Claisen Rearrangement of Prenyl Ethers of Isomeric Acetylnaphthols and Bisprenyl Ethers of 4,6- and 2,4-Diacetylresorcinols

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Claisen rearrangements of the 3-methylbut-2-enyl(prenyl) ethers **3** and **9** of 2-acetyl-1-hydroxy- and 1-acetyl-2-hydroxynaphthalenes **1** and **2** and the bis(3-methylbut-2-enyl) ethers **12** and **18** of 2,4- and 4,6-diacetylresorcinols **11** and **17** have been studied under a variety of thermal and catalytic conditions. 2-Acetyl-4-(3-methylbut-2-enyl)naphthalene-1-ol **4** was the sole product on rearrangement of compound **3**, in DMA or neat. Under catalytic conditions 3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran **7** was obtained in poor yield. An isomeric pyran, 1,2-dihydro-3,3-dimethyl-3*H*-naphtho[2,1-*b*]pyran **10** (25–43%) was obtained under both thermal and catalytic conditions from **9**. The rearrangement of **12** under thermal conditions (DMA and neat) furnished 3-acetyl-2,4-dihydroxy-5-(3-methylbut-2-enyl)acetophenone **13** and 3,8-diisopropylbenzo[1,2-*b*: 3,4-*b'*]difuran **14**. Pd^{II} mediated rearrangement of **12** gave only the partially deprenylated ether, 3-acetyl-4-hydroxy-2-(3-methylbut-2-enyloxy)acetophenone **15** (29%). While the isomeric ether **18** gave the monoprenyl ether, 5-acetyl-4-hydroxy-2-(3-methylbut-2-enyloxy)acetophenone **19** in quantitative yield (95%). The rearrangement products were characterised and their formation rationalised in terms of allowed sigmatropic shifts ([3,3] prenyl and [1,5]H) followed by loss of prenyl or acetyl groups. The reactions of prenyl ethers are both comparable to those of the corresponding allyl ethers and consistent with the greater fixed double-bond character of the naphthalene system compared to that of benzene. Prenyl derivatives of benzene and naphthalene containing *ortho*-hydroxyacetophenone units were formed which have potential in synthesis.

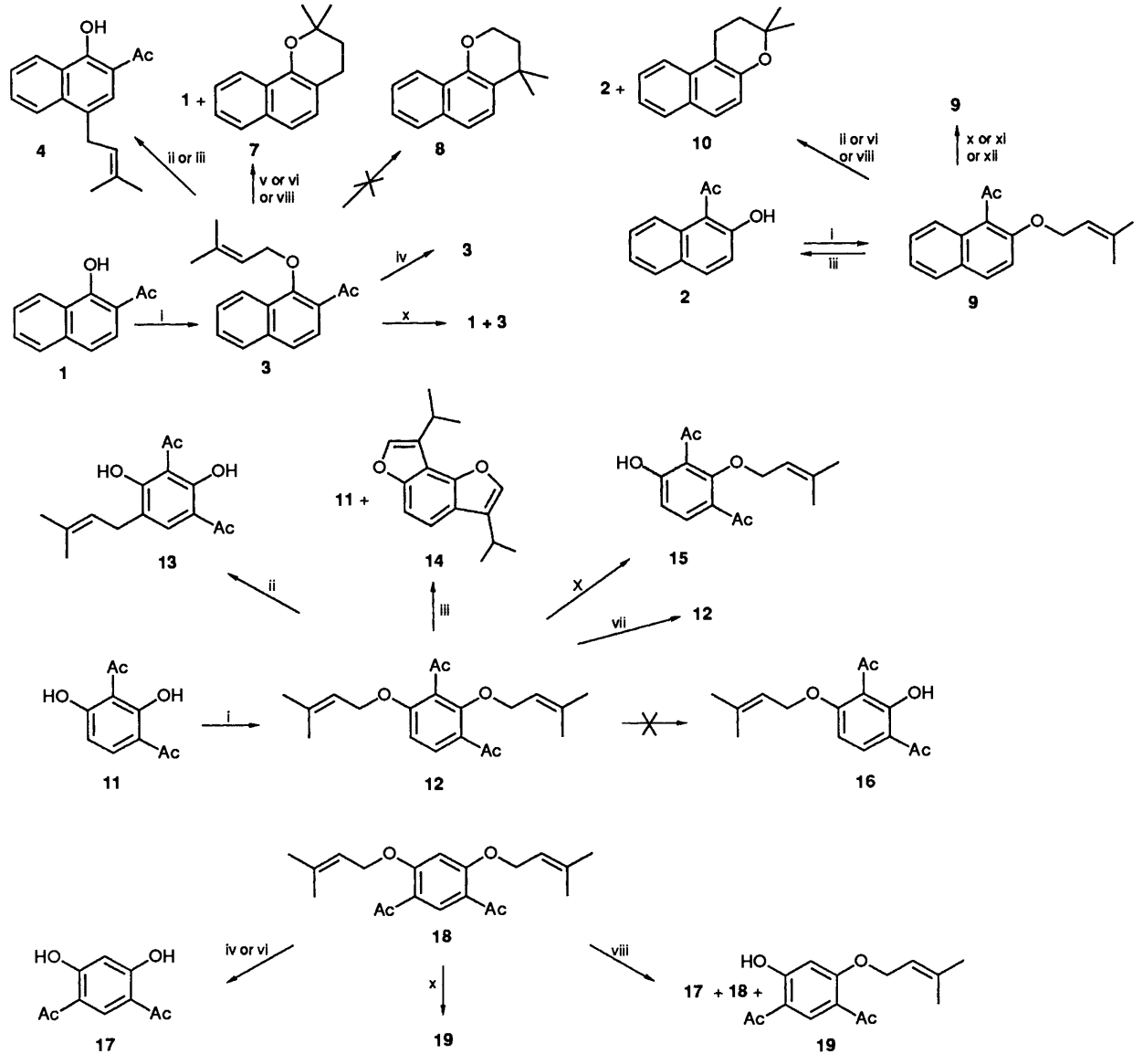
Earlier Claisen rearrangement studies of the bisallyl ethers of 4,6- and 2,4-diacetylresorcinols,[1,2] diprenyl[3] and diprop-2-ynyl[4] ethers of 4,6-diacetylresorcinol,[5,6] and allyl[7] and prop-2-ynyl[4] ethers of 2-acetyl-1-hydroxy-[8] and 1-acetyl-2-hydroxy-naphthalene,[8] gave both mechanistic details of the rearrangement and intermediates, *e.g.* allyl and prenyl substituted *ortho*-hydroxyacetophenones and allyl and prop-2-ynyl derivatives of *ortho*-hydroxyacetonaphthones, having potential as starting materials for benzo- and naphtho-pyrans. Loss of acetyl, allyl, prenyl and prop-2-ynyl groups was observed together with [1,5]sigmatropic H and acetyl shifts accompanied by the [3,3]allyl, prenyl, or prop-2-ynyl shifts.[9] Results for the allyl ethers of acetylnaphthols are consistent with the greater fixed double bond character of the naphthalene system compared to that of benzene. Similar studies on the corresponding prenyl ethers have significance since the expected products are related to natural products having *O*-prenyl,[10] *C*-prenyl or dimethylpyran,[10–12] or substituted furan[13] components. With this in mind we have extended our studies to the prenyl ethers of 2-acetyl-1-hydroxy- and 1-acetyl-2-hydroxynaphthalenes and diprenyl ethers of 2,4- and 4,6-diacetylresorcinols. The thermal studies involved heating the compound either in refluxing *N,N*-dimethylaniline (DMA) or neat at 185 °C. The catalytic studies involved either a protic or Brønsted acid (CF_3CO_2H) or an aprotic or Lewis acid [BF_3·OEt_2 and $PdCl_2(MeCN)_2$].

