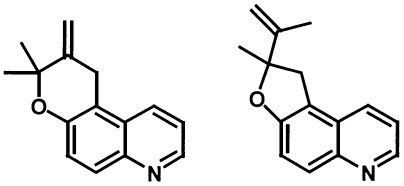
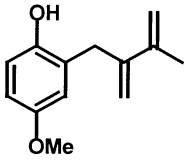
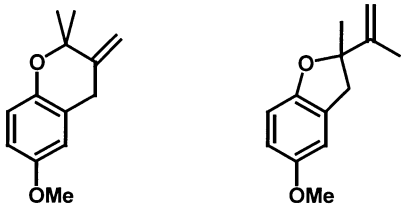
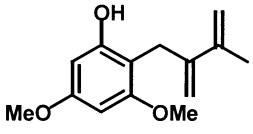
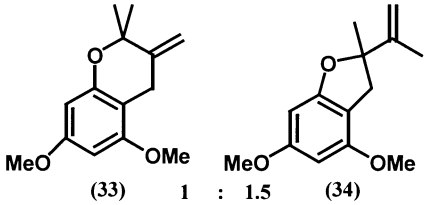
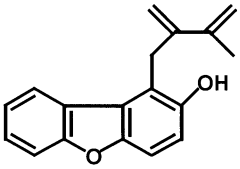
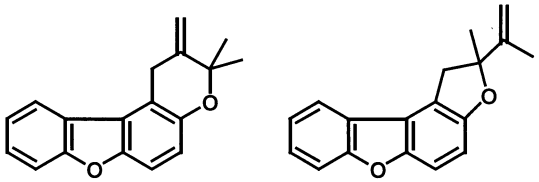
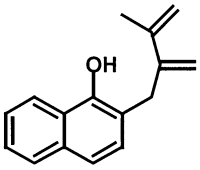
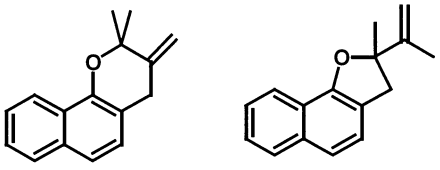
Entry	Ether	Product	Reaction time (h)	Yield[a] (%)
1.	 (1)	 (22)	48	20
2.	 (2)	 (23)	48	44
3.	 (5)	 (24)	24	62
4.	 (8)	 (25)	24	56
5.	 (9)	 (26)	3	63
6.	 (10)	 (16)	24	48

Reactions carried out in DMF in a Schlenk tube at 205°C.
[a] Isolated yields.



Scheme 9.

Table 3. Acid catalysed cyclisation products of 2-(1,3-dienylmethyl)-phenols

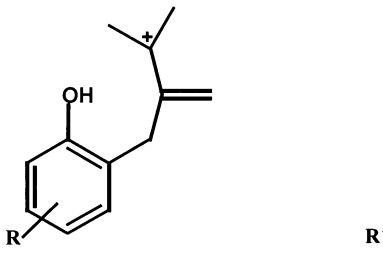
Entry	Phenol	Product	Yield[a] (%)
1.	 (10)	 (27) 4 : 1 (28)	62
2.	 (17)	 (29) 6.5 : 1 (30)	76
3.	 (23)	 (31) 3.5 : 1 (32)	62
4.	 (24)	 (33) 1 : 1.5 (34)	56
5.	 (25)	 (35) 3 : 1 (36)	60
6.	 (26)	 (37) 4 : 1 (38)	74

All reactions carried out in CH_2Cl_2 in a Schlenk tube at room temperature using TsOH (0.5 equiv.) and a trace of TFA.
[a] Isolated yields.

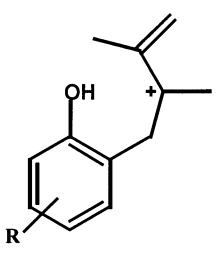
temperature in methylene chloride in the presence of *p*-toluenesulphonic acid (0.5 equiv.) and a trace of TFA. The products were a mixture of *exo*-methylene chromans and dihydrobenzofurans (Scheme 9) (Table 3).

In most cases the major product is the *exo*-methylene chroman except for the dienylmethyl phenol **24**, which gave a 1:1.5 mixture (56%) of chroman and dihydrobenzofuran. Monitoring of the ratio of chroman to dihydrobenzofuran showed the ratio did not alter over 24–48 h. It did not prove possible to separate these isomeric mixtures chromatographically.

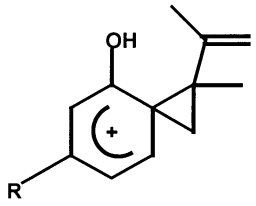
The observed product ratios could be interpreted in terms of stereoelectronic effects. The two carbocations **39** and **40** are both tertiary and allylic but in the case of **40** further stabilisation, and lower reactivity, might result from aryl π-participation **41** (R=H).



(39)



(40)



(41)

The apparently anomalous result with **24** would then be due to the buttressing effect ($A^{1,2}$-strain) of the *ortho*-methoxy group enhancing the cyclisation of **40** to the extent that the stabilising effect of the two methoxy substituents on the π-participation of the analogue of**41** is negated. In order to test this hypothesis we carried an analogous three-step sequence on 3-methoxyphenol (Scheme 10).

