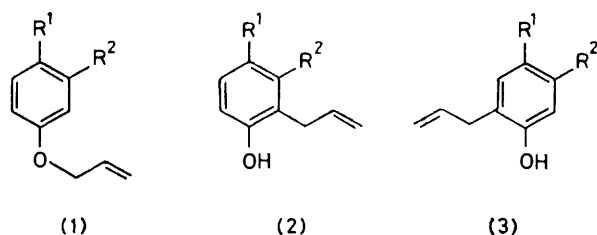


Claisen Rearrangement of *meta*-Substituted Allyl Phenyl Ethers

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Electron-releasing substituents at the 3-position of allyl phenyl ethers favour Claisen rearrangement of the allyl group to the 6-position, whereas electron-acceptors favour migration to the 2-position. 2-Acylhydroquinone 4-allyl ethers yield, predominantly, the 3-allyl isomers, probably because internal hydrogen bonding confers naphthalenoid character on the aryl residue.

ALTHOUGH the Claisen rearrangement of allyl aryl ethers has been extensively studied,¹ relatively little data are available for *meta*-substituted systems (1; R¹ = H) in which migration can in principle occur to two different *ortho*-positions, giving (2; R¹ = H) and (3; R¹ = H). Rearrangements have been described for (1; R¹ = H) in which R² = NHAc,² OMe,³⁻⁵ O-allyl,⁶ OH,⁷ Me,^{4,5,8} CF₃,^{5,9} NO₂,¹⁰ Cl,⁴ Br,^{4,5,11} CN,⁴ OAc,¹² CPh,⁴ and CO₂Me,¹⁰ and, although there is a slight tendency overall for the isomer (2; R¹ = H) to predominate when R² is electron-accepting, and for (3; R¹ = H) to predominate



when it is electron-donating, a precise assessment of its effect is difficult to make because the conditions used for the rearrangements and for work-up varied considerably.

isolated by sublimation, and its composition determined by ¹H n.m.r. spectroscopy using the methylene proton resonances for integration: those in the isomers (2; R¹ = H) are doublets of triplets (J_1 5–6, J_2 1–2 Hz), whereas those in (3; R¹ = H) are doublets (J 5–6 Hz) in which the triplet structure is obscured by additional coupling with the adjacent ring proton; it is restored by spin-decoupling of this proton. The methylene resonances in both (2; R¹ = H, R² = CF₃) and (3; R¹ = H, R² = CF₃) are broad doublets due to long-range coupling with fluorine, but both are sharpened, the former to a doublet of triplets, by fluorine decoupling.

The results, summarised in Table 1, suggest that an electron-accepting *meta*-substituent favours formation of the isomer (2; R¹ = H). Dipolar attraction of the allyl π -system preferentially to the 2-position of the ring may be involved.

Hydroquinone mono-allyl ethers (1; R¹ = OH) were similarly examined, in the absence of a solvent. The results are summarised in Table 2. A *meta*-methyl group favours migration to the position *para* to it, whilst a *meta*-*t*-butyl group directs exclusively to this position, probably due to its steric effect. Electron-accepting

TABLE 1

Claisen rearrangement of allyl phenyl ethers (1; R¹ = H) at 220 °C

R ² in (1)	Product sublimation temp./°C/mmHg	Neat			In HCONMe ₂		
		Time/h ^a	Total yield (%)	Ratio (2) : (3)	Time/h ^a	Total yield (%)	Ratio (2) : (3)
OMe	40/0.05	1.5	86	1 : 2	4.0	80	2 : 1
Me	72/0.05	2.5	85	1 : 1	4.5	90	1 : 1
H	50/0.05	1.7	80		3.0	78	
CF ₃	42/0.05		Decomp.		5.8	81	1 : 1
NO ₂			Decomp.		0.5	12 ^b	
CO ₂ Me	58/0.05	1.5	68	6 ^c : 1		Decomp.	
CHO			Decomp.			Decomp.	
COMe	78/0.05	1.0	65	2 : 1	1.0	80	2 : 1

^a Time for consumption of allyl ether. ^b In Ph₂O (less extensive decomposition than in HCONMe₂); product isolated by p.l.c. ^c A 5 : 1 mixture of (2; R = CO₂Me) and methyl 2,3-dihydro-2-methylbenzofuran-4-carboxylate.

We now report on isomer distributions resulting from Claisen rearrangements of several *meta*-substituted allyl phenyl ethers¹³ under mutually comparable conditions.