Results and Discussion

2-Acetyl-1-hydroxy- **1**,[8] 1-acetyl-2-hydroxy-naphthalene **2**,[8] gave the prenyl ethers in poor yield when treated with prenyl bromide–acetone–K_2CO_3 while 2,4-diacetylresorcinol **11**[6] failed to react. However, the respective prenyl ethers **3**, **9** and **12** (Scheme 1) were prepared in good yield (80–95%) in the presence of equimolar quantities of KI.[14] Product characterisation was on the basis of ^1H NMR spectral results (see Experimental section).

The ether **3**, an oil, when heated in refluxing DMA or neat (185 °C in an oil-bath) gave a greenish yellow product in 50 and 65% yield respectively. The product contained an *ortho*-hydroxyacetyl system (ν_{max} 1630 cm^{-1}) and the acetyl [δ 2.55 (3 H, s)] and *C*-prenyl protons [δ 1.73 (6 H, s, 2 × *gem* CH_3), 3.53 (2 H, d, $ArCH_2$), and 5.28 (1 H, t, CH=)] were readily recognised from its ^1H NMR spectrum. Three structures **4**, **5** or **6** (Schemes 1 and 2), were possible with the *C*-prenyl group at C-4, -7, or -5 of the naphthalene unit. These might be derived from the intemediate dienone structures **B**, **D** and **E** (Scheme 2), formed by successive [3,3] prenyl shifts from the initially formed intermediate, **A**, from compound **3**. The chemical shifts of the aromatic protons of 2-acetyl-1-naphthol **1**[15] or its prenyl ether **3** at increasing field strength are 8-H, 5-H, 7-H, 6-H, 4-H and 3-H. The 8-H and 5-H signals (both dd), appearing downfield, are easily recognisable. The *ortho* coupled 3-H (d) appears upfield at δ 7.1 in compound **1** and at δ 7.33 in compound **3**, somewhat deshielded in the latter in view of the presence of a free 2-acetyl group, unlike in the former where it is chelated to 1-OH. The remaining protons 7-H, 6-H and 4-H appeared as an unresolved multiplet. The upfield 3-H doublet became a singlet in the rearranged product whilst the pattern of 8-H, 5-H and the rest was undisturbed, suggesting its structure as 2-acetyl-4-(3-methyl-2-enyl)-1-naphthol **4**. The isolation of **4** as the major product and not isomers **5** and **6**, was understandable when the stabilities of the respective intermediates (**B**, **D** and **E**) were considered; intermediate **B** is the most stable with the benzene system intact.