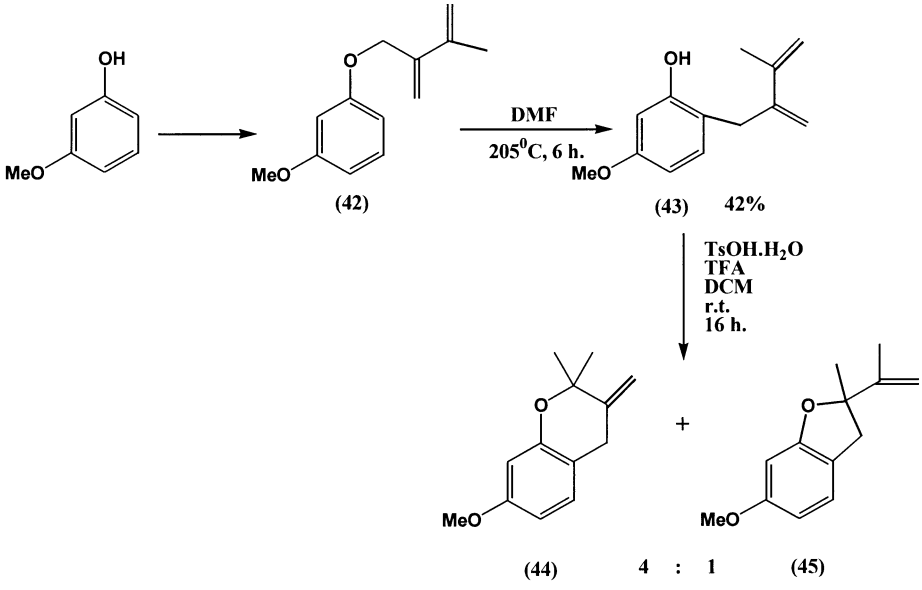
Formation of O-dienyl ether **42** occurred in 69% yield using the conditions described for Table 1. Thermal Claisen rearrangement over 6 h as described for Table 2 afforded **43** in 42% yield. Cyclisation of **43** using the conditions described in Table 3 afforded a 4:1 mixture (63%) of **44** and **45**. Thus in the absence of the buttressing effect of the additional methoxyl group in **24** the isomer ratio from **43** reverts to 'normal' 4:1 ratio, indicating **41** does not play a dominant role in determining the isomer ratio. The phenol **17**, which shows the greatest preference for chroman formation (Table 3, entry 2), has the lowest p*K*a (8.9)[17] of those studied. The increased phenoxide ion stability is thus reflected in the greater discrimination observed in this case.

5. Experimental

Melting points were determined on a Koffler hot-stage apparatus and are uncorrected. Mass spectral data were obtained on a VG Autospec instrument at 70 eV. Nuclear magnetic resonance spectra were recorded at 250 MHz on a Brucker AM 250. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane (TMS) as internal standard. Coupling constants are given in Hertz (Hz). Unless otherwise specified deuteriochloroform was used as a solvent. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=double doublet, dt=double triplet. Microanalysis were obtained using a Carbo Erba MOD11016 instrument. The term 'ether' refers to diethyl ether and petroleum ether refers to that fraction of petroleum ether with boiling point between 40 and 60°C. Column chromatography was performed with flash silica gel (Merck 9385).

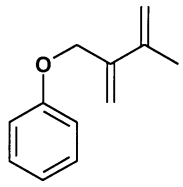
5.1. General procedure for the palladium catalysed alkylation of phenols with allene

The phenol (2 mmol) and $Pd(PPh_3)_4$ (5 mol%), or $Pd(OAc)_2$ (5 mol%) and tris-2-furylphosphine (10 mol%), were mixed in dry THF (10 ml) in a Schlenk tube. The solution was degassed by two freeze-pump-thaw cycles before addition of allene (1 bar). The reaction mixture was stirred at 80°C for 16 h, then cooled. The excess pressure was vented from the Schlenk tube and the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography.



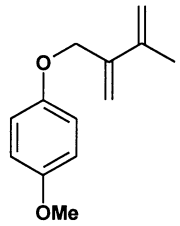
Scheme 10.

5.1.1. (3-Methyl-2-methylene-but-3-enyloxy)-benzene (1)



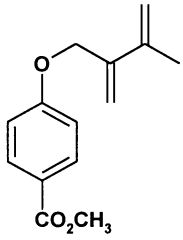
Column chromatography eluting with petroleum ether afforded the product (67%) as a colourless oil. (Found: C, 82.45; H, 8.35. $C_{12}H_{14}O$ requires: C, 82.7; H, 8.1%); δ_H 1.98 (s, 3H, Me), 4.73 (s, 2H, OCH_2), 5.08, 5.11, 5.35 and 5.39 (4×s, 4×1H, 2×C═CH_2), 6.96 (m, 3H, ArH) and 7.29 (m, 2H, ArH); *m/z* (%): 174 (M^+, 49), 159 (88), 131 (40), 94 (61), 79 (100), 65 (40), 53 (68), 41 (66) and 39 (67).

5.1.2. 1-Methoxy-4-(3-methyl-2-methylene-but-3-enyloxy)-benzene (2)



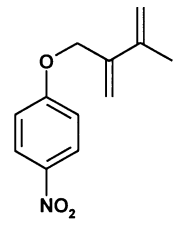
Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (69%) as a colourless oil. (Found: C, 76.6; H, 7.95. $C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.97 (s, 3H, Me), 3.77 (s, 3H, OMe), 4.67 (s, 2H, OCH_2), 5.07, 5.11, 5.34 and 5.37 (4×s, 4×1H, 2×C═CH_2) and 6.86 (m, 4H, ArH); *m/z* (%): 204 (M^+, 28), 189 (11), 123 (100), 109 (16), 95 (22) and 41 (25).

5.1.3. 4-(3-Methyl-2-methylene-but-3-enyloxy)-benzoic acid methyl ester (3)



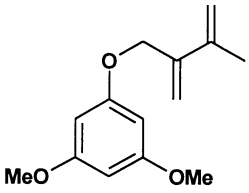
Column chromatography eluting with 24:1 v/v petroleum ether–ether afforded the product (56%) as a colourless amorphous powder, mp 42–43°C. (Found: C, 72.3; H, 7.15. $C_{14}H_{16}O_3$ requires: C, 72.4; H, 6.95%); δ_H 1.9 (s, 3H, Me), 3.81 (s, 3H, CO_2Me), 4.7 (s, 2H, OCH_2), 5.02 (s, 2H, C═CH_2), 5.29 (s, 2H, C═CH_2), and 6.87 and 7.91 (2×d, 2×2H, ArH); *m/z* (%): 232 (M^+, 16), 173 (59), 121 (68), 93 (32), 79 (100), 53 (71) and 41 (73).

