Thermal Claisen Rearrangement Studies on 4,6- and 2,4-Diacetylresorcinol Bisallyl Ethers: Observation of Loss or [1,5] Sigmatropic Shift of Acetyl Groups

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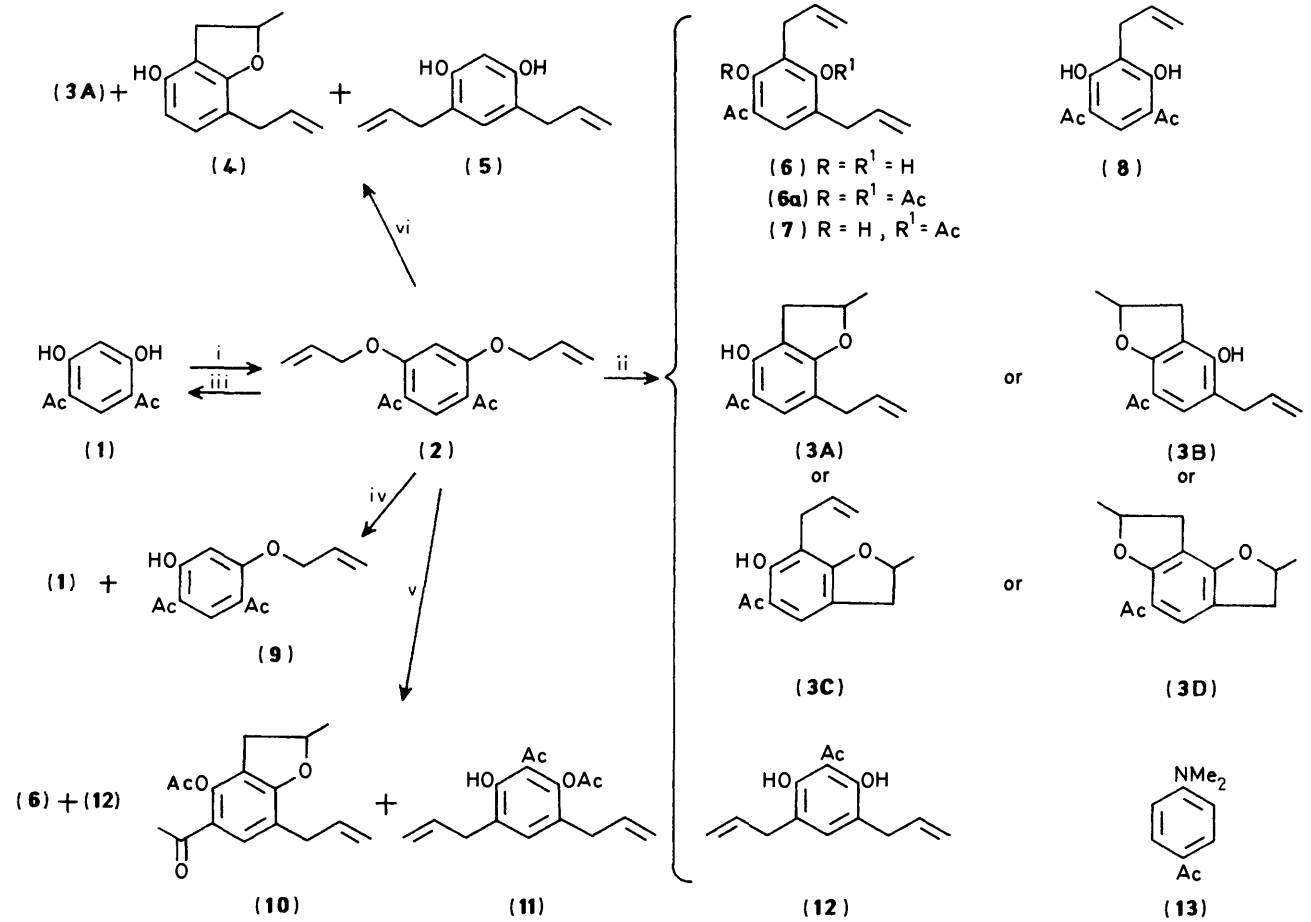
Thermal Claisen rearrangement of 4,6-diacetylresorcinol bisallyl ether (**2**) in *N,N*-dimethylaniline gave a mixture of readily characterised products. While no rearrangement occurred with lower boiling solvents (benzene and dioxane), higher boiling solvents (diphenyl ether and glycerol) gave rise to more complex rearrangement and a lowering of the yields of isolable products. Trifluoroacetic acid both at room temperature and 60 °C effected either partial or total deallylation but no rearrangement. Product formation has been rationalised in terms of symmetry allowed sigmatropic [3,3] allyl, [1,5] acetyl or [1,5] H shifts followed by allyl or acetyl group loss; the latter is a novel observation. The acetyl group, most probably eliminated as a cation, effected both *O*-acylation and nuclear acylation of the substrates. Claisen rearrangement of the bromo and nitro derivatives of compound (**2**) in which the *ortho* and *para* positions are blocked, gave products arising from bromo and nitro group elimination. Rearrangement of 2,4-diacetylresorcinol bisallyl ether (**18**) in *N,N*-dimethylaniline occurred similarly.

