Thermal Claisen Rearrangement of Allyl Ethers of Isomeric Acetylnaphthols

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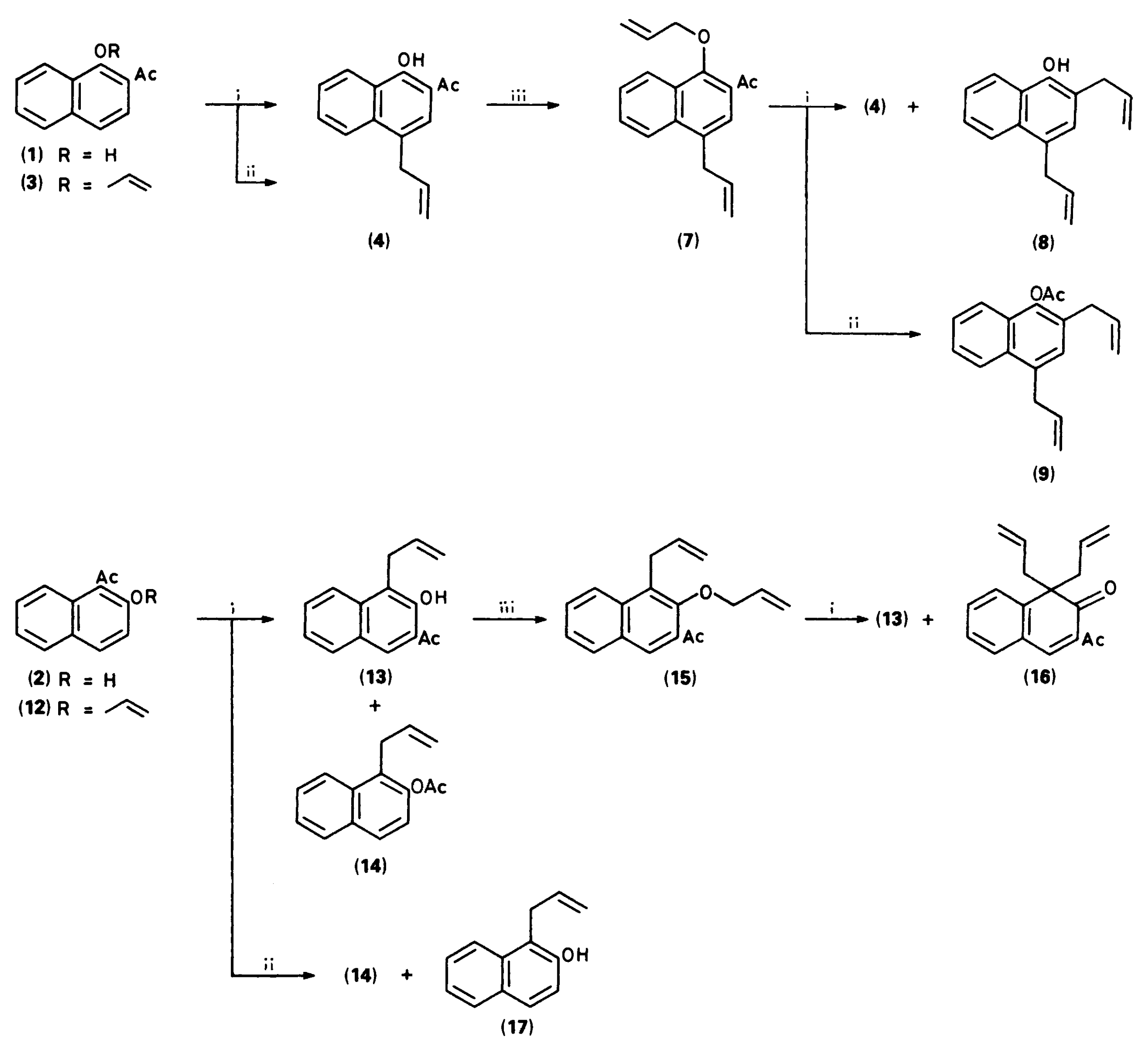
Thermal Claisen rearrangement of the allyl ethers (**3**) and (**12**) of the isomeric 2-acetyl-1-hydroxy- and 1-acetyl-2-hydroxy-naphthalenes (**1**) and (**2**) has been studied by heating each in refluxing *N,N*-dimethylaniline (DMA) and neat at 185 °C under an N_2 atmosphere. 2-Acetyl-4-allyl-1-hydroxynaphthalene (**4**), the sole product isolated from (**3**), was isolated in 56 and 88% yield respectively under the two sets of conditions. The rearrangement of the allyl ether (**12**) gave 3-acetyl-1-allyl-2-hydroxynaphthalene (**13**) (18%) and 2-acetoxy-1-allylnaphthalene (**14**) (23%) in *N,N*-DMA while in the neat rearrangement it gave (**14**) as the major product (70%) along with 1-allyl-2-hydroxynaphthalene (**17**) (20%). The rearrangement of the allyl ether (**7**), obtained on further allylation of (**4**), furnished 2,4-diallyl-1-hydroxynaphthalene (**8**), (15%) and (**4**) (15%) in DMA while it gave 1-acetoxy-2,4-diallylnaphthalene (**9**) as the sole product (67%) in the neat rearrangment. The rearrangement of the allyl ether (**15**), obtained by further allylation of (**13**), in DMA gave 3-acetyl-1,1-diallylnaphthalen-2(1*H*)-one (**16**) (20%) along with (**13**) (6%). The various rearrangement products have been characterised by their spectroscopic data (UV, IR, ^{1}H NMR, and EI-MS) and the reactions rationalised by the allowed sigmatropic shifts such as [3,3] allyl, [1,5] acetyl followed by loss of allyl or acetyl groups. The significant differences noticed in the reactions of the isomeric series of allyl ethers are consistent with the greater fixed double-bond character of the naphthalene system compared to that of benzene as well as the positional isomerism that exists in the allyl ethers. The above Claisen rearrangement studies result in the isolation of some interesting naphthylallyl derivatives with *ortho*-hydroxyacetophenone units which form useful synthetic intermediates for preparing several naphthyl-α- and γ-pyrone derivatives of pharmacological activity.