5.1.4. 1-(3-Methyl-2-methylene-but-3-enyloxy)-4-nitro-benzene (4)



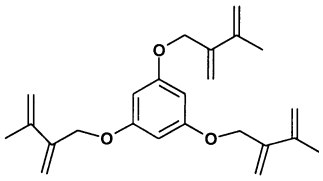
Column chromatography eluting with 49:1 v/v petroleum ether–ether afforded the product (64%) as a colourless amorphous powder, mp 45–46°C. (Found: C, 65.95; H, 6.15; N, 6.15. $C_{12}H_{13}NO_3$ requires: C, 65.75; H, 6.0; N, 6.4%); δ_H 1.98 (s, 3H, Me), 4.83 (s, 2H, OCH_2), 5.08, 5.11, 5.36 and 5.39 (4×s, 4×1H, 2×C═CH_2) and 6.99 and 8.29 (2×d, 2×2H, *J*=9.3 Hz, ArH); *m/z* (%): 219 (M^+, 2.5), 202 (15), 81 (97), 79 (100), 53 (80), and 41 (67).

5.1.5. 1,3-Dimethoxy-5-(3-methyl-2-methylene-but-3-enyloxy)-benzene (5)



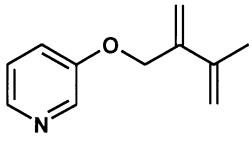
Column chromatography eluting with 49:1 v/v petroleum ether–ether afforded the product (66%) as a colourless oil. (Found: C, 71.8; H, 7.8. $C_{14}H_{18}O_3$ requires: C, 71.8; H, 7.75%); δ_H 1.97 (s, 3H, Me), 3.78 (s, 6H, 2×OMe), 4.68 (s, 2H, OCH_2), 5.09, 5.1, 5.34 and 5.35 (4×s, 4×1H, 2×C═CH_2), 6.09 (s, 1H, ArH) and 6.13 (s, 2H, ArH); *m/z* (%):234 (M^+, 82), 219 (100), 203 (24), 191 (39), 167 (71), 125 (51), 53 (44) and 41 (54).

5.1.6. 1,3,5-Tris-(3-methyl-2-methylene-but-3-enyloxy)-benzene (6)



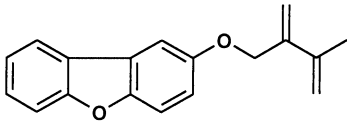
Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (33%) as a colourless oil. (Found: C, 78.9; H, 8.4. $C_{24}H_{30}O_3$ requires: C, 78.65; H, 8.25%); δ_H 1.97 (s, 9H, 3×Me), 4.66 (s, 6H, 3×OCH_2), 5.07, 5.09, 5.35 and 5.38 (4×s, 4×3H, 6×C═CH_2) and 6.19 (s, 3H, ArH); *m/z* (%): 367 (M^++1, 21), 161 (39), 145 (44), 119 (59), 105 (69), 93 (88) and 81 (100).

5.1.7. 3-(3-Methyl-2-methylene-but-3-enyloxy)-pyridine (7)



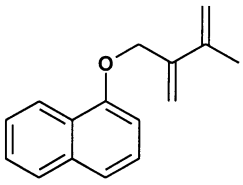
Column chromatography eluting with 3:2 v/v petroleum ether–ether afforded the product (34%) as a colourless oil. (Found: C, 75.5; H, 7.35; N, 7.75. $C_{11}H_{13}NO$ requires: C, 75.4; H, 7.5; N, 8.0%); δ_H 1.98 (s, 3H, Me), 4.78 (s, 2H, OCH_2), 5.1 and 5.38 (2×s, 2×2H, 2×C═CH_2),7.24 (m, 2H, ArH) and 8.23 and 8.35 (2×m, 2×1H, ArH); *m/z* (%): 175 (M^+,17), 160 (16), 79 (36), 53 (53), 41 (48) and 39 (100).

5.1.8. 2-(3-Methyl-2-methylene-but-3-enyloxy)-dibenzofuran (8)



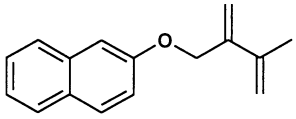
Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (60%) which crystallised from petroleum ether–ether as colourless plates, mp 74–75°C. (Found: C, 81.6; H, 6.1. $C_{18}H_{16}O_2$ requires: C, 81.8; H, 6.1%); δ_H 2.0 (s, 3H, Me), 4.81 (s, 2H, OCH_2), 5.1, 5.17, 5.37 and 5.43 (4×s, 4×1H, 2×C=CH_2), 7.08 (dd, 1H, J=2.6 and 9 Hz, ArH), 7.27–7.51 (m, 5H, ArH) and 7.89 (d, 1H, J=8 Hz, ArH); *m/z* (%): 264 (M^+, 26), 249 (20), 224 (24), 183 (100), 155 (44), 127 (30).

5.1.9. 1-(3-Methyl-2-methylene-but-3-enyloxy)-naphthalene (9)



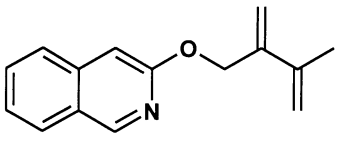
Column chromatography eluting with hexane afforded the product (78%) as a colourless oil. (Found: C, 85.65; H, 7.3. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.2%); δ_H 2.01 (s, 3H, Me), 4.9 (s, 2H, OCH_2), 5.09, 5.17, 5.4 and 5.51 (4×s, 4×1H, 2×C=CH_2), 6.83 (dd, 1H, J=1.14, 7.3 Hz, ArH), 7.33–7.49 (m, 4H, ArH), 7.8 and 8.3 (2×m, 2×1H, ArH); *m/z* (%): 224 (M^+, 31), 209 (83), 181 (10), 144 (50), 115 (100), 79 (27), 53 (27) and 41 (28).