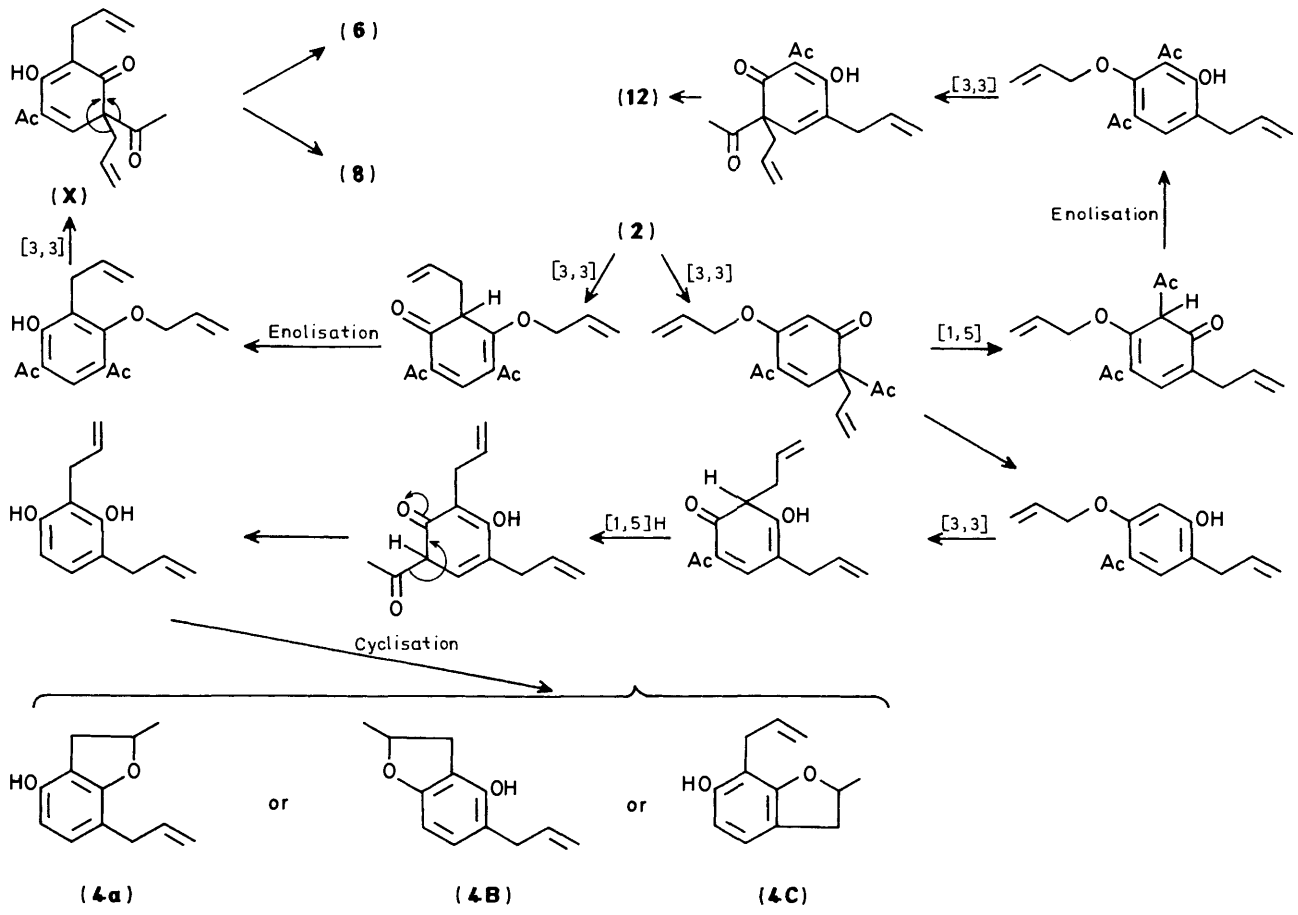
ortho And *para* Claisen rearrangements of aryl allyl ethers, characterised as [3,3] sigmatropic reactions[1] and extensively reviewed in the literature[2–9] have been of value in synthesizing coumaran and chroman systems.

In preliminary form,[10] we reported the thermal Claisen rearrangement of the bisallyl ether of 4,6-diacetylresorcinol in *N,N*-dimethylaniline. Here we report a study of the thermal Claisen rearrangement of the bisallyl ethers of 2,4- and 4,6-diacetylresorcinols and their derivatives in various solvents. Rearrangement studies on resacetophenone bisallyl ether and peonol allyl ether are also described. 4,6-Diacetyl- (**1**) and 2,4-diacetyl-resorcinol (**14**) (7%) were prepared by acetylation of resorcinol in 90 and 7% yields respectively.[11,12]

5′-Acetyl-2′,4′-diallyloxyacetophenone (**2**), was prepared by



Scheme 1. *Reagents and conditions:* i, allyl bromide–Me_2CO–K_2CO_3; ii, *N,N*-dimethylamine; iii, CF_3CO_2H at 60 °C; iv, CF_3CO_2H at 0 °C; v, Ph_2O; vi, glycerol

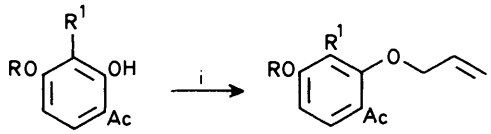


Scheme 2.

treating 4,6-diacetylresorcinol (**1**) with allyl bromide and anhydrous potassium carbonate in acetone, on thermal rearrangement in refluxing *N*,*N*-dimethylaniline for 6 h, gave compounds (**3A**), (**6**)—(**8**), (**12**), and (**13**) (Scheme 1). They were characterised readily on the basis of their spectral data (u.v., i.r., ^{1}H n.m.r. and mass; see Experimental section).

The formation of these products, rationalised in terms of symmetry allowed [3,3] and [1,5] sigmatropic shifts (Scheme 2), is based mainly, on initial rearrangement of both the allyl groups followed by the loss of (i) an acetyl group to give (**6**), (ii) an allyl group to give (**8**), and (iii) loss of one acetyl group and rearrangement of the other acetyl group to give (**12**). Compounds (**6**) and (**8**) are thus formed from a common dienone intermediate (**X**) by the loss of an acetyl or allyl group. Cyclisation of (**6**), could, theoretically, give rise to three possible structures: (**3A**), (**3B**), or (**3C**). An *ortho* hydroxyacetophenone system in the molecule ruled out structure (**3B**). Structure (**3C**) was also rejected since whilst it might be expected to undergo further cyclisation to a dicoumaran (**3D**), it resisted cyclisation with acids; the structure was therefore assigned as (**3A**). Compounds (**6**) and (**3A**) were also obtained in equivalent amounts, alternatively by the thermal rearrangement of the bisallyl ether of resacetophenone (**19**) [prepared from resacetophenone (**15**) (Scheme 3). Compound (**7**), formed by acetylation of (**6**) yielded a diacetate (**6A**) with Ac_2O–NaOAc, though not with Ac_2O–Py.

Although loss of an acetyl group during Claisen rearrangement has not been reported before, loss of allyl,[13,14] formyl,[15] carboxy,[16,17] methoxycarbonyl,[18] and allyloxy groups,[19] and



(**14**) R = H, R^1 = Ac
(**15**) R = R^1 = H
(**16**) R = Me, R^1 = H
(**17**) R = Me, R^1 = Allyl

(**18**) R = Allyl, R^1 = Ac
(**19**) R = Allyl, R^1 = H
(**20**) R = Me, R^1 = H