Our work on the thermal Claisen rearrangements[1,2] of the bisallyl ethers of 4,6- and 2,4-diacetylresorcinols[3,4] during which we observed acetyl loss and [1,5] sigmatropic H and acetyl shifts accompanied by the [3,3] allyl shifts,[5] we have now studied the allyl ethers of 2-acetyl-1-hydroxy- and 1-acetyl-2-hydroxy-naphthalene. In doing this, we hoped to gain insight into how the greater fixed double-bond character of naphthalene affected the course of rearrangement. Although the allyl ethers of acetylnaphthols not been so studied, simple naphthyl allyl ethers[6-14] have.

Results and Discussion

2-Acetyl-1-hydroxy- (**1**)[15] and 1-acetyl-2-hydroxy-naphthalene (**2**)[15] were allylated (allyl bromide/acetone/K_2CO_3) to give the respective allyl ethers (**3**) and (**12**) in quantitative yield. The former, obtained as an oil and characterised on the basis of its ^{1}H NMR spectrum (see Experimental section), on being subjected to Claisen rearrangement in refluxing dimethylaniline (DMA) gave a product consisting of pale greenish yellow crystalline needles (56%). A better yield (88%) of the same product was obtained by heating the allyl ether (**3**) neat at 185 °C in an oil-bath. This product contained an *ortho* hydroxyacetyl system (ν_{max} 1 625 cm^{-1}) all the acetyl protons [δ 2.55 (3 H, s)] and *C*-allyl protons [δ 3.62 (2 H, d, *J* 7.7 Hz, $ArCH_2$), 5.05 (2 H, m, $=CH_2$), and 6.0 (1 H, m, $CH=CH_2$)] were readily recognised from its 1H NMR spectrum. Three structures, (**4**), (**5**), or (**6**) (Scheme 1 and 2), where the C-allyl group might be located at C-4, C-7, or C-5 of the naphthalene unit, were considered possible. These might be derived from the intermediate dienone structures (**B**, **D**, and **E**) (Scheme 2), formed by successive [3,3] allyl shifts from the initially formed intermediate, **A**, from (**3**). The chemical shifts of the aromatic protons of 2-acetyl-1-naphthol (**1**)[16] or its allyl 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, whilst the *ortho* coupled 3-H (d) is upfield, δ 7.1 in (**1**) and at δ 7.4 in (**3**), somewhat deshielded in the latter in the absence of chelation. The remaining protons 7-H, 6-H, and 4-H appear unresolved as a multiplet. The upfield 3-H doublet became a singlet in the rearranged product while the pattern of 8-H, 5-H, and the rest is undisturbed, suggesting its structure as 2-acetyl-4-allyl-1-naphthol (**4**). The isolation of (**4**) as the single major product compared to the possible isomers (**5**) and (**6**) is understandable when the stabilities of the respective intermediates (**B**, **D**, and **E**) are considered; the intermediate, **B**, is the most stable with the benzene system intact.

2-Acetyl-4-allyl-1-hydroxynaphthalene (**4**) was then further allylated (allyl bromide/acetone/K_2CO_3) to give the allyl ether (**7**) in quantitative yield. The product was characterised on the basis of ^{1}H NMR spectrum (see Experimental section) and subjected to further thermal rearrangement in refluxing DMA and also by heating at 185 °C. The former reaction mixture furnished two products; (**4**) (15%) by deallylation and a new diallylnaphthol (15%) which showed the presence of two *C*-allyl protons and the absence of acetyl protons in its ^{1}H NMR spectrum. This supported its structure as 2,4-diallyl-1-naphthol (**8**). The formation of (**8**) in this rearrangement can be readily explained from the intermediate, F (Scheme 2), formed by the initial [3,3] allyl rearrangement which loses an acetyl group or an allyl group straight away or from the intermediates (**G**–**J**) (Scheme 2) obtained by further [3,3] allyl shifts. Of all the intermediates (**F**–**J**), **F** and **G** are thermodynamically more stable compared to the rest with an intact benzenoid ring, giving rise to (**4**). Probably, for the same reason, neither of the diallyl products (**10**) or (**11**) could be isolated from the less stable intermediates **I** and **J**. Neat rearrangement of (**7**) furnished the acetate of (**8**), 1-acetoxy-2,4-diallylnaphthalene (**9**) in high yield