5.1.10. 2-(3-Methyl-2-methylene-but-3-enyloxy)-naphthalene (10)



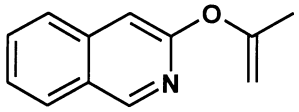
Column chromatography eluting with petroleum ether afforded the product (69%) as a colourless amorphous powder, mp 32–33°C. (Found: C, 85.55; H, 7.25. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.2%); δ_H 2.0 (s, 3H, Me), 4.84 (s, 2H, OCH_2), 5.11, 5.16, 5.39 and 5.44 (4×s, 4×1H, 2×C=CH_2), 7.16–7.43 (m, 4H, ArH) and 7.74 (m, 3H, ArH); *m/z* (%): 224 (M^+, 73), 209 (68), 181 (29), 157 (44), 144 (53), 81 (59), 69 (100).

5.1.11. 3-(3-Methyl-2-methylene-but-3-enyloxy)-isoquinoline (11)



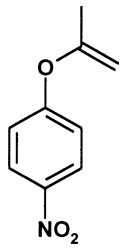
Column chromatography eluting with 49:1 v/v petroleum ether–ether afforded the product (30%) as a colourless amorphous powder, mp 47–48°C. (Found: C, 79.9; H, 6.9; N, 6.05. $C_{15}H_{15}NO$ requires: C, 79.95; H, 6.7; N, 6.2%); δ_H 2.0 (s, 3H, Me), 5.09 (s, 2H, OCH_2), 5.15, 5.2, 5.35 and 5.44 (4×s, 4×1H, 2×C=CH_2), 7.07 (s, 1H, ArH), 7.37 and 7.56 (2×dd, 2×1H, J=7.5 Hz, ArH), 7.68 and 7.88 (2×d, 2×1H, J=7.5 Hz, ArH) and 8.96 (s, 1H, ArH); *m/z* (%): 226 (M^++1, 100), 225 (M^+, 13), 146 (56), 117 (23), 73 (28) and 69 (32).

5.1.12. 3-Isopropenyloxy-isoquinoline (12)



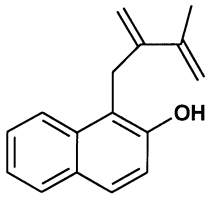
Column chromatography eluting with 9:1 v/v petroleum ether–ether afforded the product (19%) as a yellow oil. (Found: C, 77.95; H, 6.15; N, 7.3. $C_{12}H_{11}NO$ requires: C, 77.8; H, 6.0; N, 7.55%); δ_H 2.07 (s, 3H, Me), 4.4 and 4.5 (2×s, 2×1H, C=CH_2), 7.2 (s, 1H, ArH), 7.48 and 7.64 (2×dd, 2×1H, J=7.5 Hz, ArH), 7.76 and 7.95 (2×d, 2×1H, J=7.5 Hz, ArH), and 9.04 (s, 1H, ArH); *m/z* (%): 186 (M^++1, 100), 185 (M^+, 18), 146 (48), 117 (21), 73 (72) and 69 (65).

5.1.13. 1-Isopropenyloxy-4-nitro-benzene (15)



Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (42%) as a yellow oil. (Found: C, 60.55; H, 5.05; N, 8.05. $C_9H_9NO_3$ requires: C, 60.35; H, 5.05; N, 7.8%); δ_H 1.99 (s, 3H, Me), 4.44 and 4.57 (2×s, 2×1H, C=CH_2), 7.12 and 8.23 (2×d, 2×2H, J=9.2 Hz, ArH); *m/z* (%): 179 (M^+, 100), 139 (58), 109 (86), 65 (71) and 43 (48).

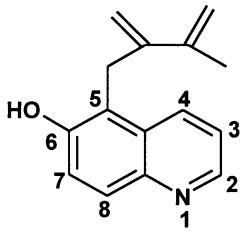
5.1.14. 1-(3-Methyl-2-methylene-but-3-enyl)-naphthalen-2-ol (16)



Column chromatography eluting with 9:1 v/v petroleum ether–ether afforded the product (50%) as a colourless amorphous powder, mp 73–74°C. (Found: C, 85.8; H, 7.1. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.2%); δ_H 2.03 (s, 3H, Me), 3.99 (s, 2H, CH_2Ar), 4.54 (s, 1H, C=CH_2), 5.06 (s, 1H, OH), 5.17 (s, 2H, C=CH_2), 5.42 (s, 1H, C=CH_2), 7.13 (d, 1H, J=8.7 Hz, ArH), 7.30–7.48 (m, 2H, ArH) and

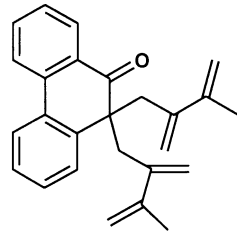
7.69–7.81 (m, 3H, ArH); *m/z* (%): 224 (M^+, 67), 209 (100), 181 (42), 157 (21) and 128 (29).

5.1.15. 5-(3-Methyl-2-methylene-but-3-enyl)-quinolin-6-ol (17)



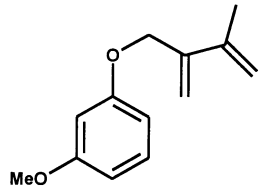
Column chromatography eluting with 7:3 v/v hexane–ethyl acetate afforded the product (60%) which crystallised from ethyl acetate–methanol as colourless prisms, mp 193–194°C. (Found: C, 79.7; H, 6.6; N, 6.1. $C_{15}H_{15}NO$ requires: C, 79.95; H, 6.7; N, 6.2%); δ_H (acetone-d_6) 2.01 (s, 3H, Me), 4.03 (s, 2H, CH_2Ar), 4.31, 5.11, 5.16 and 5.49 (4×s, 4×1H, 2×C=CH_2), 7.4 (dd, 1H, J=4.1, 8.6 Hz, ArH_3), 7.5 (d, 1H, J=9.1 Hz, ArH_7), 7.88 (d, 1H, J=9.1 Hz, ArH_8), 8.1 (d, 1H, J=8.6 Hz, ArH_4), 8.71 (d, 1H, J=4.1 Hz, ArH_2) and 8.91 (s, 1H, OH); *m/z* (%): 225 (M^+, 45), 210 (100), 182 (30), 158 (28), 130 (34).