RESULTS AND DISCUSSION

The highest and most reproducible yields were obtained by heating the allyl ethers *in vacuo* at 220 °C, either alone or in *NN*-dimethylformamide, until the starting material had been consumed. The total product was

substituents, R² in (1; R¹ = OH), of which acetyl^{14,15} and propionyl^{14,16} have been studied previously, favour migration to the position *ortho* to them, exclusively in the case of acetyl.* Strong internal hydrogen bonding, as (4), here confers naphthalenoid character¹⁴ on the molecule, and the rearrangement thus resembles that

* In one experiment in which the temperature was raised from 180 to 230 °C during 45 min,¹⁴ a low yield of the isomer (3; R¹ = OH, R² = COMe) was detected by ¹H n.m.r. spectroscopy, but this result was not reproducible.

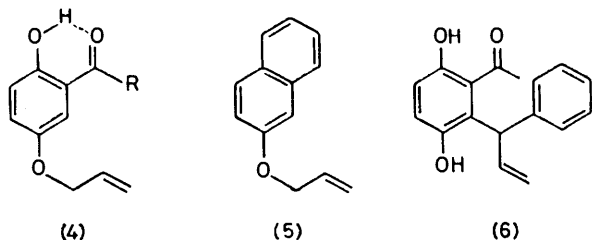
TABLE 2

Claisen rearrangement of hydroquinone allyl ethers
(1; R¹ = OH) at 220 °C

R ² in (1)	Product sublimation temp./°C/mmHg	Time/h ^a	Total yield (%)	Ratio ^b (2) : (3)
Bu ^t	64—80/0.05	0.8	61	0 : 1
Me	92/0.05	2.5	68	11 ^c : 15 ^d
CO ₂ Me	74—92/0.05	0.7	83	11 ^e : 6 ^f
CHO	74—94/0.05	0.5	85	2 : 1
COMe	81/0.05	0.5	75	1 : 0

^a Time for consumption of allyl ether. ^b For (2) and (3), R¹ = OH. ^c A 1 : 10 mixture of (2; R¹ = OH, R² = Me) and 2,3-dihydro-2,4-dimethylbenzofuran-5-ol. ^d A 1 : 2 mixture of (3; R¹ = OH, R² = Me) and 2,3-dihydro-2,6-dimethylbenzofuran-5-ol. ^e A 10 : 1 mixture of (2; R¹ = OH, R² = CO₂Me) and methyl 2,3-dihydro-5-hydroxy-2-methylbenzofuran-4-carboxylate. ^f A 10 : 1 mixture of (3; R¹ = OH, R² = CO₂Me) and methyl 2,3-dihydro-5-hydroxy-2-methylbenzofuran-6-carboxylate.

observed for 2-allyloxynaphthalene (5), which gives 1-allyl-2-naphthol exclusively.⁵



An attempt to exploit the regioselectivity of this rearrangement to provide a precursor (6) for a synthesis of a 1,4-dihydroxyanthracene was unsuccessful: 5'-cinnamyloxy-2'-hydroxyacetophenone underwent decinnamylation at 220 °C; the corresponding benzyl ether¹³ was stable at this temperature, but decomposed at 260 °C.

EXPERIMENTAL

Allyl ethers were prepared as described elsewhere,¹³ under nitrogen for those of hydroquinones. Claisen rearrangements of the allyl ethers (1 mmol), either alone or in freshly distilled *N,N*-dimethylformamide (2 ml), were carried out in a glass tube which, after evacuation at 0.01 mmHg, was closed by a Teflon 'Rotaflo' stopcock arranged so that the tube could be immersed in the heating-bath, at 220 °C, up to the plug of the stopcock, thus eliminating cold-spots on which condensation could occur. Progress of the reaction was monitored by removal of the tube from the heating-bath, rapid cooling, opening, and t.l.c. analysis; the tube was then pumped out again, and the process repeated until the allyl ether had been consumed. The total product was then sublimed (bulb-to-bulb; Tables 1 and 2) and its composition determined by ¹H n.m.r. spectroscopy at 90 MHz for 6% solutions (in CDCl₃ unless stated otherwise, using tetramethylsilane as an internal standard); resonances due to hydroxy-protons were removed by addition of D₂O. Where possible, products were separated by fractional sublimation and p.l.c.; only new or key compounds are detailed below.