The prenyl ether **3** when stirred in trifluoroacetic acid (TFA) at 0 °C was recovered unchanged whilst at room and reflux temperatures it furnished compound **1** (11%) after deprenylation and 3,4-dihydro-2,2-dimethyl-2*H*-naphtho[1,2-*b*]pyran **7** (9%)[11] by rearrangement and cyclisation. The formation of compound **7** rather than compound **8** (Scheme 3) which is normally expected by *ortho*-Claisen rearrangement followed by cyclisation, can be explained in terms of an intermediate spiro-

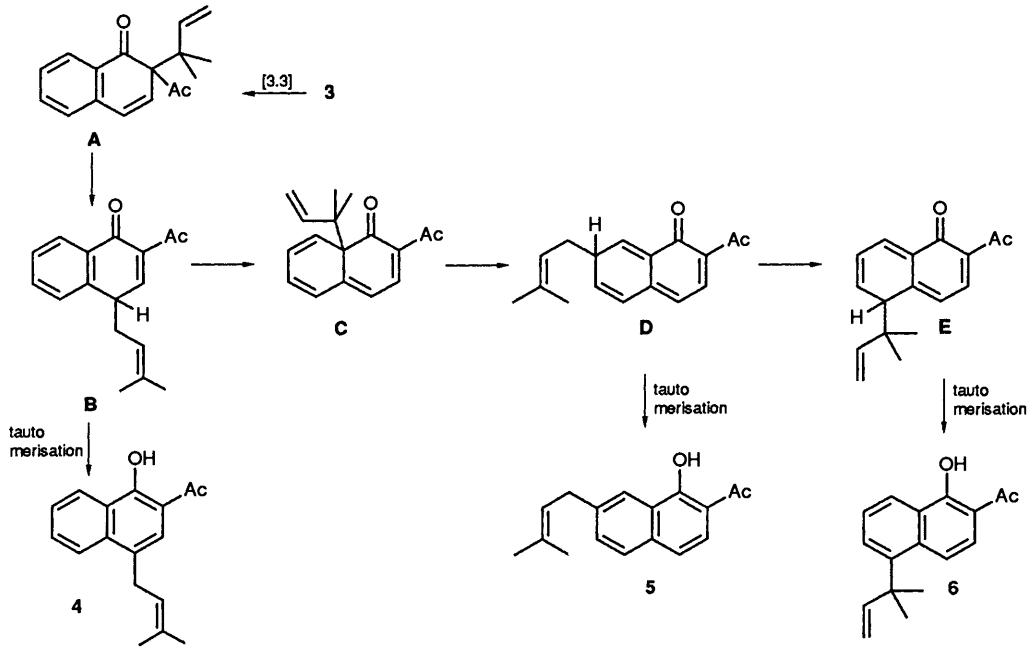


Scheme 1 *Reagents*: i, Prenyl bromide, K_2CO_3, KI, acetone reflux; ii, *N,N*-dimethylaniline, 193 °C, N_2; *iii*, neat 185 °C, N_2; iv, TFA, 0 °C, N_2; v, TFA, room temp., N_2; vi, TFA, reflux, N_2; vii, BF_3·OEt_2 in dioxane, reflux, N_2; viii, BF_3·OEt_2 in CCl_4, room temp. N_2; ix, BF_3·OEt_2 in CCl_4 reflux N_2; x, $PdCl_2(CH_3CN)_2$, dioxane, reflux, N_2; xi, $PdCl_2(CH_3CN)_2$, xylene, reflux, N_2; xii, $PdCl_2(CH_3CN)_2$, CCl_4, room temp. N_2

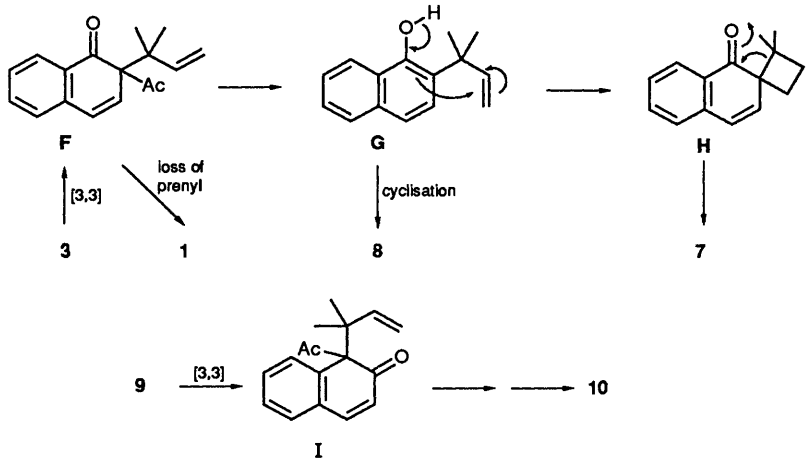
cyclobutane[16] **C**. The initially formed intermediate dienone **F** gives **G** by loss of acetyl. The intermediate **G** could then give either compound **8** by cyclisation or compound **7** by rearrangement *via* intermediate **H**. The loss of prenyl from **F** gives **1**. The same product composition **1** (8%) and **7** (6%) was obtained by treating compound **3** in the presence of BF_3·OEt_2 with Pd^{II} mediation to give the deprenylated compound **1** (16%) and the rearranged compound **4** (29%) in refluxing dioxane.

The isomeric prenyl ether **9** when subjected to Claisen rearrangement in refluxing DMA gave the deprenylated compound **2** (39%) and 1,2-dihydro-3,3-dimethyl-3*H*-naphtho-[2,1-*b*]pyran **10**[16] (3%). Formation of compound **10** probably involves a spiro intermediate[16] (cf. compound **7**). Products **2** (23 and 68%) and **10** (43 and 25%) were also obtained when **9** was heated in refluxing TFA or treated with BF_3·OEt_2, respectively. The ether **9** when heated neat gave only compound **2** (69%) resulting from deprenylation; Pd^{II} mediation had no effect starting material being recovered (74–87%). Increased amount of catalyst had little effect on the reaction. The resistance of compound **9** to rearrangement, compared to compound **3**, under similar conditions, may be due to the greater stabilities of the 2-naphthyl derivatives.