5.1.16. 10,10-Bis-(3-methyl-2-methylene-but-3-enyl)-10*H*-phenanthren-9-one (18)



Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (53%) as a colourless oil. (Found: C, 88.0; H, 7.4. $C_{26}H_{26}O$ requires: C, 88.1; H, 7.4%); δ_H 1.6 (s, 6H, 2×Me), 2.89 and 3.32 (2×d, 2×2H, J=15 Hz, 2×CH_2), 4.12, 4.75, 4.8 and 4.89 (4×s, 4×2H, 4×C=CH_2), 7.34 (m, 4H, ArH), 7.64 (m, 1H, ArH) and 8.04 (m, 3H, ArH); *m/z* (%): 354 (M^+, 22), 273 (70), 258 (100), 231 (68), 251 (65), 178 (47) and 41 (71).

5.1.17. 1-Methoxy-3-(3-methyl-2-methylene-but-3-enyloxy)-benzene (42)

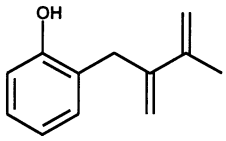


Column chromatography eluting with 4:1 v/v petroleum ether–ether afforded the product (69%) as a colourless oil. (Found: C, 76.25; H, 8.05. $C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.97 (s, 3H, Me), 3.786 (s, 3H, OMe), 4.70 (s, 2H, OCH_2), 5.07, 5.10, 5.35 and 5.38 (4×s, 4×1H, 2×C=CH_2), 6.52 (dd, 1H, J=8.9 and 8.1 Hz, ArH) and 6.50–6.53 (m, 3H, ArH); *m/z* (%): 204 (M^+, 57), 189 (100), 173 (15), 161 (44), 124 (42), 77 (38) and 41 (95).

5.2. General procedure for Claisen rearrangement of the dienyl aryl ethers

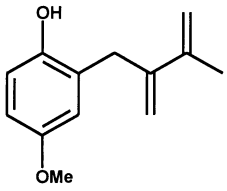
The dienyl aryl ether (0.2 g) was dissolved in *N*,*N*-dimethylformamide (2 ml) and the solution heated at 205°C for 3–48 h in a Schlenk tube. The mixture was then cooled to room temperature, water (2 ml) added and the mixture extracted with ether (3×). The organic extracts were combined, dried (anh. Na_2SO_4), filtered and the filtrate evaporated under reduced pressure. The residue was purified by flash chromatography to afford the product.

5.2.1. 2-(3-Methyl-2-methylene-but-3-enyl)-phenol (22)



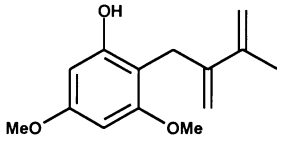
Column chromatography eluting with 13:1 v/v petroleum ether–ether afforded the product (20%) as a colourless oil. (Found: C, 81.55; H, 8.2. $C_{12}H_{14}O$ requires: C, 82.7; H, 8.1%); δ_H 1.9 (s, 3H, Me), 3.63 (s, 2H, CH_2Ar), 4.91 (s, 1H, C=CH_2), 4.92 (s, 1H, OH), 5.05 (s, 1H, C=CH_2), 5.2 and 5.23 (2×s, 2×1H, C=CH_2), 6.81–6.89 (m, 2H, ArH) and 7.09–7.14 (m, 2H, ArH); *m/z* (%): 173 (M^+-1, 7), 147 (31), 97 (59), 83 (47), 73 (49), 69 (63) and 57 (100).

5.2.2. 4-Methoxy-2-(3-methyl-2-methylene-but-3-enyl)-phenol (23)



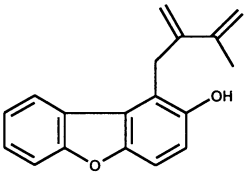
Column chromatography eluting with 16:1 v/v petroleum ether–ether afforded the product (44%) as a colourless oil. (Found: C, 76.3; H, 7.8. $C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.96 (s, 3H, Me), 3.6 (s, 2H, CH_2Ar), 3.75 (s, 3H, OMe), 4.6 (s, 1H, OH), 4.91, 5.04, 5.19 and 5.23 (4×s, 4×1H, 2×C=CH_2), and 6.67–6.78 (m, 3H, ArH); *m/z* (%): 204 (M^+,100), 189 (62), 173 (13), 147 (15), 73 (40) and 57 (34).

5.2.3. 3,5-Dimethoxy-2-(3-methyl-2-methylene-but-3-enyl)-phenol (24)



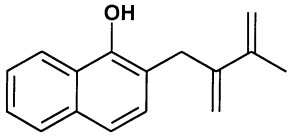
Column chromatography eluting with 9:1 v/v petroleum ether–ether afforded the product (62%) as a colourless oil. (Found: C, 71.75; H, 7. 85. $C_{14}H_{18}O_3$ requires: C, 71.75; H, 7.75%); δ_H 1.97 (s, 3H, Me), 3.6 (s, 2H, CH_2Ar), 3.77 (s, 6H, 2×OMe), 4.87 and 5.06 (2×s, 2×1H, C=CH_2), 5.12 (s, 1H, OH), 5.2 and 5.29 (2×s, 2×1H, C=CH_2) and 6.11 and 6.12 (2×s, 2×1H, ArH); *m/z* (%): 234 (M^+, 66), 219 (60), 167 (100), 73 (77), 69 (52) and 55 (67).