5-Allyloxy-2-hydroxy-*t*-butylbenzene.—This was an oil (81% yield) (Found: C, 74.6; H, 9.4. C₁₂H₁₈O₂ requires C, 74.2; H, 9.3%); δ 1.45 (s, Bu^t), 4.51 (dt, J₁ 5, J₂ 1 Hz,

CH₂O), 4.70 (br s, OH), 5.2—5.6 (m, CH₂=), 5.9—6.4 (m, =CH), and 6.5—7.1 (m, 3 × Ar-H); ν_{max.} (film) 3 700—3 120 cm⁻¹; m/e 206 (M⁺, 20%), 165 (46), 149 (27), and 41 (100).

5-Allyloxy-2-hydroxytoluene.—This was an oil (68% yield) (Found: C, 73.2; H, 7.5. C₁₀H₁₃O₂ requires C, 73.2; H, 7.3%); δ 2.16 (s, Me), 4.39 (dt, J₁ 5, J₂ 1 Hz, CH₂O), 4.84 (br s, OH), 5.0—5.5 (m, CH₂=), 5.8—6.3 (m, =CH), and 6.4—6.8 (m, 3 × Ar-H); ν_{max.} (film) 3 660—3 180 cm⁻¹; m/e 164 (M⁺, 44%), 132 (100), and 41 (13).

5-Allyloxy-2-hydroxybenzaldehyde.—This was an oil (lit.¹⁴ oil) (82% yield); δ 4.35 (dt, J₁ 5, J₂ 1 Hz, CH₂O), 5.2—5.7 (m, CH₂=), 5.8—6.5 (m, =CH), 6.8—7.4 (m, 3 × Ar-H), 9.88 (s, CHO), and 10.65 (s, OH); ν_{max.} (film) 3 460br and 1 640 cm⁻¹; m/e 178 (M⁺, 47%), 150 (9), 137 (100), 109 (38), 81 (38), and 41 (5).

5'-Allyloxy-2'-hydroxyacetophenone.—Isolated as pale yellow crystals (86% yield), m.p. 59—60 °C (lit.¹⁴ 59—69 °C); δ 2.63 (s, Me), 4.54 (dt, J₁ 5, J₂ 1 Hz, CH₂O), 5.2—5.5 (m, CH₂=), 5.7—6.4 (m, =CH), 6.8—7.4 (m, 3 × Ar-H), and 11.84 (s, OH); ν_{max.} (Nujol) 3 300—3 200 and 1 645 cm⁻¹; m/e 192 (M⁺, 34%), 151 (100), 43 (13), and 41 (10).

5'-Cinnamyloxy-2'-hydroxyacetophenone.—This was isolated as yellow needles, by sublimation at 140 °C/0.05 mmHg (90% yield), m.p. 105—107 °C (Found: C, 76.4; H, 5.8. C₁₇H₁₆O₃ requires C, 76.1; H, 6.0%); δ (C₆D₆) 1.94 (s, Me), 4.20 (dt, J₁ 5, J₂ 1 Hz, CH₂O), 5.9—6.7 (m, CH=CH), 6.8—7.3 (8 × Ar-H), and 12.26 (OH); ν_{max.} (CHCl₃) 3 560—3 240 and 1 645 cm⁻¹; m/e 268 (M⁺, 3%), 151 (1), and 117 (100). Heating of this compound at 220 °C for 20 h followed by sublimation at 95 °C/0.05 mmHg, gave 2',5'-dihydroxyacetophenone (64%), m.p. 196—198 °C.