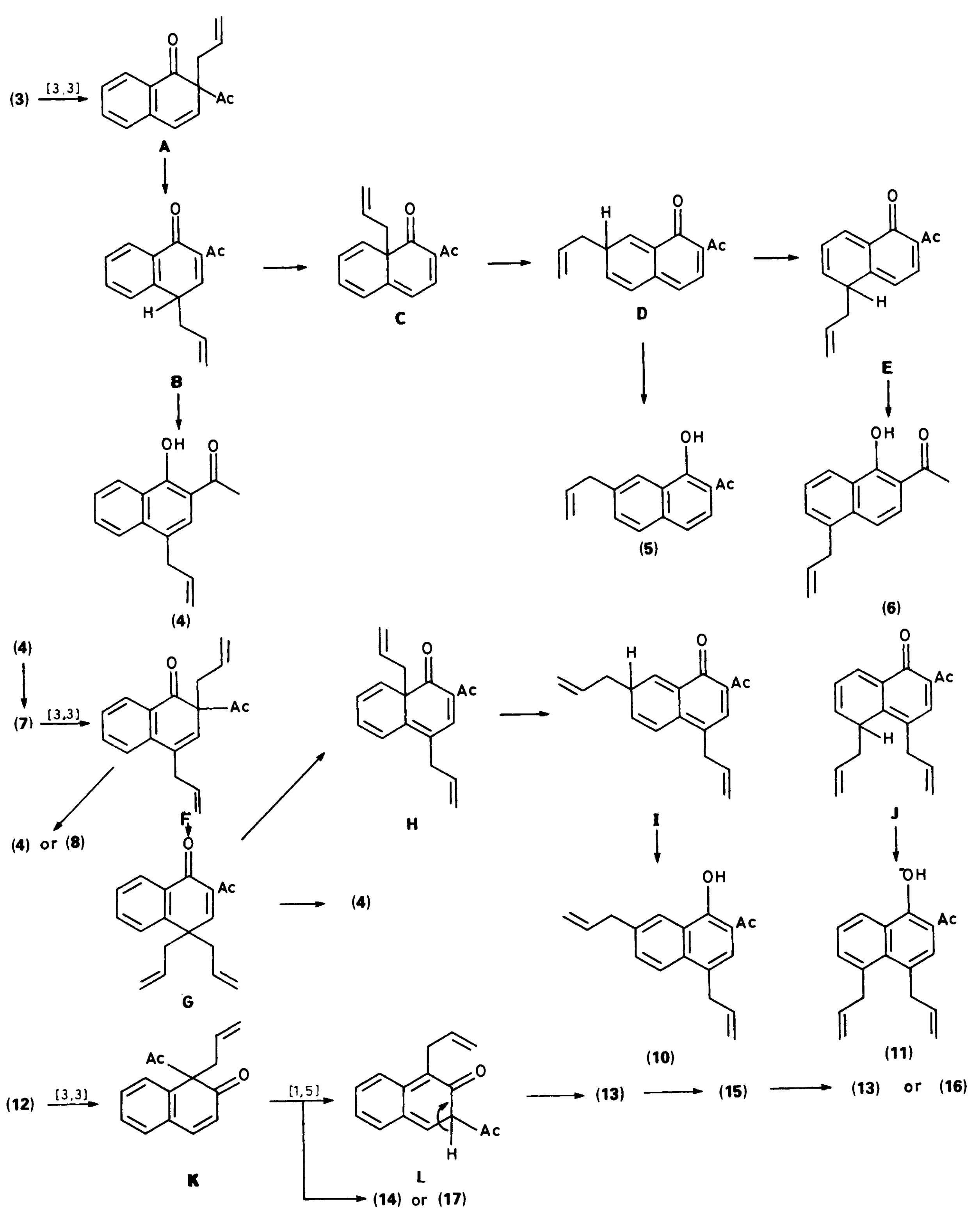


Scheme 1. *Reagents:* i, *N,N*-dimethylaniline, reflux; ii, neat rearrangement, 185 °C, N_2 atmosphere; iii, allyl bromide, K_2CO_3, acetone.

(67%). This could be recognised by the presence of characteristic *O*-acetyl protons at δ 2.30. There was no trace of (**8**) or (**4**).

The allyl ether (**12**) was then subjected to thermal Claisen rearrangement in refluxing DMA and also by heating neat at 185 °C. The former rearrangement yielded two products, one, a naphthol (18%, m.p. 72 °C) and the other a naphthyl acetate (liq. 23%). The ^{1}H NMR and IR spectra of the naphthol showed the presence of a *C*-allyl group in addition to a chelated *ortho*-hydroxyacetyl system (ν_{max} 1 640 cm^{-1}). The most easily recognisable aromatic proton of 1-acetyl-2-naphthol (**2**)[17] or its allyl ether is the 3-H very upfield signal at δ 6.95. This doublet is conspicuously absent in the above rearranged naphthol suggesting the presence of an allyl or acetyl group at this position. Its ^{1}H NMR spectrum showed a neat singlet at δ 8.23 as noted for the 4-H in 3-acetyl-2-naphthol.[17] This established the structure of the rearranged naphthol as 3-acetyl-1-allyl-2-hydroxynaphthalene (**13**). From this it is clear that it is the acetyl group that shifted to C-3 by a [1,5] acetyl shift from the initially formed intermediate **K** (Scheme 2). The naphthyl acetate, with the acetoxy protons at δ 2.2 and with the significant absence of the acetyl group at δ 2.7, was identified as 2-acetoxy-1-allylnaphthalene (**14**) which should have been formed by rearrangement of the acetyl group or by the initial loss of acetyl group from the intermediate **K** which *in situ* acetylates the naphthol (**17**). Neat rearrangement of the allyl ether (**12**) gave the naphthol (**17**) (20%) and its acetate (**14**) (70%) together accounting for 90% of the product, with conspicuous absence of (**13**), the product formed by [1,5] acetyl migration.