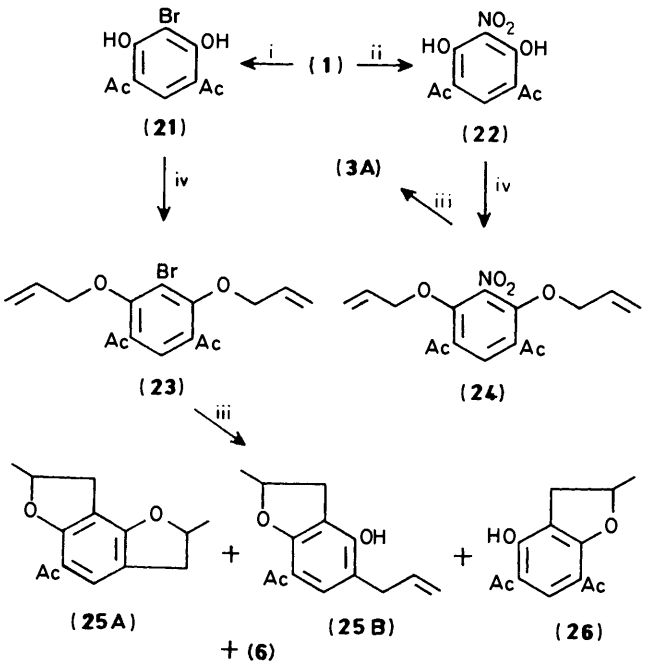
(**18**) $\xrightarrow{ii}$ (**6**) + (**7**) + (**12**) + (**25a**) + (**25b**)
(**19**) $\xrightarrow{ii}$ (**6**) + (**3A**)
(**20**) $\xrightarrow{ii}$ (**17**)

Scheme 3. *Reagents and conditions:* i, allyl bromide–Me_2CO–K_2CO_3; ii, *N*,*N*-dimethylaniline

halogen atoms[20,21] has. Although formation of the *O*-acetyl derivative (**7**) of compound (**6**) as well as a nuclear acetylated derivative of the solvent, 4-acetyl-*N*,*N*-dimethylaniline (**13**) provide ample proof of acetyl group loss, the isolated yields of the latter were far from quantitative. The acetyl group is probably lost as a cation, although its elimination as a radical cannot be ruled out, in view of the high reaction temperature. Although allyl group elimination has also been recorded in the literature,[7,22] no products arising from this source were isolated in our work. The formation of compound (**12**) is a further interesting observation explained in terms of a [1,5] sigmatropic acetyl migration followed by [3,3] sigmatropic shifts (Scheme 2). Such acetyl migration has been recorded only once before.[23]

Different solvents were also used for the Claisen rearrangement of the bisallyl ether (**2**) in order to see their effects. There was no reaction in refluxing anhydrous benzene or dioxane even after 24 h. In trifluoroacetic acid, reported to be a good Claisen solvent for the rearrangement of phenyl allyl ethers under mild conditions,[24] compounds (**9**) and (**1**), produced as a result of partial and total deallylation respectively, were obtained at room temperature; at 60 °C only compound (**1**) was obtained (Scheme 1). The novel monoallyl ether (**9**) cannot be obtained by direct allylation of the diacetylresorcinol (**1**), the diallyl ether always being formed. The reaction of compound (**2**) in refluxing diphenyl ether (b.p. 258 °C) for 6 h (Scheme 1) gave the novel benzofuran (**10**), and acetophenone (**11**), together with compounds (**6**) and (**12**). Compound (**2**) in refluxing glycerol yielded the benzofuran (**4**) for which the isomeric structures A, B, or C are possible, the resorcinol (**5**), and compound (**3A**) (Scheme 1). Although compounds (**4**) and (**5**) are both formed by loss of two acetyl groups during rearrangement, whilst formation of the latter is straightforward, that of the former with its modified skeleton and two *ortho* coupled aromatic protons, is more complex involving a sigmatropic [1,5] H shift and [3,3] rearrangements (see Scheme 1).

The bisallyl ether (**2**) provides an example where positions *para* to the *o*-allyl groups are blocked, with only one free *ortho* position; substitution of this by a bromo or nitro group results in blocking of all the *ortho* and *para* positions. Such compounds (**23**) and (**24**) were prepared (Scheme 4) and subjected to Claisen



Scheme 4. i, NBS–dioxane; ii, H_2SO_4–HNO_3; iii, *N,N*-dimethylaniline; iv, allyl bromide

rearrangement. 4,6-Diacetyl-2-bromoresorcinol (**21**) was prepared from 4,6-diacetylresorcinol (**1**) and NBS and the 2-nitro analogue (**22**) by a literature method.[25] The bisallyl ether (**23**), prepared itself from (**21**), in refluxing *N,N*-dimethylaniline gave the new dihydrobenzofurans (**25a**), (**25b**), and (**26**), compound (**6**) and minor products (Scheme 4). Since the products are formed by loss of bromine and an allyl or acetyl group, bromine is seen as an ineffective blocking agent. The 3-nitro analogue (**24**), under similar conditions underwent resinification, little of the dihydrobenzofuran (**3A**) being obtained (Scheme 2).

We have also studied the Claison rearrangement of the bisallyl ether (**18**) which has both free *ortho* and *para* positions (Scheme 3). Compound (**14**) gave the bisallyl ether (**18**) which in refluxing *N,N*-dimethylaniline rearranged to compounds (**6**), (**7**), and (**12**) [as from compound (**2**)] and an inseparable mixture of (**25a**) and (**25b**) [as from compound (**23**)]. All these products are formed by [3,3] migration of the allyl groups to the *ortho* position with subsequent acetyl loss. Unlike compound (**2**), on rearrangement compound (**18**) gave no product resulting from allyl group loss. It is possible that acetyl loss occurs in preference to allyl loss in the aromatisation step: the difference in behaviour of the allyl ethers (**2**) and (**18**) remains unexplained.

Thermal rearrangement of the allyl ether (**20**) (Scheme 3) yielded, by *ortho* rearrangement of allyl group, compound (**17**): this has been obtained earlier by the rearrangement of monoallyl ether of resacetophenone followed by methylation.[26]

Experimental

M.p.s were determined on VEB Analytik Dresden HMK hot plate and are uncorrected. The compounds were dried at room temperature or at 100 °C/0.2 mmHg for 6 h. Acme's silica gel G has been used for column (100—200 mesh) and t.l.c. and the solvent systems are indicated at appropriate places. I.r. spectra were measured on Shimadzu Infrared spectrophotometer-IR-408 or Perkin-Elmer 237 Grating Infrared spectrophotometer and u.v. spectra on Shimadzu UV-140 or Beckman DB-G spectrophotometers. All the ^1H n.m.r. values were recorded on a Perkin-Elmer R-32 at 90 MHz or a Varian CFT-20 at 80 MHz and are given as δ values with $SiMe_4$ as internal standard. The mass spectra were taken on Hitachi RMU 6L instrument.

