*Tetrahedron.* Vol. 31, pp. 2803 to 2807. Pergamon Press 1975. Printed in Great Britain

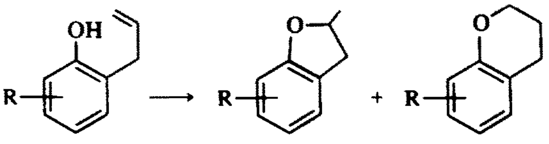
# ON THE MECHANISM OF INTRAMOLECULAR PHOTOCYCLOADDITION OF SUBSTITUTED *o*-ALLYLPHENOLS TO CYCLIC ETHERS

S. GERESH, O. LEVY, Y. MARKOVITS and A. SHANI*
Department of Chemistry, Ben-Gurion University of the Negev, Beer Sheva, Israel

(*Received in UK* 15 *November* 1974; *accepted for publication* 16 *June* 1975)

**Abstract**—Osmometric and NMR techniques were used in order to study the ionic mechanism for the intramolecular photocycloaddition reaction of *o*-allyl phenols (1) to give cyclic ethers (2)+(3). The role of the intramolecular H–bond between the OH group and the $\pi$-electrons of the allylic group was ascertained. Based on the results of the photocyclization, osmometric and NMR measurements the substituents can be divided into 3 groups according to their effect on the above intramolecular interaction.

Two, basically, different mechanisms can be rationalized for the photo-cyclization of substituted *ortho*-allyl phenols (1) to cyclic ethers (2, 3):



1 2 3

(i) An ionic addition, mainly in Markovnikof manner, of the OH group to the double bond, as a result of an intramolecular H–bond[1] and dissociation in the excited state, or via a direct protonation of the double bond.[2a–c]

(ii) A radical addition to the double bond via a phenoxy radical.[3]

We do not expect the reaction to follow a direct protonation of the excited double bond, as this mechanism is usually limited to 6- or 7-membered ring olefins and does not operate with opened-chain olefins.† The radical addition is eliminated on the basis of the acid catalysis of the reaction.[1]

We have found evidence for the intramolecular H-bond and the role of that association in the course of the photocycloaddition reaction.

In the case of an ionic reaction one would expect to observe the effect of the acidity of the phenol on the efficiency of the reaction, namely, an electron releasing group in the *para*-position will decrease the efficiency of the reaction, while in the *meta*-position will enhance it. This is based on the assumption that the substituents exert the same effect in both the ground and the excited state.[4]

We have already shown that such a correlation does not exist[5] and now demonstrate the same result with more compounds (Tables 1 and 2).

It was also found that the relative chemical yield can serve as a good measure of the relative quantum yield and thus of the efficiency of the reaction.[5]

Table 1. p$K_a$ of substituted phenols in the ground, singlet and triplet excited states in aqueous solution

| | Ground state | Singlet state<br>Bartok *et al.*[a] | <br>Wehry *et al.*[b] | <br>Avigal *et al.*[c] | Triplet state Wehry[b] |
|---|---|---|---|---|---|
| Phenol | 10·00 | 3·6 | 4·0 | 3·7 | 8·5 |
| *o*–$CH_3$ | 10·28 | 5·3 | — | — | — |
| *m*–$CH_3$ | 10·09 | 4·2 | 4·0 | — | 8·7 |
| *p*–$CH_3$ | 10·26 | 4·1 | 4·3 | 3·7 | 8·6 |
| *o*–$C_2H_5$ | 10·2 | 4·5 | — | 3·3 | — |
| *m*–$C_2H_5$ | 9·9 | 4·5 | 4·1 | — | — |
| *p*–$C_2H_5$ | 10·0 | 4·3 | 4·3 | — | — |
| *o*–Cl | 8·5 | 3·3 | — | — | — |
| *m*–Cl | 9·13 | 4·0 | 3·0 | — | 7·6 |
| *p*–Cl | 9·42 | 3·5 | 3·2 | — | 8·0 |
| *o*–$OCH_3$ | 9·98 | 5·2 | — | 4·4 | — |
| *m*-$OCH_3$ | 9·65 | 2·7 | 4·6 | 3·4 | 8·4 |
| *p*–$OCH_3$ | 10·21 | 4·7 | 5·6 | 4·1 | 8·6 |
| *p*-$\overset{+}{N}(CH_3)_3$ | 8·35 | — | 1·7 | — | — |

[a] W. Bartok, R. B. Hartman and P. J. Luchesi, *Photochem. & Photobiol.* 4, 499 (1965).