In the neat rearrangement, the formation of the naphthyl acetates (**9**) [from (**7**)] and (**14**) [from (**12**)] as major products raises some doubts with respect to the loss of acetyl groups from the intermediate structures. It was thought that the acetyl group might be lost as acetyl cation or a radical under the thermal conditions of the reaction.[2] The acetyl cation or radical is acetylating the phenol formed or any other substrate such as solvent molecules, *e.g.* DMA,[2] *in situ*, which are necessarily intermolecular processes. But in the neat rearrangement, an intramolecular rearrangement, the acetyl group is more likely to give a naphthyl acetate by a four-membered transition state, **N**, or a naphthol by hydrogen transfer through a six-membered cyclic transition state, **M**, with loss of ketene in which case the formation of either naphthol or its acetate becomes simultaneous. The latter concept may also hold good for the intermolecular processes since the ketene can itself act as an electrophile to effect acetylation. A similar mechanism may also

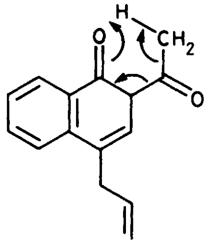


Scheme 2.

be appropriate with respect to loss of an allyl group either as an allyl cation, a radical, or an allene by hydrogen transfer through a six-membered cyclic transition state, **O**.

Compound (**13**) obtained in the above rearrangement was further allylated and the allyl ether (**15**) (95%) obtained was characterised on the basis of its ^{1}H NMR spectrum (see Experimental section) and subjected to thermal Claisen rearrangement in DMA to yield the deallylated naphthol (**13**) (6%) along with a second product (20%). Its ^{1}H NMR spectrum (see Experimental section) showed the presence of an acetyl group and two *C*-allyl groups, the signals for which had moved upfield. Its ^{1}H NMR spectrum also showed the presence of all the five aromatic protons present in the parent compound (**15**) intact. Based on the above, its structure was assigned as 3-acetyl-1,1-diallylnaphthalen-2(1H)-one (**16**) (Scheme 1).

A comparative study of the thermal Claisen rearrangement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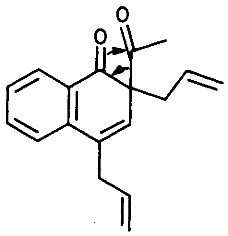
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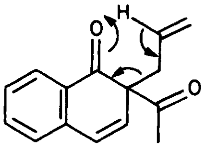
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of the 2-acetyl-1-naphthyl allyl ethers and 1-acetyl-2-naphthyl allyl ethers revealed some significant differences both between and within the two systems. These may be summarised as follows. (*a*) The rearrangement of (**7**) gave products (**4**) (allyl loss) or (**8**) or (**9**) (acetyl loss), no such products being noted from (**3**). It is likely that neither acetyl nor allyl loss is from the intermediate **A** from (**3**), since the allyl group can undergo successive [3,3] migrations to give a stable 4-allyl derivative. In the intermediate **F** from (**7**), allyl or acetyl loss becomes competitive giving both possible products (**4**) and (**8**). (*b*) Unlike intermediate **A** from the allyl ether (**3**), intermediate **K** from the allyl ether (**12**) possesses a *peri*-allyl and acetyl group, from which the latter, in preference to the former, is either lost or undergoes a [1,5] sigmatropic shift. (*c*) Sigmatropic [1,5] acetyl shifts noted only for the 2-naphthyl series and not 1-naphthyl; proceeding from the intermediates **A** or **F** the [1,5] acetyl shifts could go only to the ring junction, a position vulnerable to eventual elimination. (*d*) Migration of allyl groups into the B ring were noted in 1-naphthyl or 2-naphthyl allyl ethers because of the instability of the intermediates. (*e*) An intermediate dienone such as (**16**) could be isolated only from the 2-naphthyl series and not from the 1-naphthyl series. (*f*) All the above observations conform to the positional isomerism of the 1-naphthyl and 2-naphthyl allyl ether series, showing at the same time, the fixed double-bond character of the naphthalene system as compared to the benzene system, 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 latter and not from C-2 to C-3.

The above Claisen rearrangement studies, besides giving greater insight into the mechanistic aspects, yielded in the process some interesting acetylnaphthols with allyl groups at different positions. The naphthyl ethers might be expected to possess varied pharmacological activity.[18,19] Besides, they form useful synthetic intermediates, which are inaccessible otherwise, for the preparation of angular and linear naphtho-α- and γ-pyrone derivatives which are also reported to be pharmacologically active.[20-22]

Experimental

M.p.s were recorded on a VEB Analytik Dresden hot stage apparatus and are uncorrected. Unless stated otherwise 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 as internal standard, UV spectra were obtained in EtOH with a Shimadzu-UV-260 spectrometer, and electron impact-mass spectroscopy (EI-MS) was carried out with JEOL JMS-D 300 and Varian Mat 112S spectrophotometers. Preparative TLC (PLC) conducted on glass plates coated with silica gel-G (particle size 75μ, Acme) and column chromatography using silica gel (100–200 mesh, Acme). Spots on TLC were detected by their absorption under UV light. Solvents used were of LR grade and were purified by general methods. Commercial allyl bromide (Fluka) and *N*,*N*-dimethylaniline (E. Merck) were used. All the organic extracts were dried over $MgSO_4$.