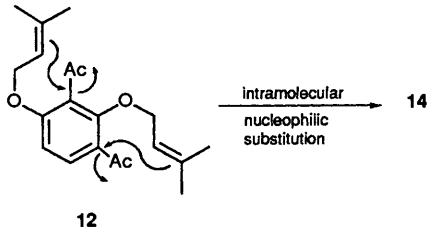
The diprenyl ether **12**, obtained by prenylation of 2,4-diacetylresorcinol **11**,[6] was subjected to Claisen rearrangement in refluxing DMA to give 3-acetyl-2,4-dihydroxy-5-(3-methylbut-2-enyl)acetophenone **13**,[3] identical with the product obtained by thermal rearrangement of 5-acetyl-2,4-bis(3-methylbut-2-enyloxy)acetophenone **18**.[3] It was formed by *para*-Claisen rearrangement followed by loss of one prenyl group. The ether **12** when heated neat gave **11** in slightly better yield (22%) and a new compound (M^+, 256) (18%). It gave no colouration with alc. $FeCl_3$ indicating involvement of the oxygen atom in an ether linkage and no free OH. Its ^1H NMR spectrum lacked both the aromatic acetyl protons indicating their loss during rearrangement. The isopropyl pattern appeared [δ 1.0 (12 H, d, 4 × *gem* CH_3) and 2.0 (2 H, m, 2 × 4-H)] in addition to a doublet for oxymethylene protons [δ 4.1 (4 H)], indicating formation of two similar isopropyl substituted furan rings. The aromatic protons appeared at δ 7.50–7.85 (2 H, m). The above spectral observations suggested that the compound was 2,3,7,8-tetrahydrodiisopropylbenzo[1,2-*b*:3,4-*b*′]difuran **14**, the formation (Scheme 4) of which was believed to be intramolecular nucleophilic substitution of an acetyl group initiated by the prenyl group.



Scheme 2



Scheme 3



Scheme 4

The ether **12** when stirred in TFA gave the deprenylated derivative **11** (95%) while it was recovered unchanged in the presence of BF_3·OEt_2. Increased amounts of catalyst had no effect on the reaction. Pd^{II} mediation gave partial deprenylation to afford **11** (31%) and a new compound (29%) which gave a red colour with alc. $FeCl_3$. Its ^1H NMR spectrum containing two different chelated acetyls (ν_{max} 1700 and 1660 cm^{-1}) [δ 2.57 and 2.60 (3 H each, s, $COCH_3$)] and only one set of *O*-prenyl protons [δ 2.76 and 2.60 (3 H each, s, *gem* CH_3), 4.65 (2 H, d, OCH_2) and 5.45 (1 H, t, CH=)] and a phenolic proton (D_2O exchangeable) at δ 13.2 (1 H, s) suggested it to be a monoprenyl ether obtained by partial deprenylation. The monoprenyl ether could have either structure **15** or **16**. The upfield shift of 5-H from δ 6.60 in compound **12** to δ 6.47 in the product must be due to the shielding effect of 4-OH, thereby suggesting its structure as 3-acetyl-4-hydroxy-2-(3-methylbut-2-enyloxy)acetophenone **15**.

The Claisen rearrangement of the diprenyl ether **18** was studied [3] under a variety of thermal conditions. Its rearrangement in the presence of catalysts [TFA, BF_3·OEt_2, and $PdCl_2(MeCN)_2$] has been reported here. It was deprenylated in TFA giving compound **17** (95%). In the presence of BF_3·OEt_2 in addition to compound **17** (10%) it gave a new compound (48%) which gave red colour with alc. $FeCl_3$. Its ^1H NMR spectrum accounted for two acetyls [δ 2.59 (6 H, s)], one chelated phenolic hydroxyl [(D_2O exchangeable) δ 12.9 (1 H, s)] and only one prenyl unit [δ 1.77 and 1.81 (3 H each, s, *gem* CH_3), 4.40 (2 H, d, OCH_2) and 5.50 (1 H, t, CH=)] suggesting it to be a monoprenyl ether **19** of **17**. An increase in temperature gave complete deprenylation and formation at **17** (98%). Since in the presence of Pd^{II}, the ether **18** gave the monoprenyl ether **19** in 95% yield, this is a convenient preparative method, direct prenylation always leading to a mixture of mono- and di-prenyl ethers.

A summary of the significant observations from the Claisen

rearrangements described are as follows (a) Thermal Claisen rearrangement of compound **3** gave a 4-prenylated derivative **4** by *para*-Claisen rearrangement while the isomer **9** gave, *via* the *ortho* rearranged product the naphthopyran **10**. (b) Deprenylation was not observed in the thermal Claisen rearrangement of compound **3** while it was the sole process in compound **9**, a result of the prenyl group being in the *peri* position in intermediate **I**, unlike in **A**. (c) The steric hindrance exerted by the *gem* methyls in the intermediate dienones, **A** or **I**, disallowed cyclisation *in situ* to give the 4,4-dimethylnaphthopyrans but, initiated rearrangement through spirocyclobutane intermediates to give the stable 2,2-dimethylnaphthopyrans **7** and **10**. (d) While Pd^{II} mediated rearrangement had no effect on compound **9**, it effected deprenylation with compound **3**, possibly as a result of the relative stability of 2-naphthyl compounds. (e) The above observations are in tune with the positional isomerism of the 1-naphthyl and 2-naphthylprenyl ether series, and the fixed double bond character of the naphthalene system unlike that in benzene, the [3,3] rearrangements being from C-1 to C-2 and C-2 to C-4 in the former and C-2 to C-1 in the later but not from C-2 to C-3. (f) Thermal rearrangement of compound **12**, in solvent, gave a *para* rearranged product **13**, but when heated neat, it gave compound **14** by intramolecular nucleophilic substitution of acetyl by prenyl group probably resulting out of greater steric compression in the neat condition. (g) Although the catalysis of CF_3CO_2H,[17] $BF_3{\cdot}OEt_2$,[18,19] and $PdCl_2$-$(CH_3CN)_2$[20] resulted in the rearranged products with allyl ethers,[7] the prenyl ethers, under similar conditions, were either recovered unchanged or gave the deprenylated derivatives.