Preparation of 3′-Acetyl-4′,6′-diallyloxyacetophenone (**2**).—A mixture of 4,6-diacetylresorcinol (**1**) (1.94 g, 0.01 mol) allyl bromide (2.6 ml, 0.03 mol), and freshly ignited potassium carbonate (10 g) was refluxed in dry acetone (100 ml) on a water-bath for 6 h. It was then filtered and distilled under reduced pressure to provide a residue which was treated with water (150 ml). The resulting solid was filtered off, washed with aqueous NaOH (2%) and water, and recrystallised from hexane–chloroform to give the bisallyl ether (**2**) as colourless shining needles (2.65 g, 96.7%), m.p. 92 °C (Found: C, 70.0; H, 6.7. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); R_F 0.31 (benzene–ethyl acetate, 9:1); $FeCl_3$ colour→ – ve; $\nu_{max.}$(KBr) 1 650 (CO), 1 630, 1 420, 1 355, 1 270, 1 225, 1 050, 990, and 910 cm^{-1}; $\lambda_{max.}$(EtOH) 248 (log ε 5.10) and 275 nm (4.82); δ_H($CDCl_3$; 90 MHz) 2.4 (6 H, s, 2 × Ac), 4.55 (4 H, d, *J* 5 Hz, 2 × OCH_2), 5.4 (4 H, m, 2 × CH_2), 6.0 (2 H, m, 2 × CH=), 6.2 (1 H, s, 3′-H), and 8.05 (1 H, s, 6′-H); *m/z* (%) 274 (M^+, 59.28), 259 (98.54), 231 (18), 219 (81), and 191 (100).

Thermal Claisen Rearrangement of the Ether (**2**) *in* N,N-*Dimethylaniline*.—The above ether (**2**) (2.5 g, 9 mmol) was refluxed in freshly distilled *N,N*-dimethylaniline (15 ml) for 6 h. After cooling to room temperature, the reaction mixture was poured onto ice cold HCl (50 ml) with stirring to give oily material which was extracted with ether (3 × 100 ml). The ether solution was washed with aqueous sodium hydroxide (20%; 3 × 50 ml) and water, dried ($MgSO_4$), and evaporated to give a reddish brown gum (1 g). The combined alkaline washings on acidification with aqueous hydrochloric acid (1:1) gave a brown solid (1.1 g). These two, the alkali-soluble and -insoluble fractions were worked up separately.

Alkali-soluble fraction. The brown precipitate (1.1 g) from the sodium hydroxide-soluble fraction showed two spots on t.l.c. (R_F 0.59 and 0.43, benzene) and column chromatography (silica gel/hexane) gave compounds (**6**) and (**8**).

Concentration of the column fractions 30—55 (hexane–benzene, 6:4, each 250 ml) gave a residue, which on crystallisation from hexane afforded colourless shining needles of 3′,5′-diallyl-2′,4′-dihydroxyacetophenone (**6**) (700 mg, 33%), m.p. 90 °C (lit.,[26] m.p. 89—90 °C) (Found: C, 72.7; H, 7.3. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%); $FeCl_3$ colour→violet; $\nu_{max.}$(KBr) 3 300—3 100 (OH), 1 630 (C=O), 1 620, 1 580, 1 500, 1 450, 1 430, 1 280, 995, 910, and 890 cm^{-1}; $\lambda_{max.}$(EtOH) 285 (log ε 5.12) and 332 nm (4.73); δ_H($CDCl_3$; 90 MHz), 2.55 (3 H, s, Ac), 3.25 (2 H, d, *J* 6 Hz, CH_2), 3.45 (2 H, d, *J* 6 Hz, CH_2), 5.1 (4 H, m, 2 × =CH_2), 5.8 (1 H, s, 4′-OH), 5.95 (2 H, m, 2 × CH=), 7.4 (1 H, s, 6′-H), and 12.9 (1 H, s, 2′-OH); *m/z* (%) 232 (M^+, 68.8) and 217 (100). It formed a diacetate (Ac_2O/Py) (**6a**), m.p. 49—50 °C; $\nu_{max.}$(KBr) 1 760 (OAc), 1 685 (CO), 1 620, 1 590, 1 450, 1 275, 995, 905, and 880 cm^{-1}; δ_H($CDCl_3$; 90 MHz), 2.3 (6 H, s, 2 × OAc), 2.5 (3 H, s, Ac), 3.25 (4 H, d, *J* 7 Hz, 2 × CH=), 5.15 (4 H, m, 2 × =CH_2), 5.75 (2 H, m, 2 × CH=), and 7.6 (1 H, s, 6′-H).

Concentration of column fractions 65—75 (hexane–benzene, 3:7, each 250 ml) gave a residue, which on crystallisation from methanol gave 5′-acetyl-3′-allyl-2′,4′-dihydroxyacetophenone (**8**) as pale brown prisms (125 mg, 5.9%), m.p. 93—94 °C (Found: C, 66.55; H, 5.95. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.02%); $FeCl_3$ colour→red; $\nu_{max.}$(KBr) 2 960—2 600 (OH), 1 650 (C=O), 1 615, 1 450, 1 245, 990, 920, and 885 cm^{-1}; $\lambda_{max.}$(EtOH) 262 (log ε 5.21) and 325 nm (4.93); δ_H($CDCl_3$; 80 MHz), 2.62 (6 H, s, 2 × Ac), 3.42 (2 H, d, *J* 6.2 Hz, CH_2), 5.07 (2 H, m, =CH_2), 5.79 (1 H, m, CH=), 8.14 (1 H, s, 6′-H), and 13.23 (2 H, s, 2α-OH); *m/z* (%) 234 (M^+, 74.26) and 219 (100).

Alkali-insoluble fraction. The dark red gum (1 g) showed three spots on t.l.c. plate (R_F 0.58, 0.44, and 0.42 benzene). It was subjected to silica gel (25 g) column chromatography to give pure compound (**3A**) and compounds (**7**) and (**12**) as a mixture.

Column fractions 30—45 (hexane–benzene, 6:4, each 250 ml) on concentration gave 5-acetyl-7-allyl-4-hydroxy-2-methyl-2,3-dihydrobenzofuran (**3A**) as a bright greenish yellow oil (250 mg, 12%) (Found: C, 72.35; H, 6.9. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%), $FeCl_3$ colour→violet; $\nu_{max.}$(film) 3 050, 2 950—2 900, 1 640 (CO), 1 615, 1 450, 1 310, 1 275, 1 245, 1 200, 1 130, 1 100, 1 045, 1 020, 1 000, and 905 cm^{-1}; $\lambda_{max.}$(EtOH) 292 nm (log ε 5.04); δ_H($CDCl_3$; 80 MHz) 1.45 (3 H, d, *J* 6.2 Hz, 2-Me), 2.45 (3 H, s, Ac), 2.55—3.4 (2 H, m, 3-CH_2), 3.2 (2 H, d, *J* 7.0 Hz, CH_2), 4.8—5.2 (3 H, m, =CH_2 and 2-H), 5.9 (1 H, m, C*H*=), 7.2 (1 H, s, 6-H), and 12.43 (1 H, s, OH); *m/z* 232 (M^+, 71.0%) and 217 (100).