2-*Acetyl*-1-*allyloxynaphthalene* (**3**).—A mixture of (**1**) (1 g, 5.38 mmol), allyl bromide (0.6 ml, 6.72 mmol), and freshly ignited K_2CO_3 (5 g) was refluxed in dry acetone (50 ml) 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 ml). The combined extracts were dried and evaporated to give a pale yellow oil (**3**) (1.2028 g, 99%). This gave no colouration with alcoholic $FeCl_3$ (Found: C, 79.6; H, 6.1. $C_{15}H_{14}O_2$ requires C, 79.65; H, 6.2%); λ_{max} 244.6 (log ε 4.8145), 286 (4.1901), and 335 nm (3.6865); ν_{max} (neat) 2 950, 1 675 (CO), 1 600, 1 190, 1 170, 1 110, 970, 925, 815, and 748 cm^{-1}; $\delta(CCl_4)$ 2.64 (3 H, s, $COCH_3$), 4.45 (2 H, d, *J* 5.6 Hz, OCH_2), 5.15–5.55 (2 H, m, $=CH_2$), 6.0 (1 H, m, $CH_2CH=$), 7.40 (1 H, d, *J* 7.9 Hz, 3-H), 7.45–7.58 (3 H, m, 4-, 6-, and 7-H), 7.7 (1 H, dd, *J* 1.1 Hz and *J* 7.9 Hz, 5-H), and 8.1 (1 H, dd, *J* 1.4 Hz and *J* 8.1 Hz, 8-H); *m*/*z* 226 (M^+, 32%), 211 [$(M - CH_3)^+$, 12.8], 185 [$(M - CH_2CHCH_2)^+$, 16.6], 184 [$(M - CH_2CO)^+$, 50], 183 [$(M - CH_3CO)^+$, 6.15], 114 (100), 43 [$(CH_3CO)^+$, 5.1], and 41 [$(CH_2CHCH_2)^+$, 6.4].

Thermal Rearrangement of (**3**).—(*a*) *In* N,N-*dimethylaniline*. Compound (**3**) (1 g, 4.42 mmol) was refluxed in freshly distilled *N*,*N*-dimethylaniline (b.p. 193 °C) (10 ml) for 7 h. The reaction mixture was poured into ice-cold HCl (300 ml) and the resulting pale green solid was filtered off, repeatedly washed with water, and dried. The product, 2-acetyl-4-allyl-1-hydroxynaphthalene (**4**), showed a major spot on TLC, R_F 0.4 (hexane–EtOAc, 95:5) and crystallised as pale greenish yellow needles (560 mg, 56%), m.p. 92 °C (from light petroleum). It gave a bright green colour with alcoholic $FeCl_3$ (Found: C, 79.6; H, 6.1. $C_{15}H_{14}O_2$ requires C, 79.65; H, 6.2%); λ_{max} 217 (log ε 4.3141), 218.2 (4.3077), 259.8 (4.3799), 287.8 (3.5808), 298.4 (3.556), 309.2 (3.2248), and 372.8 nm (3.6888); ν_{max} 3 750 (OH), 1 625, 1 575, 1 450, 1 365, 1 330, 1 082, 980, and 910 cm^{-1}; $\delta(CCl_4)$ 2.55 (3 H, s, $COCH_3$), 3.62 (2 H, d, *J* 7.7 Hz, $ArCH_2$), 5.05 (2 H, m, $=CH_2$), 6.0 (1 H, m, $CH_2CH=$), 7.27 (1 H, s, 3-H), 7.4–7.6 (2 H, m, 6- and 7-H), 7.78 (1 H, dd, *J* 1.1 Hz and *J* 7.9 Hz, 5-H), 8.4 (1 H, dd, *J* 1.4 Hz and *J* 8.1 Hz, 8-H), and 13.84 (1 H, s, OH); *m*/*z* 226 (M^+, 100%), 211 [$(M - CH_3)^+$, 54.1], 199 [$(M - CH_2CH)^+$, 5.7], 184 [$(M - CH_2CO)^+$, 8.2], 183 [$(M - CH_3CO)^+$, 45.9], 165 (24.6), 43 [$(CH_3CO)^+$, 90.2], and 28 [$(CO)^+$, 39.3].

(*b*) *Neat under a* N_2 *atmosphere*. Compound (**3**) (1 g, 4.42 mmol) was heated at 185 °C for 3 h. The resulting yellowish brown material (950 mg) was worked up by passage over a column of silica gel (50 g). The initial hexane fractions (5 × 250 ml) on concentration gave a pale greenish yellow crystalline solid, characterised as (**4**) (880 mg, 88%). Further elution yielded no further pure material.