5.2.4. 1-(3-Methyl-2-methylene-but-3-enyl)-dibenzofuran-2-ol (25)



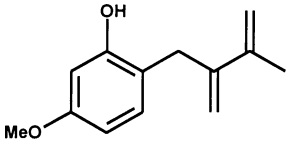
Column chromatography eluting with 16:1 v/v petroleum ether–ether afforded the product (56%) as a colourless amorphous powder, mp 129–130°C. (Found: C, 81.55; H, 6.25. $C_{18}H_{16}O_2$ requires: C, 81.8; H, 6.1%); δ_H 2.05 (s, 3H, Me), 4.1 (s, 2H, CH_2Ar), 4.66 (s, 1H, C=CH_2), 4.84 (s, 1H, OH), 5.18 (s, 2H, C=CH_2), 5.44 (s, 1H, C=CH_2), 6.99 (d, 1H, J=8.7 Hz, ArH), 7.29 (m, 1H, ArH), 7.37 (d, 1H, J=8.7 Hz, ArH), 7.43 (m, 1H, ArH), 7.54 (d, 1H, J=8 Hz, ArH) and 7.72 (d, 1H, J=8 Hz, ArH); m/z (%): 264 (M^+, 100), 249 (65), 197 (92), 147 (32), 135 (39), 73 (78) and 57 (68).

5.2.5. 2-(3-Methyl-2-methylene-but-3-enyl)-naphthalen-1-ol (26)



Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded the product (63%) as a colourless amorphous powder, mp 60–61°C. (Found: C, 85.5; H, 7.25. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.2%); δ_H 2.0 (s, 3H, Me), 3.79 (s, 2H, CH_2Ar), 4.99, 5.08, 5.26 and 5.33 (4×s, 4×1H, 2×C=CH_2), 5.5 (s, 1H, OH), 7.24 (d, 1H, J=3.14 Hz, ArH), 7.39–7.48 (m, 3H, ArH), and 7.77 and 8.17 (2×m, 2×1H, ArH); m/z (%): 224 (M^+, 20), 209 (100), 194 (9), 165 (13) and 128 (36).

5.2.6. 5-Methoxy-2-(3-methyl-2-methylene-but-3-enyl)-phenol (43)

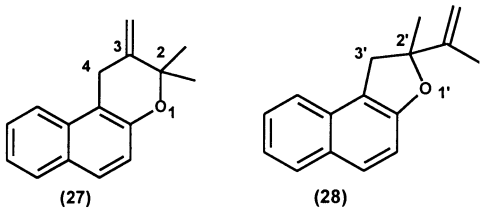


Column chromatography eluting with 4:1 v/v petroleum ether–ether afforded the product (42%) as a colourless oil. (Found: C, 76.95; H, 7.95. $C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.95 (s, 3H, Me), 3.55 (s, 2H, CH_2Ar), 3.75 (s, 3H, OMe), 4.70 (s, 1H, OH), 4.90, 5.03, 5.19 and 5.26 (4×s, 4×1H, 2×C=CH_2), 6.44 (m, 2H, ArH) and 6.93 (d, 1H, J=8.2 Hz, ArH); m/z (%): 204 (M^+, 70), 175 (35), 137 (100), 77 (37) and 55 (24).

5.3. General procedure for acid catalysed cyclisation of 2-(1,3-dienylmethyl) phenols

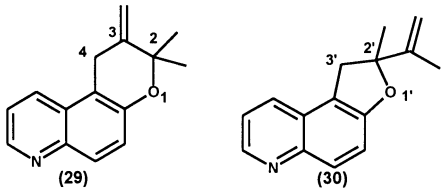
A solution of the dienyl phenol (0.1 g), *p*-toluenesulfonic acid monohydrate (0.5 equiv.), trifluoroacetic acid (0.01 ml) in CH_2Cl_2 (5 ml) was stirred at room temperature overnight, then neutralised with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were washed with water, dried (anh. Na_2SO_4) and the solvent removed under reduced pressure. The residue was purified by column chromatography.

5.3.1. 3,3-Dimethyl-2-methylene-2,3-dihydro-1*H*-benzo-[*f*]chromene (27) and 2-isopropenyl-2-methyl-1,2-dihydro-naphtho[2,1-*b*] furan (28)



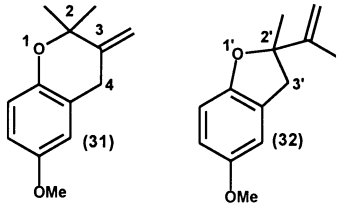
Column chromatography eluting with petroleum ether afforded a 4:1 mixture of (**27**) and (**28**) (62%) as a colourless oil. (Found: C, 85.6; H, 7.15. $C_{16}H_{16}O$ requires: C, 85.65; H, 7.19%); δ_H 1.54 (s, 6H, 2×2-Me), 1.64 (s, 3H, 2′-Me), 1.87 (s, 3H, CH_3–C=), 3.29 and 3.51 (2×d, 2×1H, J=15.5 Hz, 3′-CH_2, 3.82 (s, 2H, 4-CH_2), 4.88 (s, 2H, C=CH_2), 5.14 and 5.15 (2×s, 2×1H, C=CH_2) and 7.02–7.81 (m, 12H, ArH); m/z (%): 224 (M^+, 47), 209 (26), 193 (8), 181 (10), 147 (20), 133 (14) and 73 (100).

5.3.2. 3,3-Dimethyl-2-methylene-2,3-dihydro-1*H*-pyrano-[3,2-*f*] quinoline (29) and 2-isopropenyl-2-methyl-1,2-dihydro-furo[3,2-*f*] quinoline (30)



Column chromatography eluting with 7:3 v/v petroleum ether–ether afforded a 6.5:1 mixture of (**29**) and (**30**) (76%) as a colourless oil. (Found: C, 79.85; H, 6.65; N, 6.4. $C_{15}H_{15}NO$ requires: C, 79.95; H, 6.7; N, 6.2%); δ_H 1.55 (s, 6H, 2×2-Me), 1.65 (s, 3H, 2′-Me), 1.88 (s, 3H, CH_3–C=), 3.29 and 3.51 (2×d, 2×1H, 3′-CH_2), 3.8 (s, 2H, 4-CH_2, 5.0) and 5.16 (s, 2H, C=CH_2) and 7.26, 7.38, 7.91, 8.2 and 8.75 (5×m, 5×2H, ArH); m/z (%): 226 (M^++1, 100), 225 (M^+, 20), 210 (8), 158 (8) and 73 (10).