[b] E. L. Wehry and L. B. Rogers, *J. Am. Chem. Soc.* 87, 4234 (1965).

[c] I. Avigal, J. Feitelson and M. Ottolenghi, *J. Chem. Phys.* 50, 2614 (1969).

The absence of the expected correlation still does not eliminate the ionic-type mechanism. It might be that the solvent effect and change of acidity from water to nonpolar organic solvent is the reason for the observed results. So far we have approached (by conductometric measurements) the p$K_a$ values of some phenols in organic solvents having low dielectric constant (2·2). The p$K_a$ values for benzene solutions of some phenols were found of the order of magnitude of 18–20, which means very weak acidity (if at all, in practical meaning) compared to aqueous solutions. Even if we draw upon the analogy of enhanced acidity upon photoexcitation (in aqueous medium), then the enhanced acidity in organic solvents will most likely yield phenols whose acidity is still very weak (p$K \simeq$ 12–14). It might be that with these low acidities, the effects of the substituents are negligible.

The yields of recovered starting material may just reflect the net result of competition between the cycloaddition and the radical decomposition of the phenols. Thus, we may explain the differences between the methyl- and ethyl-substituted phenols by the accelerated formation of benzyl radical from the latter one; or fast chlorine split-

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† In a recent paper, it was shown that in hydroxylic medium even an 8-membered ring is protonated as well as tetra-substituted simple olefins.

Table 2. Photochemical yield, chemical shift and association of substituted ortho-allyl phenols

| | Starting material (R=) | Photochemical yield (%) | Starting material recovered (%) | Change in chemical shift | $\beta_2$ l/mole NMR | Association osmometry | $\beta_2$ l/mole osmometry |
|---|---|---|---|---|---|---|---|
| **1** | -H | 11 | 66 | No | | No | |
| **4** | *o*-$CH_3$ | 27 | 57 | No | | No | |
| **5** | *m*-$CH_3$ | 55 | 25 | No | | No | |
| **6** | *p*-$CH_3$ | 32 | 21 | No | | No | |
| **7** | *o*-$C_2H_5$ | 20 | 30 | No | | No | |
| **8** | *p*-$C_2H_5$ | 8 | 11 | No | | No | |
| **9** | *o*-Cl | 10 | 13 | No | | No | |
| **10** | *m*-Cl | 6 | 61 | [a] | | [a] | |
| **11** | *p*-Cl | 8 | 14 | No | | No | |
| **12** | *o*-$OCH_3$ | — | 60 | No | | No | |
| **13** | *m*-$OCH_3$ | 37 | 5 | [a] | | [a] | |
| **14** | *p*-$OCH_3$ | 37 | 5 | [a] | | [a] | |
| **15** | *o*-$COOCH_3$ | — | 93 | No | | No | |
| **16** | *m*-$COOC_2H_5$ | 4 | 70 | [a] | | [a] | |
| **17** | *p*-$COOCH_3$ | 28 | 48 | Yes | 3·2 | Yes | 10·3 |
| **18** | *o*-$COCH_3$ | — | 74 | No | | No | |
| **19** | *m*-$COCH_3$ | 8 | 11 | Yes | 2·1 | [b] | |
| **20** | *p*-$COCH_3$ | 13 | 66 | Yes | 3·2 | Yes | 17·8 |
| **21** | *o*-$NO_2$ | — | 54 | No | | No | |
| **22** | *p*-$NO_2$ | 2 | 84 | Yes | 2·9 | Yes | 7·5 |

[a] Not measured.

[b] Conflicting results were obtained, probably due to impurities.

ting in the *ortho* and *para* positions (probably because of resonance effects), while smaller rate with the meta isomer;[6] or resonance stabilization of the phenoxy radical with *para* acetyl group, an effect which does not occur with the acetyl in the *meta* position. Typical irradiation could be described as in Fig. 1, which illustrates very fast reaction at the beginning, which slows down, while more decompositions occurs over that period of time. The representing compound has the highest chemical and probably quantum yield.

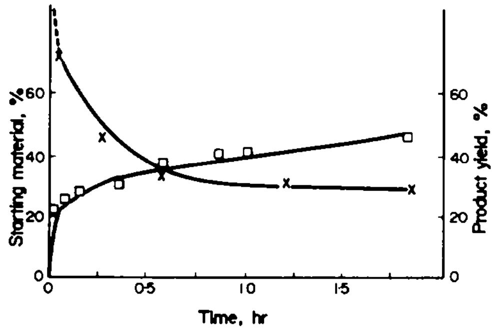


Fig. 1. Disappearance of the starting material and appearance of the product vs time of irradiation of 5.