2-*Acetyl*-4-*allyl*-1-*allyloxynaphthalene* (**7**).—A mixture of compound (**4**) (1 g, 4.42 mmol), allyl bromide (0.48 ml, 5.53 mmol), and freshly ignited K_2CO_3 (5 g) was refluxed in dry acetone (50 ml) for 3 h. Work-up gave a pale yellow oil (1.165 g, 99%) gave no colouration with alcoholic $FeCl_3$ (Found: C, 81.2; H, 6.7. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%); λ_{max} 216.4 (log ε 4.2911), 253.4 (4.3156), 290.2 (3.6839), and 340.6 nm (3.2470); ν_{max} 2 990, 2 925, 1 660 (CO), 1 618, 1 600, 1 590, 1 410, 1 360, 1 150, 1 100, 1 070, 990, and 910 cm^{-1}; $\delta(CCl_4)$ 2.67 (3 H, s, $COCH_3$), 3.72 (2 H, d, *J* 7.7 Hz, $ArCH_2$), 4.48

(2 H, d, *J* 5.6 Hz, OC*H*$_2$), 5.1 (2 H, m, 4-CH$_2$CHC*H*$_2$), 5.5 (2 H, m, OCH$_2$CHC*H*$_2$), 6.0 (2 H, m, 2 × CH$_2$C*H*=), 7.4 (1 H, s, 3-H), 7.45–7.55 (2 H, m, 6- and 7-H), 7.9 (1 H, dd, *J* 1.1 Hz and *J* 7.9 Hz, 5-H), and 8.17 (1 H, dd, *J* 1.4 Hz and *J* 8.1 Hz, 8-H); *m*/*z* 266 (M^+, 23.3%), 226 [(M – CH$_2$CCH$_2$)$^+$, 9.1], 225 [(M – CH$_2$CHCH$_2$)$^+$, 7.8], 224 [(M – CH$_2$CO)$^+$, 11.6], 223 [(M – CH$_3$CO)$^+$, 5.8], 183 (54.5), 165 (23.4), 152 (28.6), 43 [(CH$_3$CO)$^+$, 100], and 41 [(CH$_2$CHCH$_2$)$^+$, 40.2].

Thermal Rearrangement of Compound (**7**).—(*a*) *In* N,N-*dimethylaniline*. Compound (**7**) (1 g, 3.76 mmol) was refluxed in freshly distilled *N*,*N*-dimethylaniline (10 ml) for 1 h. The reaction mixture after work-up gave a reddish brown gum (800 mg) which showed two major spots on TLC R_F 0.62 and 0.75 (hexane–EtOAc, 9:1). The above product mixture was resolved by PLC to yield compound (**4**) (125 mg, 14.7%) and 2,4-diallyl-1-hydroxynaphthalene (**8**) (125 mg, 14.8%) as a pale brown oil. The latter gave a dark brown colour with alcoholic FeCl$_3$ (Found: C, 85.6; H, 7.1. C$_{16}$H$_{16}$O requires C, 85.7; H, 7.1%); ν_{max} 3 525 (OH), 2 925, 1 600, 1 590, 1 450, 1 090, 990, and 910 cm^{-1}; δ 3.52 (2 H, d, *J* 7.7 Hz, 2-C*H*$_2$CHCH$_2$), 3.72 (2 H, d, *J* 7.7 Hz, 4-C*H*$_2$CHCH$_2$), 4.95–5.5 (4 H, m, 2 × =CH$_2$), 6.0 (3 H, m, 2 × C*H*=CH$_2$ and OH), 7.05 (1 H, s, 3-H), 7.4–7.52 (2 H, m, 6- and 7-H), 7.95 (1 H, dd, *J* 1.1 Hz and *J* 7.9 Hz, 5-H), and 8.21 (1 H, dd, *J* 1.4 Hz and *J* 8.1 Hz, 8-H).

(*b*) *Neat under a* N$_2$ *atmosphere*. Compound (**7**) (1 g, 3.76 mmol) was heated at 185 °C under a N$_2$ atmosphere for 1 h. Work-up of the reaction mixture gave a yellow oily product which afforded a major spot on TLC, R_F 0.58 (hexane–EtOAc, 9:1). The above product mixture was resolved by PLC into a single dominant band which yielded 1-acetoxy-2, 4-diallylnaphthalene (**9**) as a yellow oily compound (670 mg, 67%) (Found: C, 81.2; H, 6.7. C$_{18}$H$_{18}$O$_2$ requires C, 81.2; H, 6.8%); λ_{max} 224.8 (log ε 4.4699) and 286.4 nm (3.6710); ν_{max}(neat) 2 950, 1 755 (CO), 1 640, 1 600, 1 440, 1 368, 1 150, 1 080, 990, and 910 cm^{-1}; δ(CCl$_4$) 2.3 (3 H, s, OCOCH$_3$), 3.32 (2 H, d, *J* 7.7 Hz, 2-C*H*$_2$CHCH$_2$), 3.69 (2 H, d, *J* 7.7 Hz, 4-C*H*$_2$CHCH$_2$), 4.9–5.2 (4 H, m, 2 × =CH$_2$), 5.89 (2 H, m, 2 × C*H*=CH$_2$), 7.1 (1 H, s, 3-H), 7.2–7.4 (2 H, m, 6- and 7-H), 7.65 (1 H, dd, *J* 1.1 Hz and *J* 7.9 Hz, 5-H), and 7.85 (1 H, dd, *J* 1.4 Hz and *J* 8.1 Hz, 8-H); *m*/*z* 266 (M^+, 10.3%), 224 [(M – CH$_2$CO)$^+$, 100], 183 [(M – CH$_2$CO, – CH$_2$CHCH$_2$)$^+$, 12.3], 165 (23.2), 152 (23.2), and 43 [(CH$_3$CO)$^+$, 9.6].