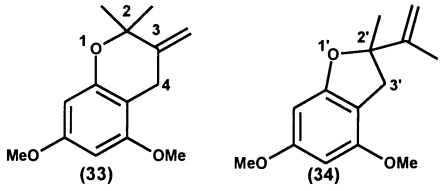
5.3.3. 6-Methoxy-2,2-dimethyl-3-methylene-chroman (31) and 2-isopropenyl-5-methoxy-2-methyl-2,3-dihydro-benzofuran (32)



Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded a 3.5:1 mixture of (**31**) and (**32**) (62%) as a colourless oil. (Found: C, 76.35; H, 7.95.

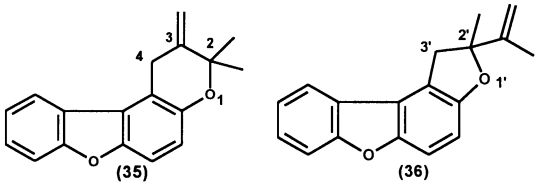
$C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.46 (s, 6H, 2×2-Me), 1.54 (s, 3H, 2′-Me),1.83 (s, 3H, CH_3–C═), 2.98 and 3.23 (2×d, 2×1H, J=15.7 Hz, 3′-CH_2), 3.5 (s, 2H, 4-CH_2), 3.75 (s, 6H, 2×OCH_3), 4.83 (s, 1H, C═CH_2), 5.0 (s, 2H, C═CH_2),5.08 (s, 1H, C═CH_2), 6.6–6.76 (m, 6H, ArH); *m/z* (%): 204 (M^+, 34), 189 (100), 174 (11), 161 (8) and 146 (9).

5.3.4. 5,7-Dimethoxy-2,2-dimethyl-3-methylene-chroman (33) and 2-isopropenyl-4,2-dimethoxy-2-methyl-2,3-dihydro-benzofuran (34)



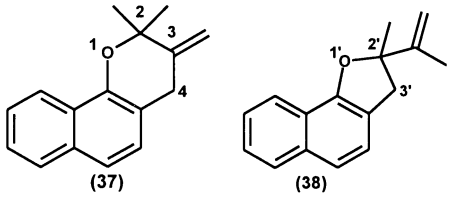
Column chromatography eluting with 49:1 v/v petroleum ether–ether afforded a 1:1.5 mixture of (**33**) and (**34**) (56%) as a colourless oil. (Found: C, 72.05; H, 7.9. $C_{14}H_{18}O_3$ requires: C, 71.75; H, 7.75%); δ_H 1.47 (s, 6H, 2×2-Me), 1.54 (s, 3H, 2′-Me), 1.81 (s, 3H, CH_3–C═), 2.89 and 3.11 (2×d, 2×1H, J=15 Hz, 3′-CH_2), 3.33 (s, 2H, 4-CH_2), 3.77 (m, 12H, 4×OCH_3), 4.82 (s, 1H, C═CH_2), 5.02 (s, 2H, C═CH_2), 5.07 (s, 1H, C═CH_2) and 6.0–6.07 (m., 4H, ArH); *m/z* (%): 234 (M^+, 70), 219 (56), 133 (65), 97 (59), 83 (42), 73 (44) and 57 (77).

5.3.5. 3,3-Dimethyl-2-methylene-2,3-dihydro-1*H*-4,7-dioxa-benzo[*c*]fluorene (35) and 2-isopropenyl-2-methyl-1,2-dihydro-benzo[*d*]benzo[1,2-*b*;4,3-*b*′] difuran (36)



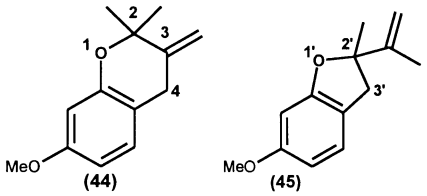
Column chromatography eluting with 99:1 v/v petroleum ether–ether afforded a 3:1 mixture of (**35**) and (**36**) (60%) as a colourless oil (Found: C, 82.05; H, 5.95. $C_{18}H_{16}O_2$ requires: C, 81.8; H, 6.1%); δ_H 1.55 (s, 6H, 2×2-Me), 1.65 (s, 3H, 2′-Me), 1.89 (s, 3H, CH_3–C═), 3.4 and 3.62 (2×d, 2×1H, J=16 Hz, 3′-CH_2), 4.01 (s, 2H, 4-CH_2), 4.89 and 5.17 (2×s, 2×2H, 2×C═CH_2), 6.9–7.1 (m, 2H, ArH), 7.3–7.6 (m, 6H, ArH) and 7.8–8.0 (m, 4H, ArH); *m/z* (%): 264 (M^+, 40), 249 (100), 221 (31), 168 (42) and 139 (69).

5.3.6. 2,2-Dimethyl-3-methylene-3,4-dihydro-2*H*-benzo-[*h*]chromene (37) and 2-isopropenyl-2-methyl-2,3-dihydro-naphtho[1,2-*b*] furan (38)



Column chromatography eluting with petroleum ether afforded a 4:1 mixture of (**37**) and (**38**) (74%) as a colourless oil. (Found: C, 85.4; H, 7.2. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.2%); δ_H 1.58 (s, 6H, 2×2-Me), 1.64 (s, 3H, 2′-Me), 1.86 (s, 3H, CH_3–C═), 3.18 and 3.42 (2×d, 2×1H, J=15.4 Hz, 3′-CH_2), 3.65 (s, 2H, 4-CH_2), 4.87, 5.07, 5.09, and 5.17 (4×s, 4×1H, 2×C═CH_2), 7.14 (d, 1H, J=8.4 Hz, ArH), 7.25–7.46 (m, 7H, ArH), 7.74 (m, 2H, ArH) and 8.0 and 8.2 (2×m, 2×1H, ArH); *m/z* (%): 224 (M^+, 97), 209 (100), 181 (40), 83 (25), 69 (49) and 57 (79).