Experimental

M.p.s were recorded on a VEB Analytik Dresden hot stage apparatus and are uncorrected. Unless otherwise stated UV spectra were obtained in MeOH with a Shimadzu-UV-260 spectrophotometer, IR spectra were recorded in $CHCl_3$ on a Shimadzu-IR-408 spectrophotometer, ^1H NMR spectra were recorded on a Perkin-Elmer R32 (90 MHz) spectrometer in $CDCl_3$ using TMS [$(CH_3)_4Si$] as internal standard (*J* values in Hz), and electron impact mass spectroscopy (EI-MS) was carried out with JEOL-D 300 and Varian Mat 112S spectrometers. Preparative TLC (PLC) conducted on glass plates coated with silica gel-G (particle size 75, Acme) and column chromatography using silica gel (100–200 mesh, Acme). Spots on TLC were detected under UV light. Solvents used were of LR grade and were purified by general methods. Commercial [3-methylbut-2-enyl bromide and $BF_3{\cdot}OEt_2$ (Fluka)] and [DMA, TFA and $PdCl_2$ (E. Merk)] were used. All the organic extracts were dried over $MgSO_4$. All the rearrangements were carried out under N_2 atmosphere.

2-Acetyl-1-(3-methylbut-2-enyloxy)naphthalene **3**.—A mixture of compound **1** (1 g, 5.38 mmol), 3-methylbut-2-enyl bromide (0.58 cm^3, 6.72 mmol), and freshly ignited K_2CO_3 (5 g), were refluxed in dry acetone (50 cm^3) for 3 h. The acetone solution was distilled under reduced pressure and the resulting product was treated with water and extracted with $CHCl_3$ (3 × 50 cm^3). The combined extracts were dried and evaporated to give a *pale yellow oil* **3** (96 mg, 7%) which gave no colouration with alc. $FeCl_3$ (Found: C, 80.2; H, 6.9. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.0%); λ_{max}/nm 213 (log ε 3.93) and 244 (3.70); ν_{max}(neat)/cm^{-1} 2950, 2900, 1685(CO), 1650, 1590, 1450, 1250, 1230, 1190, 1100, 1060, 860, 750, 710 and 610; δ(CCl_4) 1.73 (6 H, s, 2 × *gem* CH_3), 2.63 (3 H, s, $COCH_3$), 4.48 (2 H, d, *J* 8, OCH_2), 5.53 (1 H, t, *J* 8, CH=), 7.33 (1 H, d, *J* 9, 3-H), 7.35–7.59 (3 H, m, 4-, 6- and 7-H), 7.69 (1 H, dd, *J* 1.1 and 7.9, 5-H) and 8.13 (1 H, dd, *J* 1.4 and 8.1, 8-H); *m/z* 254 (M^+, 100%), 239 [(M − CH_3), 36], 211 [(M − $COCH_3$), 25], 199 [M − $C(CH_3)_2CH$, 12], 186 [(M − $CH_2CCH_3CHCH_2$), 60], 171 (35), 155 (19), 69 [$(CH_3)_2CCHCH_2$, 55] and 43 [($COCH_3$), 70].

The above prenylation when carried out in presence of KI (0.89 g, 5.38 mmol) resulted in the formation of compound **3** (1.09 g, 80%).

Claisen Rearrangement of Compound **3**.—(*a*) *In* N,N-*dimethylaniline*. Compound **3** (1 g, 3.94 mmol) was refluxed in freshly distilled DMA (b.p. 193 °C) (10 cm^3) for 1 h. The reaction mixture was poured into ice-cold HCl (300 cm^3) and the resulting pale greenish yellow mass was extracted with $CHCl_3$ (3 × 100 cm^3). The combined extracts were dried and evaporated to give crystalline *2-acetyl-4-(3-methylbut-2-enyl)-1-naphthol* **4** which showed a major spot on TLC, R_F 0.55 (hexane–ethyl acetate, 95:5), and crystallised as pale greenish yellow needles (500 mg, 50%), m.p. 68 °C (from light petroleum; b.p. 60–80 °C). It gave a bright green colour with alcoholic $FeCl_3$ (Found: C, 80.1; H, 7.0. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.0%); λ_{max}/nm 223 (log ε 4.18), 264 (4.14), 272 (4.13), 290 (3.46), 300 (3.40), 314 (3.18) and 374 (3.4539); ν_{max}/cm^{-1} 2950, 1630 (CO), 1400, 1330 and 985; δ(CCl_4) 1.73 (6 H, s, 2 × *gem* CH_3), 2.55 (3 H, s, $COCH_3$), 3.53 (2 H, d, *J* 8, $ArCH_2$), 5.28 (1 H, t, *J* 8, CH=), 7.33 (1 H, s, 3-H), 7.35–7.70 (2 H, m, 6- and 7-H), 7.83 (1 H, dd, *J* 1.1 and 7.9, 5-H), 8.43 (1 H, dd, *J* 1.4 and 8.1, 8-H) and 13.80 (1 H, s, OH), *m/z* (M^+, 100%), 239 [(M − CH_3), 24], 211 [(M − $COCH_3$), 24], 199 [M − $C(CH_3)_2CH$, 32], 186 [(M − $CH_2CCH_3CHCH_2$), 14] and 43 [($COCH_3$), 80].