It is also seen from table 2 that those phenols with polar substituents in the ortho position do not react. We earlier postulated[5] that either intramolecular or intermolecular hydrogen bonding is the reason for this. In principle we can postulate 5 different H-bonds:

(a) *Intramolecular* (i) between the OH group and the $\pi$ electrons of the double bond; (ii) between the OH group and polar group in the *ortho* position.

(b) *Intermolecular* (i) between the OH group and $\pi$ electrons of a double bond (we expect this type to exist, if at all, to a very minor extent); (ii) between 2 hydroxyl groups; (iii) between OH group and a polar substituent of another molecule.

In order to have a better understanding of the mechanism and the behavior of the phenols in nonpolar organic solvents in the ground state we have checked the possible aggregation and H-bonding by osmometric and NMR techniques in benzene as solvent. From the mean aggregation number ($\bar{n}$) dependence on the solute concentration, assuming a monomer-dimer equilibrium, the dimerization constants were evaluated.

An intermolecular association can be described by the following equilibrium:

$$2A \rightleftharpoons A_2 \quad \text{and} \quad \beta_2 = [A_2]/[A]^2$$

where A and $A_2$ are the molar concentration of the monomer and dimer respectively, and $\beta_2$ is the dimerization constant.

The analytical solute concentration, B, and the osmometric concentration S can be expressed as:

$$B = A + 2\beta_2 A^2 \quad S = A + \beta_2 A^2$$

Solving the above two equations gives:

$$\beta_2 = (B-S)/(2S-B)^2$$

Table 3 illustrates the results of the above treatment for *p*-nitro *o*-allyl phenol in benzene at 37°C.

Only for three systems (Table 2) intermolecular association was assumed based on the observed change in the mean aggregation number ($\bar{n} = B/S$) with the solute concentration. In all other systems studied $\bar{n}$ was found concentration independent and close to unity. The small departures from unity were related to the presence of

Table 3. Osmometric results for *p*-nitro *o*-allyl phenol in benzene, 37°C

| B($10^2 \times$ mole/l) | S($10^2 \times$ mole/l) | $\tilde{n}$ | $\beta_2$(l/mole) |
|---|---|---|---|
| 1·21 | 1·13 | 1·06 | 6·8 |
| 1·70 | 1·53 | 1·11 | 9·2 |
| 3·58 | 3·17 | 1·13 | 5·3 |
| 4·72 | 4·03 | 1·17 | 6·1 |
| 6·06 | 4·91 | 1·23 | 8·1 |
| 6·83 | 5·48 | 1·25 | 7·8 |
|  |  |  | $\beta_{av} = 7·5 \pm 1·3$ |

impurities of lower molecular weight than the phenol studied.

Since the osmometric measurements do not discriminate between the various types of intermolecular interactions (H-bonding, dipole-dipole, etc.) NMR measurements were carried out in order to evaluated the contribution of intermolecular H-bonding. The calculated $\beta_2$ from the chemical shift dependence on solute concentration[7] is consistently lower than those obtained from osmometric measurements as expected (Table 2).

From Table 2 one can easily see three different groups of substituent effects, while the olefinic group has its own effect.

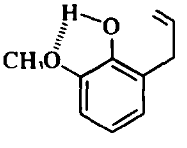
(i) Polar substituents *ortho* to the OH group;

(ii) Polar substituents *meta* or *para* to the OH group;

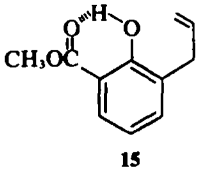
(iii) Non-polar substituents *ortho*, *meta* and *para* to the OH group.

The first group include **15**(*c*-$COOCH_3$), **18**(*o*-$COCH_3$), **21**(*o*-$NO_2$). It also includes **12**(*o*-Me) which is not so polar but can form an intramolecular H-bond between the substituent and the OH group, which is strong enough to prevent photocycloaddition, as with the first three compounds.† We see neither aggregation nor change in chemical shift upon dilution, as expected for a strong intramolecular hydrogen bond. The O$\underline{H}$ in NMR appears at low field, as expected.