Separation of compounds (**7**) *and* (**12**). Column fractions 50—80 (hexane–benzene, 2:8, each 250 ml) on concentration gave a residue (350 mg), which showed two spots on t.l.c. plate (R_F 0.44 and 0.42, benzene). This mixture was subjected to preparative t.l.c. using benzene as the developing solvent and the preparative bands were extracted with chloroform to yield compounds (**7**) and (**12**).

Evaporation of the solvent from preparative band R_F 0.44 gave 4′-acetoxy-3′,5′-diallyl-2′-hydroxyacetophenone (**7**) as a pale greenish yellow oil (150 mg, 6%) (Found: C, 70.0; H, 6.55. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); $FeCl_3$ colour→bluish green; $\nu_{max.}$(film) 3 050, 1 750 (OAc), 1 635 (CO), 1 460, 1 435, 1 370, 1 325, 1 270, 1 190, 1 155, 1 110, 1 050, 990, 950, and 905 cm^{-1}; $\lambda_{max.}$(EtOH) 262 (log ε 4.98) and 330 nm (4.56); δ_H ($CDCl_3$; 80 MHz) 2.31 (3 H, s, OAc), 2.59 (3 H, s, Ac), 3.30 (4 H, m, 2 × CH_2), 5.50 (4 H, m, 2 × =CH_2), 6.09 (2 H, m, CH=), 7.49 (1 H, s, 6′-H), and 12.63 (1 H, s, 2′-OH); *m/z* 274 (M^+, 24.77%). It resisted acetylation with Ac_2O–Py, but gave a diacetate with Ac_2O–NaOAc and this compound was found to be identical with (**6a**) (mixed m.p., co-t.l.c., and i.r.).

Evaporation of the solvent from preparative band R_F 0.42 gave 3′,5′-diallyl-2′,6′-dihydroxyacetophenone (**12**) as a pale yellow oil (150 mg, 7%) (Found: C, 72.35; H, 7.0. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%), $FeCl_3$ colour→violet; $\nu_{max.}$(film) 3 050, 1 650 (CO), 1 620, 1 590, 1 455, 1 410, 1 370, 1 300, 1 230, 1 180, 1 160, 1 100, 980, 910, 880, and 840 cm^{-1}; $\lambda_{max.}$(EtOH) 258 (log ε 5.18) and 342 nm (4.69); δ_H ($CDCl_3$; 80 MHz) 2.38 (3 H, s, Ac), 3.43 (4 H, m, 2 × CH_2), 5.05 (4 H, br d, *J* 9.7 Hz, 2 × =CH_2), 5.9 (2 H, m, 2 × CH=), 6.09 (1 H, s, 6′-OH), 7.23 (1 H, s, 4′-H), and 12.72 (1 H, s, 2′-OH); *m/z* 232 (M^+, 52%).

Isolation of 4-*acetyl*-N,N-*dimethylaniline* (**13**) *from the solvent.* The aqueous acidic portion of the reaction mixture was neutralised with aqueous sodium hydroxide (50%) to give an oil, which was extracted into ether (3 × 100 ml). The ether solution was washed, dried ($MgSO_4$) and evaporated to give a dark red liquid (15 ml). It showed two spots on t.l.c. (R_F 0.76 and 0.13, benzene). This was chromatographed [silica gel (100 g)/hexane] to give *N*,*N*-dimethylaniline (13 ml) and compound (**13**).

4-*Acetyl*-N,N-*dimethylaniline* (**13**). Evaporation of the column fractions 25—35 (hexane–benzene, 1:9, each 250 ml) followed by crystallisation from aqueous ethanol gave (**13**) as pale brown needles (25 mg, 0.13%), m.p. 102 °C (lit.,[27] 99 °C); $\nu_{max.}$($CHCl_3$), 2 930, 1 680 (CO), 1 600, 1 520, 1 440, and 1 350 cm^{-1}.

Reactions of Compound (**2**) *in Trifluoroacetic Acid.—Room temperature.* Trifluoroacetic acid (3 ml) was added dropwise to compound (**2**) (1 g, 3.6 mmol) with stirring at 0 °C. Stirring was continued at room temperature for a further 24 h after which the reaction mixture was treated with ice cold water (10 ml) and extracted with chloroform (3 × 10 ml). The combined extracts were dried ($MgSO_4$) and concentrated to give a residue which showed two spots on t.l.c. (R_F 0.75 and 0.53, benzene–ethyl acetate, 9:1). The above reaction mixture was subjected to preparative t.l.c. using benzene–ethyl acetate (9:1) as the developing solvent and the bands were extracted with chloroform to give compounds (**1**) (12.3%) and (**9**) (70%).

Evaporation of the solvent from preparative band R_F 0.75 gave a residue, which on crystallisation from methanol gave 5′-acetyl-4′-allyloxy-2′-hydroxyacetophenone (**9**) as colourless prisms (600 mg, 70%), m.p. 95 °C (Found: C, 65.95; H, 6.5. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.02%); $FeCl_3$ colour→violet; $\nu_{max.}$(KBr) 1 670 (CO), 1 625, 1 445, 1 270, 1 220, 1 050, 980, and 905 cm^{-1}; $\lambda_{max.}$(EtOH) 255 and 318; δ_H($CDCl_3$; 80 MHz) 2.6 (6 H, s, 2 × Ac), 4.6 (2 H, d, *J* 5.3 Hz, OCH_2), 5.43 (2 H, m, =CH_2), 5.9 (1 H, m, CH=), 6.43 (1 H, s, 3′-H), 8.32 (1 H, s, 6′-H), and 12.88 (1 H, s, 2′-OH).

At 60 °C. A mixture of TFA (3 ml) and compound (**2**) (1 g) was heated on a water-bath at 60 °C for 1 h after which it was diluted with water. The solid which separated when crystallised from methanol yielded (**1**) as colourless needles (600 mg).

Thermal Rearrangement of Bisallyl Ether (**2**) *in Diphenyl Ether.*—The bisallyl ether (**2**) (500 mg, 1.8 mmol) in diphenyl ether (5 ml) was refluxed for 6 h after which the reaction mixture was chromatographed [silica gel column (75 g)/hexane].