(*b*) *By heating neat at* 185 °C. Compound **3** (1 g, 3.94 mmol) was heated at 185 °C for 3 h. The resulting yellow oil (950 mg) was separated by PLC (hexane–ethyl acetate, 95:5). The major band, R_F 0.55, was extracted to give compound **4** (650 mg, 65%).

(*c*) *In trifluoroacetic acid*. Compound **3** (1 g, 3.94 mmol) was stirred in TFA (10 cm^3) at 0 °C for 6 h. The mixture was then poured into an excess of water and extracted with $CHCl_3$ (3 × 100 cm^3). The combined extracts when dried and concentrated gave recovered starting ether **3** (900 mg, 90%). Stirring at room temperature for 6 h yielded compound **1** (70 mg, 10%) and compound **7**.

Compound **7** was a yellow oil (81 mg, 9%) which gave no colouration with alc. $FeCl_3$ (Found: C, 84.5; H, 7.1. Calc. for $C_{15}H_{16}O$: C, 84.9; H, 7.5%); δ(CCl_4) 1.35 (6 H, s, 2 × *gem* CH_3), 1.82 (2 H, t, *J* 7, $ArCH_2CH_2$), 2.97 (2 H, t, *J* 7, $ArCH_2$), 7.16–7.60 (5 H, m, 5-, 6-, 7-, 8- and 9-H) and 8.22 (1 H, dd, *J* 1.4 and 8.1, 10-H).

(*d*) *In boron trifluoride–diethyl ether*. Compound **3** (1 g, 3.94 mmol) was stirred at room temperature for 2 h in CCl_4 (25 cm^3) containing $BF_3{\cdot}OEt_2$ (0.49 cm^3, 3.89 mmol). The solvent was removed under reduced pressure and the residue treated with an excess of water and extracted with $CHCl_3$ (3 × 100 cm^3). The combined extracts were dried and concentrated under reduced pressure to give a yellow oil mixture (850 mg) which was column chromatographed to give the products **1** (64 mg, 9%) and **4** (55 mg, 6%), obtained earlier.

(*e*) *With palladium chloride–bis(acetonitrile)*. Compound **3** (1 g, 3.94 mmol) was refluxed for 6 h in dioxane (25 cm^3) containing $PdCl_2$–$(MeCN)_2$ (0.204 g, 0.79 mol). The reaction mixture was then filtered and the filtrate evaporated under reduced pressure to give a brown oily mixture (850 mg) which was column chromatographed to give compounds **1** (120 mg, 16%) and **4** (290 mg, 29%).

1-Acetyl-2-(3-but-2-enyloxy)naphthalene **9**. A mixture of compound **2** (1 g, 5.38 mmol), 3-methylbut-2-enyl bromide (0.58 cm^3, 6.72 mmol), freshly ignited K_2CO_3 (5 g), and KI (0.89 g, 5.37 mmol) were refluxed in dry acetone (50 cm^3). Work-up gave a pale brown oil (1.23 g, 90%) which gave no colouration with alc. $FeCl_3$ (Found: C, 80.2; H, 6.9. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.0%); λ_{max}/nm 220 (log ε 4.43), 280 (3.28), and 335 (2.98);

ν_{max}(neat)/cm^{-1} 3080, 3000, 2950, 1718(CO), 1638, 1600, 1590, 1520, 1480, 1440, 1380, 1340, 1285, 1160, 1060, 1010, 978, 900, 820 and 760; δ(CCl_4) 1.68 (3 H, s, *gem*, CH_3), 1.74 (3 H, s, *gem*, CH_3), 2.55 (3 H, s, $COCH_3$), 4.56 (2 H, d, *J* 8, OCH_2), 5.41 (1 H, t, *J* 8, CH=), 7.15 (1 H, d, *J* 9, 3-H) and 7.30–7.82 (5 H, m, 4-, 5-, 6-, 7- and 8-H); *m/z* 254 (M^+, 52%), 212 (13), 199 [M − $(CH_3)_2CH$, 12], 186 [(M − $CH_2CCH_3CHCH_2$), 58], 171(42), 144(100), 115(46), 69 [$(CH_3)_2CHCH_2$, 20] and 43 ($COCH_3$, 23).

Claisen Rearrangement of Compound **9**.—(*a*) *In* N,N-*dimethylaniline*. Compound **9** (1 g, 3.94 mmol) was refluxed in freshly distilled DMA (10 cm^3) for 90 min. Work-up gave a reddish brown gum (800 mg) which showed two major spots on TLC, R_F 0.76 and 0.36 (hexane–ethyl acetate, 95:5). It was resolved by PLC to give compound **2** (286 mg, 39%) and 1,2-dihydro-2,2-dimethylnaphtho[2,1-*b*]pyran **10**.