The second group includes **16**(*m*-$COOCH_3$), **17**(*p*-$COOCH_3$), **19**(*m*-COMe), **20**(*p*-COMe), **22**(*p*-$NO_2$). These compounds exhibit strong intermolecular H-bonding, which manifests itself in aggregation and can be watched by the change in chemical shift of the O$\underline{H}$ upon dilution. In addition, it was shown that these compounds do undergo photocyclization and it appears that they go through the triplet photoexcited state.[5] It seems reasonable, therefore, that in these compounds, there exists some sort of competition between the intermolecular H-bond of the OH group and a polar substituent and an intramolecular interaction of the OH group with the olefinic system (see below).



**12**

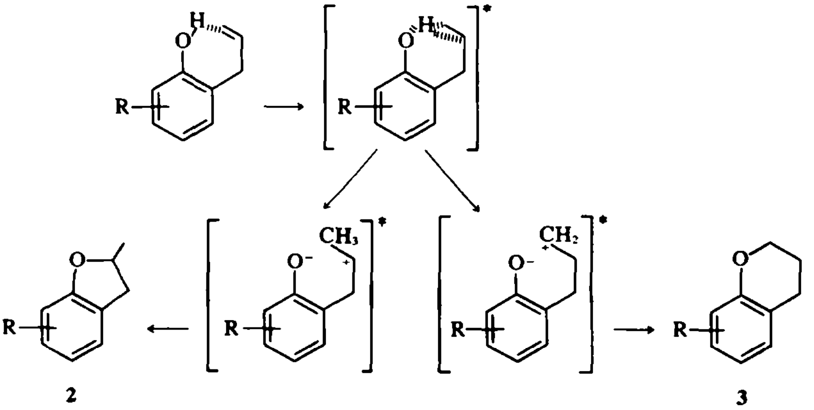


**15**

The third group includes compounds **1**, **4**–**11**, **13**, **14**. It was found that no intermolecular association occurred, and all of the compounds underwent photocycloaddition, presumably through the singlet excited state.[5] We have also observed the phenomenon that with simple substituted phenols (i.e. phenols substituted with a similar non-polar group which do not contain the allylic group *ortho* to the OH group) in the same solvent, benzene, intermolecular association does occur. This fact points out the existence of an intermolecular H-bond in simple phenols, probably through OH----OH interactions. Therefore, it appears that the *ortho*-allyl group plays an important role in preventing such intermolecular interactions in non-polar substituted *ortho*-allyl phenols. On the other hand, these intramolecular H-bonds between the OH group and the π electrons of the *ortho*-allyl group lead to the photocyclization. These bonds are strengthened in the excited state, as the acidity of the phenol is increased about $10^6$ times and then the Markovnikof-type addition occurs. This is further illustrated in Scheme 1.

The above results may also explain the role of solvent in the reaction. We have noted that no reaction takes place in alcoholic solution,[5] while a drop of efficiency occurs in dioxane solution.[1] These solvents form a strong hydrogen bond with the phenolic OH group, namely, strong solute-solvent interaction is formed, which destroys the weak intramolecular interaction depicted in the above scheme.

The different values[8] of inter- and intramolecular H-bonds between an OH group and an O or a Cl atom represent different methods of measurements, assumptions and calculations. The difference between these H-bonds is of the order of 0·5 kcal/mole, which is negligi-



Scheme 1.

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†One of the referees suggested that the lack of reactivity of the above compounds is due to deactivation of the excited state by intramolecular proton transfer.

ble in comparison with the energy level of the excited state of the phenol.

It is therefore interesting to note the difference in the behavior of **12**(*o*-Me) and **9**(*o*-Cl). While the first one does not photocyclize, the other does react. In both cases the intramolecular H-bond forms a 5-membered ring, so we may assume that O–H---Cl interaction in the excited state is weaker than both O–H---O and O–H---π electron interactions.