Analysis of Mixtures.—The following allyl CH₂O resonances (dt, J₁ 5—6, J₂ 1—2 Hz, when 2,6-disubstituted; br d, J₁ 5—6 Hz, when *ortho* to H, becoming a dt on spin-decoupling of this H), and other listed resonances, were integrated to give the composition of the mixtures resulting from Claisen rearrangements. (a) 3-Methoxyphenol : 2-allyl, δ 3.51 [δ (C₆D₆) 3.53]; 6-allyl, δ 3.37 [δ (C₆D₆) 3.25]. (b) 3-Methylphenol : 2-allyl and 6-allyl, δ 3.33—3.56 [δ (C₆D₆) 3.15—3.45] with partial overlap; Me resonances, overlapping at δ 2.35, separated by addition of Eu(fod)₃. (c) 3-Trifluoromethylphenol : 2-allyl, δ 3.44 [δ (C₆D₆) 3.51]; 6-allyl, δ 3.44 [δ (C₆D₆) 3.21]; spectra of solutions in C₆D₆ measured at 80 MHz, with ¹⁹F decoupling at 75.291 520 MHz. (d) 2,5-Dihydroxytoluene : 4-allyl, δ (C₆D₆) 3.08; 6-allyl, δ (C₆D₆) 3.25; 2,3-dihydro-2,6-dimethylbenzofuran-7-ol : δ 1.49 (d, J 6.5 Hz, 2-Me), 2.19 (s, 6-Me), 2.75 (dd, J₁ 15, J₂ 7.5 Hz), and 3.26 (dd, J₁ 15, J₂ 7.5 Hz); 2,3-dihydro-2,4-dimethylbenzofuran-5-ol : δ 1.52 (d, J 6.5 Hz, 2-Me), 2.24 (s, 4-Me), 2-H and 3-H resonances as for the 2,6-dimethyl isomer.

Resonances are listed separately for the following compounds, which were isolated in a pure state.

2-Allyl-3-nitrophenol.—This was an oil (Found: C, 60.2; H, 5.6; N, 7.5. C₉H₉NO₃ requires C, 60.3; H, 5.0; N, 7.8%); δ 3.63 (dt, J₁ 6, J₂ 2 Hz, -CH₂-), 5.0—5.6 (m, CH₂= + OH), 5.8—6.4 (m, =CH), 7.07 (dd, J₁ 8.5, J₂ 2 Hz, 6-H), 7.39 (t, 8.5 Hz, 5-H), and 7.73 (dd, J₁ 8.5, J₂ 2 Hz, 4-H); ν_{max.} (film) 3 680—3 200 cm⁻¹; m/e 179 (M⁺, 25%), 178 (25), 162 (100), 161 (30), 150 (93), 145 (77), 139 (98), and 133 (34).

2-Allyl-5-nitrophenol.—This was an oil (Found: C, 60.6; H, 5.1; N, 7.2. C₉H₉NO₃ requires C, 60.3; H, 5.0; N, 7.8%); δ 3.53 (br d, J 6 Hz, -CH₂-), 5.0—5.4 (m, CH₂=), 5.48 (s, OH), 5.8—6.4 (m, =CH), 7.28 (d, J 8.5 Hz, 3-H), 7.70 (d, J 2.5 Hz, 6-H), and 7.78 (dd, J₁ 8.5, J₂ 2.5 Hz, 4-H);

ν_{\max} . (film) 3 680—3 200 cm^{-1} ; m/e 179 (M^+ , 100%) and 164 (16).

Methyl 2-Allyl-3-hydroxybenzoate.—This was isolated as colourless crystals, m.p. 72—74 °C (Found: C, 68.6; H, 6.7. $\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C, 68.8; H, 6.3%); δ 3.69 (dt, J_1 6, J_2 2 Hz, $-\text{CH}_2-$), 3.81 (s, Me), 4.8—5.2 (m, $\text{CH}_2=$), 5.32 (s, OH), 5.7—6.3 (m, =CH), 6.90 (dd, J_1 8, J_2 2 Hz, 4-H), 7.06 (t, J 8 Hz, 5-H), and 7.34 (dd, J_1 8, J_2 2 Hz, 6-H); ν_{\max} . (Nujol) 3 480—3 220 and 1 696 cm^{-1} ; m/e 192 (M^+ , 100%), 177 (73), 161 (50), 133 (25), 105 (26), and 77 (18).

Methyl 2,3-Dihydro-2-methylbenzofuran-4-carboxylate.—This was an oil (Found: C, 68.4; H, 6.3. $\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C, 68.8; H, 6.3%); δ 1.43 (d, J 6.5 Hz, 2-Me), 3.05 (dd, J_1 17, J_2 7.5 Hz, $1 \times 3\text{-H}$), 3.64 (dd, J_1 17, J_2 8.5 Hz, $1 \times 3\text{-H}$), 3.83 (s, OMe), 4.6—5.2 (m, 2-H), 6.85 (dd, J_1 8, J_2 1.5 Hz, 7-H), 7.10 (t, J 8 Hz, 6-H), and 7.43 (dd, J_1 8, J_2 1.5 Hz, 5-H); ν_{\max} . (film) 1 725 cm^{-1} ; m/e 192 (M^+ , 41%), 177 (33), 161 (20), 159 (21), and 133 (21).