Compound **10** was obtained as a green oil (31 mg, 3%) which gave no colouration with alc. $FeCl_3$ (Found: C, 84.6; H, 7.2. Calc. for $C_{15}H_{16}O$: C, 84.9; H, 7.5%); δ 1.36 (6 H, s, 2 × *gem* CH_3), 1.90 (2 H, t, *J* 7, $ArCH_2CH_2$), 2.99 (2 H, t, *J* 7, $ArCH_2$), 7.00 (1 H, d, *J* 9, 5-H) and 7.15–7.80 (5 H, m, 6-, 7-, 8-, 9- and 10-H).

(*b*) *By heating neat at* 185 °C. Compound **9** (1 g, 3.94 mmol) was heated at 185 °C for 3 h to give a pale brown oil (950 mg) which was separated by PLC to give compound **2** (498 mg, 68%).

(*c*) *In trifluoroacetic acid.* Compound **9** (1 g, 3.94 mmol) was refluxed in TFA (10 cm^3) for 2 h. Work-up gave a red oil (800 mg) which showed two major spots on TLC, R_F 0.76 and 0.36 (hexane–ethyl acetate, 95:5). It was resolved by PLC to give compounds **2** (230 mg, 34%) and **10** (360 mg, 43%).

(*d*) *With boron trifluoride–diethyl ether.* Compound **9** (1 g, 3.94 mmol) was taken in CCl_4 (25 cm^3) containing BF_3·OEt_2 (0.49 cm^3, 3.89 mmol) and stirred at room temperature for 4 h; work-up gave a brown oil (875 mg) which was separated by PLC to give compounds **2** (498 mg, 68%) and **10** (220 mg, 25%).

(*e*) *With palladium chloride–bis(acetonitrile).* Compound **9** (1 g, 3.94 mmol) in dioxane (25 cm^3) containing $PdCl_2$-$(CH_3CN)_2$ (0.204 g, 0.78 mmol) was refluxed for 10 h. Work-up followed by column chromatography gave recovery of compound **9** (825 mg, 83%). The same reaction in refluxing xylene gave recovery of compound **9** (740 mg, 74%). Increased amounts of Pd^{II} (1.02 g, 3.94 mmol) at room temperature gave recovery of compound **9** (875 mg, 88%).

3-*Acetyl*-2,4-*bis*(3-*methylbut*-2-*enyloxy*)*acetophenone* **12**.—A mixture of 2,4-diacetylresorcinol **11** (1 g, 5 mmol), 3-methylbut-2-enyl bromide (0.6 cm^3, 10.3 mmol), and freshly ignited K_2CO_3 (5 g) was refluxed in acetone (50 cm^3) for 6 h. Work-up gave recovery of compound **11** (700 mg, 70%).

The above prenylation carried out for 3 h in the presence of KI (0.89 g, 5.376 mmol) however, gave the compound as a pale yellow solid (1.61 g, 95%), m.p. 62 °C (from benzene), which gave no colouration with alc. $FeCl_3$ (Found: C, 72.6; H, 8.1. $C_{20}H_{26}O_4$ requires C, 72.7; H, 7.9%); λ_{max}(EtOH)/nm 205 (log ε 3.96), 245 (4.08), 268 (3.91) and 347 (3.57); ν_{max}(Nujol)/cm^{-1} 2930, 2860, 1690 (CO), 1600, 1460, 1390, 1310, 1260, 1085, 980 and 910; δ(CCl_4) 1.60 (12 H, s, 4 × *gem* CH_3), 2.35 (3 H, s, 3-$COCH_3$), 2.42 (3 H, s, 1-$COCH_3$), 4.26 (2 H, d, *J* 7, 1-OCH_2), 4.48 (2 H, d, *J* 7, 3-OCH_2), 5.32 (2 H, t, *J* 7, 2 × CH=), 6.60 (1 H, d, *J* 9, 5-H) and 7.40 (1 H, d, *J* 9, 6-H); *m/z* 330 (M^+, 1%), 287 [(M − $COCH_3$), 1], 263 (41), 262 [(M − CH_2CCH_3CH-CH_2), 84], 247 [(M − $CH_2CCH_3CHCH_2$ − CH_3), 33], 219 [(M − $CH_2CCH_3CHCH_2$ − CH_3 − CO), 66], 207 [(M − $CH_2CCH_3CHCH_2$ − $C(CH_3)_2CH$, 85], 201 (21), 192 (22), 189 (19) and 43 ($COCH_3$, 100).

Claisen Rearrangement of Compound **12**.—(*a*) *In* N,N-*dimethylaniline*. Compound **12** (1 g, 3 mmol) was refluxed in freshly distilled DMA (10 cm^3) for 90 min. Work-up followed by column chromatography yielded 3-acetyl-2,4-dihydroxy-5-(3-methylbut-2-enyl)acetophenone **13**[5] (87 mg, 11%).

(*b*) *By heating neat at* 185 °C. Compound **12** (1 g, 3 mmol) was heated at 185 °C for 2 h. The resulting pale brown oil showed two major spots on TLC, R_F 0.65 and 0.53 (hexane–ethyl acetate, 85:15). Separation by column chromatography gave compound **11** (129 mg, 22%) and a new compound (liq. 18%) which gave no colouration with alc. $FeCl_3$ (Found: C, 77.8; H, 8.8. $C_{16}H_{22}O_2$ requires C, 78.0; H, 8.9%); λ_{max}/nm 193 (log ε 3.63) and 270 (3.12); δ 1.0 (12 H, d, *J* 8, 4 × *gem* CH_3), 2.0 (2 H, m, 4-H), 4.1 (4 H, d, *J* 8, 2 × OCH_2) and 7.50–7.85(2) H, m, 2 × Ar-H); *m/z* 256 (M^+, 6), 149 (25), 97 (24), 71 (41), 69 (44), 65 (38), 63 (53), 60 (25), 57 (75), 47 (24), 43 [$(CH_3)_2CH$, 100] and 41 (73).