1-*Acetyl*-2-*allyloxynaphthalene* (**12**).—A mixture of compound (**2**) (1 g, 5.38 mmol), allyl bromide (0.6 ml, 6.72 mmol), and freshly ignited K$_2$CO$_3$ (5 g) was refluxed in dry acetone (50 ml) for 3 h. The reaction mixture after work-up gave the title compound (**12**) as a low-melting solid (1.1 g, 99%) which crystallised as colourless shining cubes, m.p. 48 °C (from hexane–CHCl$_3$). It gave no colouration with alcoholic FeCl$_3$ (Found: C, 79.6; H, 6.1. C$_{15}$H$_{14}$O$_2$ requires C, 79.65; H, 6.2%); λ_{max} 224 (log ε 4.6169), 333.2 (3.4648), and 379.2 nm (3.6466); ν_{max} 2 850, 1 680 (CO), 1 620, 1 600, 990, and 910 cm^{-1}; δ(CCl$_4$) 2.5 (3 H, s, COCH$_3$), 4.4 (2 H, d, *J* 5.6 Hz, OCH$_2$), 5.2 (2 H, m, =CH$_2$), 5.85 (1 H, m, C*H*=CH$_2$), 6.95 (1 H, d, 3-H), 7.15–7.75 (5 H, m, 4-, 5-, 6-, 7-, and 8-H); *m*/*z* 226 (M^+, 43.2%), 211 [(M – CH$_3$)$^+$, 21.6], 185 [(M – CH$_2$CHCH$_2$)$^+$, 19.8], 184 [(M – CH$_2$CO)$^+$, 48], 183 [(M – CH$_3$CO)$^+$, 100], 169 [(M – CH$_2$CHCH$_2$O)$^+$, 64.3], 114 (90.7), 43 [(CH$_3$CO)$^+$, 3], and 41 [(CH$_2$CHCH$_2$)$^+$, 4.2].

Thermal Rearrangement of Compound (**12**).—(*a*) *In* N,N-*dimethylaniline*. Compound (**12**) (1 g, 4.42 mmol) was refluxed in freshly distilled *N*,*N*-dimethylaniline (10 ml) for 5 h. Work-up gave a yellowish brown gum (80 mg) which showed two major spots on TLC, R_F 0.35 and 0.66 (hexane–EtOAc, 9:1). The above product mixture was resolved by PLC to yield compounds 3-acetyl-1-allyl-2-hydroxynaphthalene (**13**) and 2-acetoxy-1-allylnaphthalene (**14**). Compound (**13**) crystallised as yellow needles (180 mg, 18%), m.p. 72 °C (from light petroleum) and gave dark green colour with alcoholic FeCl$_3$ (Found: C, 79.6; H, 6.1. C$_{15}$H$_{14}$O$_2$ requires C, 79.65; H, 6.2%); λ_{max} 222 (log ε 4.2725), 253.6 (4.5168), 294.6 (3.4811), 304.6 (3.8254), and 395 nm (3.2840); ν_{max} 2 925, 2 850, 1 640 (CO), 990, 960, 910, and 885 cm^{-1}; δ 2.7 (3 H, s, COCH$_3$), 3.8 (2 H, d, *J* 7.7 Hz, ArCH$_2$), 5.0 (2 H, m, =CH$_2$), 6.0 (1 H, m, C*H*=CH$_2$), 7.22–7.9 (4 H, m, 5-, 6-, 7-, and 8-H), 8.23 (1 H, s, 4-H), and 11.92 (1 H, s, OH); *m*/*z* 226 (M^+, 100%), 211 [(M – CH$_3$)$^+$, 48.3], 199 [(M – CH$_2$CH)$^+$, 12.5], 184 [(M – CH$_2$CO)$^+$, 5.7], 183 [(M – CH$_3$CO)$^+$, 36.7], 165 (21.7), 43 [(CH$_3$CO)$^+$, 40.0], and 28 [(CO)$^+$, 5.7].

Compound (**14**) was a yellow oil (230 mg, 23%) (Found: C, 79.6; H, 6.1. Calc. for C$_{15}$H$_{14}$O$_2$: C, 79.65, H, 6.2%); λ_{max} 223.2 (log ε 4.6909), 267 (3.6865), 278 (3.6885), 288.4 (3.5768), and 305 nm (2.5302); ν_{max} 3 050, 2 950, 1 750 (C=O), 1 635, 1 600, 990, 910, and 860 cm^{-1}; δ 2.2 (3 H, s, OCOCH$_3$), 3.66 (2 H, d, *J* 7.7 Hz, ArCH$_2$), 4.95 (2 H, m, =CH$_2$), 5.9 (1 H, m, C*H*=CH$_2$), 7.1 (1 H, d, *J* 9 Hz, 3-H), and 7.2–8.0 (5 H, m, 4-, 5-, 6-, 7-, and 8-H); *m*/*z* 226 (M^+, 39.1%), 211 [(M – CH$_3$)$^+$, 17.9], 185 [(M – CH$_2$CHCH$_2$)$^+$, 6.6], 184 [(M – CH$_2$CO)$^+$, 100], 169 (45.4), 152 (33.1), 43 [(CH$_3$CO)$^+$, 65.7], and 41 [(CH$_2$CHCH$_2$)$^+$, 5.9].