Methyl 4-Allyl-3-hydroxybenzoate.—This was an oil (Found: C, 68.7; H, 6.2. $\text{C}_{11}\text{H}_{12}\text{O}_3$ requires C, 68.8; H, 6.3%); δ 3.40 (br d, J 6 Hz, $-\text{CH}_2-$), 3.84 (s, Me), 4.9—5.2 (m, $\text{CH}_2=$), 5.54 (br s, OH), 5.7—6.2 (m, =CH), 7.12 (d, J 8 Hz, 5-H), 7.48 (d, J 2 Hz, 2-H), and 7.50 (dd, J_1 8, J_2 2 Hz, 6-H); ν_{\max} . (Nujol) 3 660—3 100 and 1 665 cm^{-1} ; m/e 192 (M^+ , 100%), 177 (13), 161 (79), 133 (72), 105 (44), and 77 (35).

2-Allyl-3-hydroxybenzaldehyde.—This was an oil (Found: C, 80.6; H, 6.0. $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires C, 80.3; H, 6.2%); δ 3.93 (dt, J_1 6, J_2 1 Hz, $-\text{CH}_2-$), 4.9—5.3 (m, $\text{CH}_2=$), 5.36 (s, OH), 5.8—6.3 (m, =CH), 7.10 (dd, J_1 8, J_2 1.8 Hz, 4-H), 7.31 (t, J 8 Hz, 5-H), 7.47 (dd, J_1 8, J_2 1.8 Hz, 6-H), and 10.17 (s, CHO); ν_{\max} . (Nujol) 3 380—3 080 and 1 665 cm^{-1} ; m/e 162 (M^+ , 51%), 147 (100), 144 (42), and 115 (62).

4-Allyl-3-hydroxybenzaldehyde.—This was an oil (Found: C, 80.7; H, 6.4. $\text{C}_{10}\text{H}_{10}\text{O}_2$ requires C, 80.3; H, 6.2%); δ 3.44 (br d, J 6 Hz, $-\text{CH}_2-$), 4.9—5.3 (m, $\text{CH}_2=$), 5.43 (br s, OH), 5.7—6.3 (m, =CH), 6.7—7.5 (m, $3 \times \text{Ar-H}$), 9.88 (s, CHO), ν_{\max} . (Nujol) 3 360—3 060, 1 670 cm^{-1} , and m/e 162 (M^+ , 5), 147 (2), 119 (5), 91 (12), and 43 (100).

2'-Allyl-3'-hydroxyacetophenone.—This was an oil (Found: C, 75.0; H, 6.9. $\text{C}_{11}\text{H}_{12}\text{O}_2$ requires C, 75.0; H, 6.8%); δ 2.55 (s, Me), 3.62 (dt, J_1 6, J_2 2 Hz, $-\text{CH}_2-$), 4.9—5.2 (m, $\text{CH}_2=$), 5.8—6.2 (m, =CH), 6.23 (br s, OH), and 6.8—7.6 (m, $3 \times \text{Ar-H}$); ν_{\max} . (film) 3 580—3 040 and 1 675 cm^{-1} ; m/e 176 (M^+ , 8%), 161 (100), 150 (4), 133 (24), 155 (16), 105 (24), and 43 (78).

4'-Allyl-3'-hydroxyacetophenone.—This was isolated as colourless crystals, m.p. 62—64 °C (Found: C, 75.0; H, 6.9. $\text{C}_{11}\text{H}_{12}\text{O}_2$ requires C, 75.0; H, 6.8%); δ 2.54 (s, Me), 3.42 (br d, J 6 Hz, $-\text{CH}_2-$), 4.9—5.3 (m, $\text{CH}_2=$), 5.7—6.3 (m, =CH), 7.05 (br s, OH), 7.15 (d, J 8 Hz, 5'-H), 7.44 (dd, J_1 8, J_2 2 Hz, 6'-H), and 7.58 (d, J 2 Hz, 2'-H); ν_{\max} . (Nujol) 3 400—3 100 and 1 650 cm^{-1} ; m/e 176 (M^+ , 91%), 161 (100), 133 (29), and 43 (23).