## EXPERIMENTAL

*Instrumentation.* NMR spectra were recorded in $C_6H_6$, $CDCl_3$, or $CCl_4$ on a Varian XL-100 instrument. TMS used as internal reference (δ = 0). In the association experiments, $C_6H_6$ was used as solvent and as internal reference, while external locked on $H_2O$. IR spectra were taken as thin films in NaCl disks or as KBr pellets on Perkin-Elmer 137 Infracord with polystyrene as reference. UV spectra were taken on Perkin-Elmer 400 in cyclohexane and ethanol, and with t-BuOK as base. The vapor pressure lowering (osmometric) measurements were performed by means of a Hewlett-Packard Osmometer, Model 302B at 37° by a technique described elsewhere.[9] The conductometric measurements were made with a LKB conductivity bridge, the solutions being kept at 37° by a thermostated vessel. GLC measurements for identification and quantum yield were run on a Varian Aerograph 2100; 5 ft (⅛ in. i.d.) column, 3% SE30 on acid washed chromosorb W. TLC analytical plates were prepared from Kieselgel $GF_{254}$ Merck; elution was accomplished with ether-petrol. ether solution and detection was either by UV lamp, or by spraying a 0·5% soln of $KMnO_4$ in a saturated soln of $Cu(OAc)_2$. For preperative separation Kieselgel $PF_{254}$ Merck was used (1 mm thickness). Microanalyses were carried out by the Hebrew University microanalytical laboratory. Melting points were determined on Fisher-Johns apparatus (uncorrected).

Solvents. Benzene and cyclohexane were distilled over sodium; t-BuOH was redistilled; ether was dried first on $CaCl_2$ and then over sodium and distilled; pet. ether was dried over $CaCl_2$ and then distilled (b.p. 64–70°).

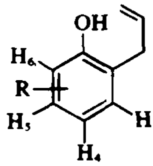
Irradiation. In each case, 1·5 g of compound in 300 ml benzene (or cyclohexane) ($1{\cdot}5\times10^{-2}$–$3{\cdot}5\times10^{-2}$ M) were irradiated for 20 hr. under $N_2$, with 450 Watt Hanovia lamp, in quartz vessel. For more details see our previous work.[5]

Substituted *ortho* allyl phenols. All compounds were prepared according to known procedures in the lit.[10–13] Compounds **1**, **4–6**, **21–14** and **15–17** were reported in our previous work.[5] Only the new compounds are described here. All compounds show the OH group at ~3500 $cm^{-1}$ and terminal olefin at ~900 $cm^{-1}$. The NMR spectra consist of 3 olefinic protons and 2 allylic ones in the *ortho* allylic group as described below:

The three aromatic hydrogens appear either as singlets, doublets or double doublets, sometimes with meta coupling. In the case of meta substitution two isomers usually formed.

In cases where R is polar (in A) $H_6$ is shifted to lower field, next to $H_4$. The coupling constants for the doublets are 6–8 c/s, while the meta coupling is 2 c/s. The data are collected in Table 4.

Table 4. NMR data* of substituted *ortho*-allyl phenols



| Compound | OH | $H_3$ | $H_4$ | $H_5$ | $H_6$ |
|---|---|---|---|---|---|
| **7** | 4·94(d) | | 6·86(t) | | — |
| **8** | 4·91(s) | 6·86(s) | — | 6·86(d) | 6·60(d) |
| **9** | 5·46(s) | 7·12(d) | 6·78(t) | 6·98(d) | — |
| **10** | 5·80(s) | 6·88(d) | 6·70(d) | — | 6·66(s) |
| **11** | 5·84(s) | 7·00(s) | — | 6·90(d) | 6·60(d) |
| **18** | 12·29(s) | 7·18(d) | 6·68(dd) | 7·40(d) | — |
| **19** | 5·40(s) | 6·96(d) | 7·18(d) | — | 7·14(s) |
| **20** | 5·10(s) | 7·18(d) | — | 7·10(d) | 6·70(d) |
| **21** | 10·93(s) | 7·40(d) | 6·86(t) | 7·94(d) | — |
| **22** | 6·1 (s) | 7·96(s) | — | 7·96(d) | 6·80(d) |

*Chemical shifts, δ, are expressed in ppm measured downfield from TMS as internal reference. s, singlet; d, doublet; t, triplet; dd, double doublet; m, multiplet.

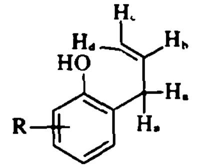
All rearrangements were conducted under $N_2$.

2-Allyl-6-ethyl phenol. The thermal rearrangement of the phenyl allyl ether was conducted in diphenyl ether at 220° for 4 hr. (22% yield). $R_f$ in 5% ether–pet. ether is 0·48 (Found: C, 81·74; H, 8·98. Calc. for $C_{11}H_{14}O$: C, 81·48; H, 8·64%).