(*b*) *Neat under a* N$_2$ *atmosphere*. Compound (**12**) (1 g, 4.42 mmol) was heated at 185 °C under a N$_2$ atmosphere for 90 min. Work-up provided a yellow gum (950 mg) which showed two major spots on TLC R_F 0.46 and 0.66 (hexane–EtOAc, 9:1). The above product mixture was resolved by PLC to yield compounds (**14**) (700 mg, 70%) and 1-allyl-2-hydroxynaphthalene (**17**) (200 mg, 20%) which crystallised as colourless needles, m.p. 56 °C (lit.,[6] m.p. 56 °C) (from light petroleum) and gave dark green colour with alcoholic FeCl$_3$ (Found: C, 84.7; H, 6.5. Calc. for C$_{13}$H$_{12}$O: C, 84.8; H, 6.5%); ν_{max}(neat) 3 400 (OH), 3 050, 1 600, 990, 910, 810, and 740 cm^{-1}; δ 3.75 (2 H, d, *J* 7.7 Hz, ArCH$_2$), 4.96 (2 H, m, =CH$_2$), 6.0 (2 H, m, C*H*=CH$_2$ and OH), 6.85 (1 H, d, *J* 9 Hz, 3-H), and 7.15–7.85 (5 H, m, 4-, 5-, 6-, 7-, and 8-H).

3-*Acetyl*-1-*allyl*-2-*allyloxynaphthalene* (**15**).—A mixture of compound (**13**) (1 g, 4.42 mmol), allyl bromide (0.48 ml, 5.53 mmol), and freshly ignited K$_2$CO$_3$ (5 g) was refluxed in dry acetone (50 ml) for 90 min. Work-up gave a yellow oil (1.165 g, 99%) which showed no colouration with alcoholic FeCl$_3$ (Found: C, 81.1; H, 6.75. C$_{18}$H$_{18}$O$_2$ requires C, 81.2; H, 6.8%); λ_{max}(CHCl$_3$) 196.8 (log ε 3.9515), 201.6 (3.9438), 223.4 (3.8998), 247 (4.5624), 284.6 (3.8800), and 336.6 nm (3.3115); ν_{max} 2 950, 1 680 (CO), 1 620, 990, and 910 cm^{-1}; δ(CCl$_4$) 2.58 (3 H, s, COCH$_3$), 3.85 (2 H, d, *J* 7.7 Hz, ArCH$_2$), 4.3 (2 H, d, *J* 5.6 Hz, OCH$_2$), 5.0 (2 H, m, 1-CH$_2$CHC*H*$_2$), 5.3 (2 H, m, OCH$_2$CHC*H*$_2$), 6.0 (2 H, m, 2 × C*H*CH$_2$), 7.3–7.9 (4 H, m, 5-, 6-, 7-, and 8-H), and 8.2 (1 H, s, 4-H); *m*/*z* 266 (M^+, 3.6%), 226 [(M – CH$_2$CCH$_2$)$^+$, 27.5], 225 [(M – CH$_2$CHCH$_2$)$^+$, 27.4], 224 [(M – CH$_2$CO)$^+$, 35.7], 223 [(M – CH$_3$CO)$^+$, 7.5], 183 (46.4), 171 (83.3), 157 (29.8), 129 (58.9), 43 [(CH$_3$CO)$^+$, 100), and 41 [(CH$_2$CHCH$_2$)$^+$, 58.3].

Thermal Rearrangement of Compound (**15**).—(*a*) *In* N,N-*dimethylaniline*. Compound (**15**) (1 g, 3.76 mmol) was refluxed in freshly distilled *N*,*N*-dimethylaniline (10 ml) for 5 h. Work-up gave a brown gum (750 mg) which showed two major spots on TLC, R_F 0.55 and 0.70 (hexane–EtOAc, 9:1). The above product mixture was resolved by PLC to yield compounds (**13**) (50 mg, 6%) and 3-acetyl-1,1-diallylnaphthalen-2(1H)-one (**16**) (200 mg, 20%) as a yellow oil (Found: C, 81.2; H, 6.7. C$_{18}$H$_{18}$O requires C, 81.2; H, 6.8%; λ_{max}(CHCl$_3$) 200.4 (log ε 3.7675), 219.8 (3.7450), 243.4 (4.1443), and 324.4 nm (4.1710); ν_{max} 2 950, 1 690–1 645br (two CO), 1 600, 990, and 910 cm^{-1}; δ 2.55 (3 H, s, $COCH_3$), 2.8 (4 H, m, 2 × $ArCH_2$), 4.7–5.0 (4 H, m, 2 × $=CH_2$), 5.1 (2 H, m, 2 × $CH=CH_2$), 7.3–7.7 (4 H, m, 5-, 6-, 7-, and 8-H), and 8.09 (1 H, s, 4-H); m/z 226 (M^+, 17.6%), 225 [$(M - CH_2CHCH_2)^+$, 7.1], 224 [$(M - CH_2CO)^+$, 7.7], 223 [$(M - CH_3CO)^+$, 13.1], 181 (10.7), 165 (14.3), 152 (29.8), 43 [$(CH_3CO)^+$, 100], and 41 [$(CH_2CHCH_2)^+$, 13.7].

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