2-Allyl-5-t-butylhydroquinone.—This was isolated as colourless crystals, m.p. 116—118 °C (Found: C, 75.6; H, 8.7. $\text{C}_{13}\text{H}_{18}\text{O}_2$ requires C, 75.7; H, 8.7%); δ 1.42 (s, Bu^t), 3.34 (br d, J 6 Hz, $-\text{CH}_2-$), 4.49 (s, OH), 4.56 (s, OH), 5.0—5.3 (m, $\text{CH}_2=$), 5.8—6.2 (m, =CH), 6.46 (s, 6-H), and 6.77 (s, 3-H); ν_{\max} . (Nujol) 3 680—3 100 cm^{-1} ; m/e 206 (M^+ , 5%) and 191 (100).

Methyl 6-Allyl-2,5-dihydroxybenzoate.—This was an oil (Found: C, 63.6; H, 6.0. $\text{C}_{11}\text{H}_{12}\text{O}_4$ requires C, 63.5; H, 5.8%); δ 3.75 (dt, J_1 6, J_2 1 Hz, $-\text{CH}_2-$), 3.96 (s, Me), 4.3—

5.3 (m, $\text{CH}_2=$ + 5-OH), 5.8—6.3 (m, =CH), 6.78 (d, J 9 Hz, 3-H), 7.00 (d, J = 9 Hz, 4-H), and 10.35 (s, 2-OH); ν_{\max} . (film) 3 700—3 040 and 1 670 cm^{-1} ; m/e 208 (M^+ , 38%), 176 (100), and 148 (24).

Methyl 4-Allyl-2,5-dihydroxybenzoate.—This was an oil (Found: C, 63.4; H, 5.9. $\text{C}_{11}\text{H}_{12}\text{O}_4$ requires C, 63.5; H, 5.8%); δ 3.37 (br d, J 6 Hz, $-\text{CH}_2-$), 3.96 (s, Me), 4.7—5.3 (m, $\text{CH}_2=$ + 5-OH), 5.7—6.3 (m, =CH), 6.63 (s, 3-H + 6-H), and 10.32 (s, 2-OH); ν_{\max} . (film) 3 660—3 100 and 1 670 cm^{-1} ; m/e 208 (M^+ , 38%), 176 (100), 149 (7), and 148 (18).

6-Allyl-2,5-dihydroxybenzaldehyde.—This was isolated as yellow crystals, m.p. 88—89 °C (Found: C, 67.0; H, 4.8. $\text{C}_{10}\text{H}_{10}\text{O}_3$ requires C, 67.4; H, 4.8%); δ 3.74 (dt, J_1 5, J_2 2 Hz, $-\text{CH}_2-$), 4.6—5.3 (m, $\text{CH}_2=$ + 5-OH), 5.7—6.4 (m, =CH), 6.79 (d, J 9 Hz, 3-H), 7.08 (d, J 9 Hz, 4-H), 10.15 (s, CHO), and 11.51 (s, 2-OH); ν_{\max} . (Nujol) 3 560—3 200 and 1 630 cm^{-1} ; m/e 178 (M^+ , 100%), 160 (31), and 131 (29).

4-Allyl-2,5-dihydroxybenzaldehyde.—This was a yellow oil (Found: C, 67.8; H, 5.0. $\text{C}_{10}\text{H}_{10}\text{O}_3$ requires C, 67.4; H, 4.8%); δ 3.43 (br d, J 6 Hz, $-\text{CH}_2-$), 4.6—5.3 (m, $\text{CH}_2=$ + 5-OH), 5.7—6.4 (m, =CH), 6.89 (s, 3-H), 6.97 (s, 6-H), 9.79 (s, CHO), and 10.79 (s, 2-OH); ν_{\max} . (Nujol) 3 560—3 100 and 1 630 cm^{-1} ; m/e 178 (M^+ , 100%), 163 (25), and 134 (3).

6'-Allyl-2',5'-dihydroxyacetophenone.—This was isolated as yellow crystals, m.p. 103—104 °C (lit.¹⁴ 104—106 °C); δ 2.62 (s, Me), 3.40 (dt, J_1 5, J_2 1 Hz, $-\text{CH}_2-$), 4.7—5.4 (m, $\text{CH}_2=$ + 5-OH), 5.9—6.4 (m, =CH), 6.80 (d, J 9 Hz, 4'-H), 6.97 (d, J 9 Hz, 3'-H), and 10.00 (br s, 2-OH); ν_{\max} . (Nujol) 3 600—3 100 and 1 680 cm^{-1} ; m/e 192 (M^+ , 63%), 177 (73), 174 (59), 131 (41), 103 (21), and 43 (100).

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