(*c*) *In trifluoroacetic acid.* Compound **12** (1 g, 3 mmol) was stirred in TFA (10 cm^3) at 0 °C for 3 h. Work-up followed by crystallisation gave compound **11** (558 mg, 95%).

(*d*) *With boron trifluoride–diethyl ether.* Compound **12** (1 g, 3 mmol) was refluxed for 6 h in dioxane (25 cm^3) containing BF_3·OEt_2 (0.0076 cm^3, 0.6 mmol). Work-up gave recovery of compound **12** (900 mg, 90%). A similar result was obtained with BF_3·OEt_2 (0.015 cm^3, 1.2 mmol).

(*e*) *With palladium chloride–bis(acetonitrile).* Compound **12** (1 g, 3 mmol) was refluxed for 45 min in dioxane (25 cm^3) containing $PdCl_2(MeCN)_2$ (151 mg, 0.6 mmol). Work-up gave a brown oil (800 mg) which showed two major spots on TLC, R_F 0.34 and 0.53 (hexane–ethyl acetate, 85:15). Separation by column chromatography yielded compound **11** (180 mg, 31%) and a new compound 3-*acetyl*-4-*hydroxy*-2-(3-*methylbut*-2-*enyloxy*)*acetophenone* **15** (230 mg, 29%). This crystallised as needles, from hexane–chloroform m.p. 51 °C. It gave a red colour with alc. $FeCl_3$ (Found: C, 68.5; H, 6.8. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%); λ_{max}/nm 204 (log ε 4.22), 2.40 (4.15), 271 (4.18) and 312 (3.78); ν_{max}(neat)/cm^{-1} 2910, 1700 (CO), 1660, (chelated CO), 1600, 1585, 1485, 1415, 1355, 1260, 1200, 1145, 1080, 1060, 980, 925 and 785; δ2.76 (3 H, s, *gem* CH_3), 2.80 (3 H, s, *gem* CH_3), 2.57 (3 H, s, 3-$COCH_3$), 2.1 (3 H, s, 1-$COCH_3$), 4.65 (2 H, d, *J* 7.87, OCH_2), 5.45 (1 H, t, *J* 6.75, CH=), 6.47 (1 H, d, *J* 9, 5-H), 7.80 (1 H, d, *J* 9, 6-H) and 13.2 (1 H, s, OH); *m/z* 262 (M^+, 30), 261 [(M − 1), 1], 207 [M − $C(CH_3)_2CH$, 2], 194 [(M − $CH_2CCH_3CHCH_2$, 42], 179 [(M − $CH_2CCH_3CHCH_2$, −CH_3), 52], 69 [$C(CH_3)_2$-$CHCH_2$, 100], 43 ($COCH_3$, 28) and 41 (62).

Claisen Rearrangement of 5-*Acetyl*-2,4-*bis*(3-*methylbut*-2-*enyloxy*)*acetophenone* **18**.—(*a*) *In trifluoroacetic acid.* Compound **18** (1 g, 3 mmol) in TFA (10 ml) was stirred at 0 °C for 24 h. Work-up followed by crystallisation gave compound **17** (559 mg, 95%).

(*b*) *With boron trifluoride–diethyl ether.* Compound **18** (1 g, 3 mmol) taken in CCl_4 (25 cm^3) containing BF_3·OEt_2 (0.007 cm^3, 0.6 mmol) was stirred at room temperature for 7 d. Work-up gave a pale yellow solid (800 mg) which showed three major spots on TLC, R_F 0.67, 0.47 and 0.29 (hexane–ethyl acetate, 85:15). Separation by column chromatography gave compounds **17** (60 mg, 10%), **18** (49 mg, 4%) and a new compound **19**. The same reaction at reflux temperature gave compound **17** (578 mg, 98%).

Compound **19** was obtained as needles (380 mg, 48%), m.p. 83–87 °C (from hexane–chloroform) which gave a red colour with alc. $FeCl_3$ (Found: C, 68.6; H, 6.7. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%); λ_{max}/nm 193 (log ε 4.08), 247 (3.60), 275 (4.25) and 315 (3.82); δ 1.77 (3 H, s, *gem* CH_3), 1.81 (3 H, s, *gem* CH_3, 2.59 (6 H, s, 2 × $COCH_3$), 4.40 (2 H, d, *J* 7, OCH_2), 5.50 (1 H, t, *J* 7, CH=), 6.42 (1 H, s, 3-H), 8.31 (1 H, s, 6-H) and 12.9 (1 H, s, OH); *m/z* 262 (M^+, 12), 247 [(M − CH_3), 4], 207 [M − $C(CH_3)_2CH$, 2], 194[(M − $CH_2CCH_3CHCH_2$), 44],

179 [(M − $CH_2CCH_3CHCH_2$), $-CH_3$, 72], 69 [$C(CH_3)_2$-$CHCH_2$, 100], 43 ($COCH_3$, 29) and 41 (61).

(*c*) *With palladium chloride–bis(acetonitrile)*. Compound **18** (1 g, 3 mmol) in dioxane (25 cm^3) containing $PdCl_2(MeCN)_2$ (157 mg, 0.6 mmol) was refluxed for 4 h. Work-up and column chromatography gave compound **19** (750 mg, 95%).

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