Hexane fractions 1—5 (each 250 ml) gave diphenyl ether (4.5 ml): further hexane elution and then hexane–benzene mixtures yielded compounds (**6**) (10.6%), (**12**) (6%), and compounds (**10**) and (**11**) as a mixture (60 mg). This product mixture was subjected to preparative t.l.c. using benzene–ethyl acetate (9:1) as the developing solvent and the bands were extracted with chloroform to give compounds (**10**) and (**11**).

Concentration of the chloroform solution from band 1 gave 4-acetoxy-5-acetyl-7-allyl-2-methyl-2,3-dihydrobenzofuran (**10**) as a pale yellow oil (25 mg, 2.5%) (Found: C, 70.0; H, 6.6. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); $FeCl_3$ colour→−ve; $\nu_{max.}$(film) 2 920, 2 900, 1 725 (OAc), 1 675 (Ac), 1 615, 1 590, 1 435, 1 370, 990, and 900 cm^{-1}; δ_H($CDCl_3$; 80 MHz) 1.5 (3 H, d, *J* 6.2 Hz, 2-Me), 2.28 (3 H, s, OAc), 2.61 (3 H, s, Ac), 2.78—3.39

(4 H, m, CH_2 and 3-CH_2), 5.03 (3 H, m, =CH_2 and 2-H), 5.93 (1 H, m, CH=), and 7.58 (1 H, s, 6-H).

Evaporation of chloroform from band 2 gave 6′-acetoxy-3′,5′-diallyl-2′-hydroxyacetophenone (**11**) as a pale violet semisolid (25 mg, 2.5%) (Found: C, 70.0; H, 6.7. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); $FeCl_3$ colour→deep green; $\nu_{max.}$(film) 3 450—3 250 (OH), 1 720 (OAc), 1 680 (Ac), 1 600, 1 570, 990, and 910 cm^{-1}; δ_H($CDCl_3$; 80 MHz), 2.16 (3 H, s, OAc), 2.38 (3 H, s, Ac), 3.45 (2 H, d, *J* 5.9 Hz, CH_2), 3.67 (2 H, d, *J* 5.7 Hz, CH_2), 5.15 (4 H, br d, 2 × =CH_2), 6.06 (2 H, m, 2 × CH=), 6.12 (1 H, s, 2′-OH), and 7.25 (1 H, s, 4′-H).

Thermal Rearrangement of the Bisallyl Ether (**2**) *in Glycerol.*—The bisallyl ether (**2**) (500 mg, 1.82 mmol) was refluxed in freshly distilled glycerol (5 ml) for 45 min. The reaction mixture was treated with water (50 ml) and the resulting syrupy solution was extracted with chloroform (3 × 50 ml). The combined extracts were dried ($MgSO_4$) and evaporated to give a dark gum which (400 mg) on preparative t.l.c. using benzene as developing solvent gave compounds (**3A**) (14.7%), (**4**), and (**5**).

Concentration of the solvent from preparative t.l.c. band 2 (R_F 0.36) gave 7-allyl-4-hydroxy-2-methyl-2,3-dihydrobenzofuran (**4**) as a pale pink semisolid (30 mg, 8.7%) (Found: C, 75.7; H, 7.5. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.41%); $FeCl_3$ colour→brown; $\nu_{max.}$($CHCl_3$) 3 450—3 300 (OH), 3 000, 1 610, 1 600, 1 500, 1 445, 975, and 900 cm^{-1}; $\lambda_{max.}$(EtOH) 280 nm; δ_H ($CDCl_3$; 80 MHz) 1.45 (3 H, d, *J* 6.2 Hz, 2-Me), 2.58—3.43 (2 H, m, 3-CH_2), 3.25 (2 H, d, *J* 6.0 Hz, CH_2), 5.03 (3 H, m, =CH_2 and 2-H), 5.8—6.15 (2 H, m, CH= and OH), 6.24 (1 H, d, *J* 8.0 Hz, 5-H), and 6.8 (1 H, d, *J* 8.0 Hz, 6-H).

Evaporation of the chloroform solution from band 3 (R_F 0.22) gave 4,6-diallylresorcinol (**5**) as a reddish semisolid (30 mg, 8.7%) (Found: C, 75.7; H, 7.6. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.41%); $FeCl_3$ colour→blue; $\nu_{max.}$($CHCl_3$) 3 450—3 300 (OH), 3 000, 1 615, 1 500, 1 440, 990, and 910 cm^{-1}; δ_H($CDCl_3$; 80 MHz), 3.31 (4 H, d, *J* 5.7 Hz, 2 × CH_2), 5.11 (4 H, m, 2 × =CH_2), 6.06 (2 H, m, 2 × CH=), 6.35 (2 H, br s, 2 × OH), 6.79 (1 H, s, 2-H), and 7.25 (1 H, s, 5-H).

Preparation of 5′-Acetyl-3′-bromo-2′,4′-dihydroxyacetophenone (**21**).—A mixture of 4,6-diacetylresorcinol (**1**) (1.94 g, 10 mmol), *N*-bromosuccinimide (2.67 g, 15 mmol), and freshly distilled dioxane (25 ml) was refluxed for 10 h after which it was poured onto ice cold water (150 ml) with stirring. The resulting solution was treated with aqueous sodium hydroxide (20%) to decompose the excess of *N*-bromosuccinimide. The reaction mixture was neutralised with aqueous HCl (1:1) and kept at 0 °C for 24 h. The pale red solid which separated was filtered off and recrystallised from chloroform–methanol to give the title compound (**21**) as colourless shining flakes (2.65 g, 97%) (Found: C, 43.85; H, 3.25. $C_{10}BrO_4$ requires C, 43.97; H, 3.32%); $FeCl_3$ colour→red; $\nu_{max.}$(KBr) 1 630 (CO) and 760 (CBr); $\lambda_{max.}$(EtOH) 264 nm; δ_H($CDCl_3$; 90 MHz) 2.68 (6 H, s, 2 × Ac), 8.21 (1 H, s, 6′-H), and 12.1 (2 H, s, 2 × OH).

Preparation of 5′-Acetyl-2′,4′-diallyloxy-3′-bromoacetophenone (**23**).—A mixture of compound (**21**) (1 g, 3.6 mmol), allyl bromide (1 ml, 10 mmol), and freshly ignited potassium carbonate (5 g) was refluxed in dry acetone for 24 h. Work-up as for compound (**2**) afforded a pale brown precipitate which on crystallisation from aqueous alcohol gave the title compound (**23**) as colourless prisms (730 mg, 56.5%) (Found: C, 53.95; H, 4.8. $C_{16}H_{17}BrO_4$ requires C, 54.40; H, 4.85%); $FeCl_3$ colour→−ve; $\nu_{max.}$(KBr) 1 670 (CO) 1 580, 1 530, 1 450, 1 410, 1 355, 1 270, 1 220, 1 050, 1 000, 910, and 715 cm^{-1} (CBr); $\lambda_{max.}$(EtOH) 245 (log ε 4.85) nm; δ_H($CDCl_3$; 90 MHz) 2.6 (6 H, s, 2 × Ac), 4.52 (4 H, d, *J* 5 Hz, 2 × OCH_2), 5.35 (4 H, m, 2 × =CH_2), 6.1 (2 H, m, 2 × CH=), and 7.9 (1 H, s, 6′-H).