5.3.7. 7-Methoxy-2,2-dimethyl-3-methylene-chroman (44) and 2-isopropenyl-6-methoxy-2-methyl-2,3-dihydro-benzofuran (45)



Column chromatography eluting with hexane afforded a 4:1 mixture of (**44**) and (**45**) (63%) as a colourless oil. (Found: C, 76.8; H, 8.2. $C_{13}H_{16}O_2$ requires: C, 76.45; H, 7.9%); δ_H 1.44 (s, 6H, 2×2-Me), 1.52 (s, 3H, 2′-Me), 1.80 (s, 3H, CH_3C═C), 3.15 and 3.50 (2×d, 2×1H, J=14.8 Hz, 3′-CH_2), 3.55 (s, 2H, 4-CH_2), 3.81 (s, 6H, 2×OCH_3), 4.85 (s, 1H, C═CH_2), 5.0 (s, 2H, C═CH_2), 5.12 (s, 1H, C═CH_2) and 6.82–6.60 (m, 6H, ArH); *m/z* (%): 204 (M^+, 100), 189 (85), 161 (61), 137 (68) and 41 (46).

Acknowledgements

We thank Leeds University and the Thailand Research Fund (TRF) of the Royal Golden Jubilee Project for support.

References

1. For reviews see: (a) Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 3590–3593. (b) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067–3125.
2. For recent examples see: (a) Grigg, R.; Kordes, M. *Eur. J. Org. Chem.* **2001**, 707–712. (b) Grigg, R.; Rasparini, M.; MacLachlan, W. *Chem. Commun.* **2000**, 2241–2242. (c) Kang, S.-K.; Baik, T.-G.; Kulak, A. N.; Ha, Y.-H.; Lim, Y.; Pak, J. *J. Am. Chem. Soc.* **2000**, *122*, 11529–11530. (d) Chang, H.-M.; Cheng, C.-H. *Org. Lett.* **2000**, *2*, 3439–3442. (e) Gai, X.; Grigg, R.; Collard, S.; Muir, J. E. *Chem. Commun.* **2000**, 1765–1766. (f) Grigg, R.; MacLachlan, W. S.; MacPherson, D. T.; Sridharan, V.; Suganthan, S.; Thornton-Pett, M.; Zhang, J. *Tetrahedron* **2000**, *56*, 6585–6594. (g) Zenner, J. M.; Larock, R. C. *J. Org. Chem.* **1999**, *64*, 7312–7322. (h) Kato, F.; Hiratsuka, Y.; Mitsui, T.; Watanabe, T.; Hiro, K. *Heterocycles* **1999**, *50*, 83–87.
3. For a review see: Yamamoto, Y.; Radhakrishnan, U. *Chem. Soc. Rev.* **1999**, *28*, 199–207.
4. Grigg, R.; Montieth, M.; Sridharan, V.; Terrier, C. *Tetrahedron* **1998**, *54*, 3885–3894.
5. Coulson, D. R. *J. Org. Chem.* **1973**, *38*, 1483–1490.
6. For recent references see: (a) Grigg, R.; Savic, V.; Tambyrajah, V. *Tetrahedron Lett.* **2000**, *41*, 3003–3006. (b) Bayler, A.; Canty, A. J.; Ryan, J. H.; Skelton, B. W.; White, A. H. *Chem.Commun.* **2000**, 575–578. (c) Brunel, J. M.; Hirlemann, M.-H.; Henmann, A.; Buono, G. *Chem. Commun.* **2000**, 1869–1870. (d) Hovestad, N. J.; Hoare,

J. L.; Jastrzebsk, J. T. B. H.; Canty, A. J.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1999**, *18*, 2970–2980. (e) Catellani, M.; Frigmeni, F.; Rangoni, A. *Angew.-Chem., Int. Ed. Engl.* **1997**, *36*, 112–119. (f) Shaw, B. L. *Chem.Commun.* **1998**, 1361–1362.

7. Hazai, L. *Advances in Heterocyclic Chemistry*; Katritzsky, A. R., Ed.; Academic: New York, 1991; Vol. 52, pp. 155–158.
8. Muzart, J.; Genet, J. P.; Denis, A. *J. Organomet. Chem.* **1987**, *326*, C23.
9. (a) Goux, C.; Lhoste, P.; Sinou, D. *Synlett* **1992**, 725–727. (b) Balavoine, G.; Bram, G.; Guibe, F. *Nov. J. Chem.* **1978**, *2*, 207–209. (c) Goux, C.; Massacret, M.; Lhoste, P.; Sinou, D. *Organometallics* **1995**, *14*, 4585–4593.
10. Nay, B.; Peyrat, J.-F.; Vercauteren, J. *Eur. J. Org. Chem.* **1999**, 2231–2234.
11. (a) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579–586. (b) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205–247.
12. van der Baan, J. L.; Bickelhaupt, F. *Tetrahedron Lett.* **1986**, *27*, 6267–6270.
13. Auburn, P. R.; Whelan, J.; Bosnich, B. *Organometallics* **1986**, *5*, 1533–1537.
14. Ikariva, T.; Ishikawa, Y.; Hirai, K.; Yoshikawa, S. *Chem. Lett.* **1982**, 1815–1818.
15. Nashed, N. T.; Sayer, J. M.; Jerina, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 1723–1730.
16. For related buttressing effects see: Grigg, R.; Heaney, F.; Markandu, J.; Surendrakumar, S.; Thornton-Pett, M.; Warnock, W. J. *Tetrahedron* **1991**, *47*, 4007–4030.
17. Perrin, D. D. *Dissociation Constants of Organic Acids and Bases in Aqueous Solution*; Butterworths: London, 1972.