Thermal Rearrangement of the Bromoallyl Ether (**23**) *in* N,N-*Dimethylaniline.*—Compound (**23**) (700 mg, 1.9 mmol) was refluxed in *N*,*N*-dimethylaniline (5 ml) for 6 h after which work-up of the mixture gave a dark red gum (650 mg). It showed 10 spots on a t.l.c. plate (R_F 0.72, 0.7, 0.59, 0.48, 0.36, and 0.27, benzene) and R_F 0.7, 0.66, 0.61, and 0.43, benzene–ethyl–acetate, 9:1). The above reaction mixture was column chromatographed [silica gel (15 g)/hexane] to yield compounds A—J of which B, D, E, and F were obtained in very low yields and could not be analysed completely.

Characterisation of compound A: a mixture of two new dihydrobenzofurans (**25a**) *and* (**25b**). Column fractions 5—10 (hexane–benzene, 9:1; each 25 ml) on concentration gave a greenish yellow residue which on further purification using preparative t.l.c. followed by crystallisation gave an inseparable mixture of (**25a**) and (**25b**) as colourless needles (30 mg, 6.52%) (Found: C, 72.3; H, 7.0. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%); $FeCl_3$ colour→green; $\nu_{max.}$(KBr) 3 400—3 250 (OH), 1 640, 1 610, 1 430, 1 340, 1 210, 1 085, 1 020, 995, 910, and 815 cm^{-1}; $\lambda_{max.}$(EtOH) 240, 270, and 368 nm; δ_H($CDCl_3$; 90 MHz) 1.3 (3 H, d, *J* 6 Hz, 2-Me), 1.45 (3 H, d, *J* 6 Hz, 2′-Me), 2.45 (3 H, s, Ac), 2.6—3.2 (2 H, m, 3-CH_2), 3.3 (2 H, d, *J* 7 Hz, CH_2), 5.0 (3 H, m, =CH_2 and 2-H), 6.0 (1 H, m, CH=), 6.9 (1 H, s, OH), and 7.25 (1 H, s, 6-H).

Identification of compound C as compound (**6**). Column fractions 30—45 (hexane–benzene, 6:4, each 250 ml) gave compound (**6**) (75 mg, 16.3%) identical with an authentic spectrum (see earlier). Further elution of the column (fractions 90—115, benzene, each 100 ml) gave a greenish yellow oil (80 mg). T.l.c. showed that this was a mixture (R_F 0.7, 0.66, 0.61, and 0.43, benzene–ethyl acetate, 9:1). This on further purification by preparative t.l.c. gave compounds G, H, I, and J. Compounds G, H, and J could not be analysed further due to insufficient quantities.

Characterisation of compound I: 5,7-*diacetyl*-4-*hydroxy*-2-*methyl*-2,3-*dihydrobenzofuran* (**26**). Compound I was obtained as a pale yellow oil (25 mg, 5.38%) (Found: C, 66.8; H, 6.45. $C_{13}H_{14}O_4$ requires C, 66.65; H, 6.02%); $FeCl_3$ colour→violet; $\nu_{max.}$(film) 2 930, 1 675, 1 630, 1 590, 1 470, 1 430, 1 360, 1 280, 1 220, 1 025, and 820 cm^{-1} δ_H($CDCl_3$; 80 MHz) 1.54 (3 H, d, *J* 6.1 Hz, 2-Me), 2.58 (3 H, s, Ac), 2.61 (3 H, s, Ac), 2.6—3.4 (2 H, m, 3-CH_2), 4.99—5.17 (1 H, m, 2-H), 8.32 (1 H, s, 6-H), and 12.8 (1 H, s, OH).

Preparation of 5′-Acetyl-2′,4′-dihydroxy-3′-nitroacetophenone (**22**).[25]—Compound (**1**) (3.88 g, 20 mmol) and nitric acid (*d*, 1.42; 40 ml) were warmed to 80 °C. After work-up, it gave the title compound (**22**) as pale yellow hexagonal plates from dilute alcohol (4 g, 83.6%), m.p. 235 °C (lit.,[25] 235 °C) (Found: C, 50.3; H, 3.6; N, 5.6. $C_{10}H_9NO_6$ requires C, 50.2; H, 3.8; N, 5.8%); $FeCl_3$ colour→bright orange red; $\nu_{max.}$(KBr) 1 660 (CO), and 1 525 and 1 350 (NO_2); $\lambda_{max.}$(EtOH) 252 and 312 nm; δ_H (Me_2SO; 90 MHz) 2.75 (6 H, s, 2 × Ac) and 8.6 (1 H, s, 6′-H).

Preparation of 5′-Acetyl-2′,4′-diallyloxy-3′-nitroacetophenone (**24**).—A mixture of compound (**22**) (1.8 g, 7.5 mmol), allyl bromide (2.5 ml, 28 mmol), and anhydrous potassium carbonate (5 g) was refluxed in dry acetone (50 ml) for 6 h. Work-up of the mixture and purification of the product by silica gel column chromatography gave a residue, which on crystallisation from hexane gave compound (**24**) as pale yellow prisms (1.5 g, 62.5%), m.p. 73 °C (Found: C, 59.85; H, 5.8. $C_{16}H_{17}NO_6$ requires C, 60.18; H, 5.36%); $FeCl_3$ colour→−ve; $\nu_{max.}$(KBr) 1 675, 1 620, 1 525, 1 420, 1 350, 1 275, 1 210, 1 080, 995, 925, and 895 cm^{-1}; $\lambda_{max.}$(EtOH) 232 nm (log ε 4.70); δ_H ($CDCl_3$; 90 MHz) 2.6 (6 H, s, 2 × Ac), 4.5 (4 H, d, *J* 6 Hz, 2 × OCH_2), 5.3 (4 H, m, 2 × =CH_2), 5.9 (2 H, m, CH=), and 8.05 (1 H, s, 6′-H).

Thermal Rearrangement of the Nitroallyl Ether (**24**) *in* N,N-*Dimethylaniline*.—The above allyl ether (**24**) (1 g, 3.1 mmol) was refluxed in *N,N*-dimethylaniline (10 ml) for 6 h. Work-up of the mixture gave a tar (300 mg) which on successive extraction with chloroform and acetone provided a dark red gum (150 mg). This on repetitive column and preparative chromatography on silica gel yielded compound (**3A**) (3.4%) and four other compounds which could not be identified because of paucity of material.

Preparation of 3′-Acetyl-2′,4′-diallyloxyacetophenone (**18**).—A mixture of 2,4-diacetylresorcinol (**14**) (0.970 g, 5 mmol) allyl bromide (1.3 ml, 15 mmol), and potassium carbonate (10 g) was refluxed for 12 h in dry acetone (50 ml). Work-up yielded the title compound (**18**) as a bright greenish yellow viscous liquid (1.2 g, 87.59%) (Found: C, 70.05; H, 6.55. $C_{16}H_{18}O_4$ requires C, 70.05; H, 6.61%); $FeCl_2$ colour→−ve; $\nu_{max.}$(film) 3 050, 1 700, 1 670, 1 580, 1 475, 1 410, 1 350, 1 260, 1 230, 1 070, 985, 925, and 810 cm^{-1}; $\lambda_{max.}$(EtOH) 235 (log ε 5.0) and 268 nm (5.38); δ_H($CDCl_3$; 90 MHz), 2.5 (3 H, s, Ac), 2.6 (3 H, s, Ac), 4.4 (2 H, d, *J* 5.5 Hz, OCH_2), 4.6 (2 H, d, *J* 5.5 Hz, OCH_2), 5.3 (4 H, m, 2 × $=CH_2$), 5.95 (2 H, m, 2 × CH=), 6.75 (1 H, d, *J* 9 Hz, 5′-H), and 7.7 (1 H, d, *J* 9 Hz, 6′-H).

Thermal Rearrangement of Compound (**18**) *in* N,N-*Dimethylaniline*.—The above allyl ether (**18**) (1 g, 3.6 mmol) was refluxed in *N,N*-dimethylaniline for 6 h. Work-up gave a dark reddish gum (1.1 g) which on silica gel (25 g) column chromatography gave two new dihydrobenzofurans as a mixture (**25a**) and (**25b**) (4.7%) and compounds (**6**) (17.7%), (**7**) (5%), and (**12**) (5.9%).

Preparation of 2′,4′-Diallyloxyacetophenone (**19**).—A mixture of resacetophenone (**15**) (3.04 g, 20 mmol), allyl bromide (3.45 ml, 40 mmol), and freshly fused potassium carbonate (10 g) was refluxed in dry acetone (100 ml) for 12 h. The reaction mixture was filtered and the filtrate was distilled under reduced pressure. The resulting residue was treated with water and extracted with ether (3 × 50 ml) and the extract washed with aqueous sodium hydroxide (30%), water, and dried ($MgSO_4$). On evaporation it gave a residue, which crystallised from hexane to give the title compound as colourless shining needles (2.75 g, 59.2%), m.p. 40—41 °C (Found: C, 72.0; H, 6.5. $C_{14}H_{16}O_3$ requires C, 72.39; H, 6.94%); $FeCl_3$ colour→−ve; $\nu_{max.}$(KBr) 1 660 (CO), 1 620, 1 420, 1 355, 1 290, 1 225, 1 055, 990, and 925 cm^{-1}; $\lambda_{max.}$(EtOH) 232 (log ε 4.98), 268 (5.11), and 304 nm (4.93); δ_H($CDCl_3$; 90 MHz) 2.6 (3 H, s, Ac), 4.6 (4 H, d, *J* 5 Hz, 2 × OCH_2), 5.35 (4 H, m, 2 × $=CH_2$), 6.0 (2 H, m, 2 × CH=), 6.45—6.55 (2 H, m, 3′- and 5′-H), and 7.8 (1 H, d, *J* 9 Hz, 6′-H).

Thermal Rearrangement of Compound (**19**) *in* N,N-*Dimethylaniline*.—The above allyl ether (**19**) (1 g, 4.3 mmol) was refluxed in *N,N*-dimethylaniline (10 ml) for 6 h. Work-up and preparative t.l.c. gave compounds (**6**) (40%) and (**3A**) (40%).

Preparation of 2′-Allyloxy-4′-methoxyacetophenone (**20**).—A mixture of peonol (**16**) (1.66 g, 1 mmol), allyl bromide (1.72 ml, 20 mmol), and potassium carbonate (5 g) was refluxed in acetone (100 ml) for 10 h. Work-up afforded the title compound (**20**) as an oil (1.8 g, 87.3%) (Found: C, 68.9; H, 7.0. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.94%); $FeCl_3$ colour→−ve; $\nu_{max.}$($CHCl_3$) 1 660 (CO), 1 640, 1 600, 1 570, 1 500, 1 480, 1 420, 1 380, 1 350, 1 290, 1 240, 1 060, 990, 920, and 830 cm^{-1}; $\lambda_{max.}$(EtOH) 268 (log ε 5.12) and 304 nm (4.93); δ_H($CDCl_3$; 90 MHz) 2.6 (3 H, s, Ac), 3.8 (3 H, s, OMe), 4.6 (2 H, d, *J* 7 Hz, OCH_2), 5.4 (2 H, m, $=CH_2$), 5.1 (1 H, m, CH=), 6.4—6.6 (2 H, m, 3′- and 5′-H), and 7.85 (1 H, d, *J* 9 Hz, 6′-H).

Thermal Rearrangement of Compound (**20**) *in* N,N-*Dimethylaniline*.—The allyl ether (**20**) (1 g, 4.8 mmol) was refluxed in *N,N*-dimethylaniline (10 ml) for 6 h. Work-up afforded 3′-allyl-2′-hydroxy-4′-methoxyacetophenone (**17**) which crystallised as yellow needles from methanol (800 mg, 80%), m.p. 59 °C (lit.,[26] 61 °C) (Found: C, 69.3; H, 6.9. $C_{12}H_{14}O_3$ requires C, 69.88; H, 6.84%); $FeCl_3$ colour→violet; $\nu_{max.}$(KBr) 1 640 (CO), 1 600, 1 580, 1 450, 1 410, 1 270, 990, 915, and 820 cm^{-1}; $\lambda_{max.}$(EtOH) 282 nm (log ε 4.83); δ_H($CDCl_3$; 90 MHz) 2.5 (3 H, s, Ac), 3.35 (2 H, br d, CH_2), 3.85 (3 H, s, OMe), 4.95 (2 H, m, $=CH_2$), 5.9 (1 H, m, CH=), 6.45 (1 H, d, *J* 9 Hz, 5′-H), 7.6 (1 H, d, *J* 9 Hz, 6′-H), and 12.8 (1 H, s, OH).

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