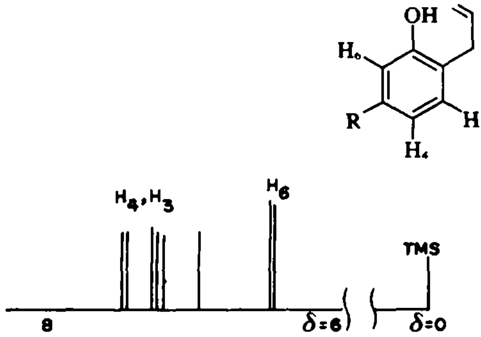
2-*Allyl*-3-(*and* 5) *ethylphenol.* The conditions as above, 6½ hr, (32% yield). $R_f$ in 5% ether-pet. ether is 0·23. No separation was achieved under different conditions (Found: C, 81·64; H, 8·78. Calc. for $C_{11}H_{14}O$: C, 81·48; H, 8·64%).

2-*Allyl*-3-(*and* 5) *chlorophenol.* Thermal rearrangement without solvent, at 200° for 20 min. (75% yield). Ratio 3-chloro:5-chloro 1:4. $R_f$ in 7% ether-pet. ether, 0·08 for 3-chloro, 0·1 for 5-chloro, m.p. 43° (Found: C, 63·89; H, 5·46. Calc. for $C_9H_9ClO$: C, 64·09; H, 5·35%).

2-*Allyl*-6-*acetylphenol.* Thermal rearrangement in dichlorobenzene for 6 hr. (30% yield). $R_f$ in 10% ether-pet. ether is 0·46 (Found: 74·89; H, 6·71. Calc. for $C_{11}H_{12}O_2$: C, 75·00; H, 6·82%).



$H_a$, δ 3.45 d, $J_{H_a,H_b} = 6_{cs}$ (2H)
$H_b$, δ 5·2–5·8, m (1 H)
$H_c$, $H_d$, δ 5·0 d, J = 13 cs ($J_{H_c,H_d,H_a} = 2$ cs)(2H)



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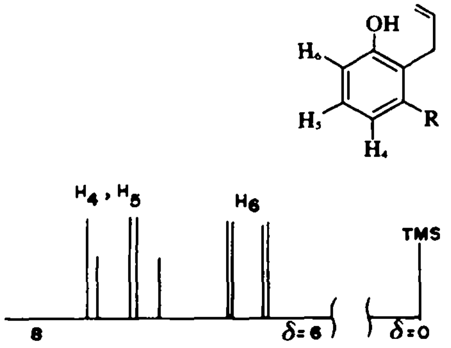

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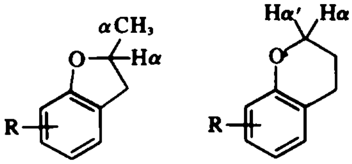
Table 5. NMR data* of substituted 2-methylcoumarans and chromans



| Compound (2, 3) | benzylic hydrogens | $H_\alpha$ | $H_{\alpha'}$ | $\alpha$–CH$_3$ | $R_f$ in ether–pet. ether | Anal. |
|---|---|---|---|---|---|---|
| $o$–C$_2$H$_5$ | 2·6(m) | 4·8(m) | 4·1(t) | 1·4(d) | 0·61(10%) | Found: C, 81·65; H, 8·59<br>Calc. for $C_{11}H_{14}O$: C, 81·48; H, 8·64 |
| $p$–C$_2$H$_5$ | 2·8(m) | 4·8(m) | 4·1(t) | 1·3(d) | 0·8(10%) | Found: C, 81·32; H, 8·57 |
| $o$–Cl | 3·4(m) | 4·98(m) | 4·18(t) | 1·45(d) | 0·77(5%) | Found: C, 64·21; H, 5·47<br>Calc. for $C_9H_9ClO$: C, 64·09; H, 5·35 |
| $m$–Cl | 3·3(m) | 4·85(m) | 4·1(t) | 1·4(d) | 0·39(10%) | Found: C, 64·15; H, 5·50 |
| $p$–Cl | 2·9(m) | 4·88(m) | 4·05(t) | 1·5(d) | 0·69(35%) | Found: C, 64·17; H, 5·60 |
| $m$–COCH$_3$ | 3·0(m) | 4·8(m) | 4·15(t) | 1·4(d) | 0·39(25%) | Found: C, 74·87; H, 6·78<br>Calc. for $C_{11}H_{12}O_2$: 75·00; H, 6·82 |
| $p$–COCH$_3$ | 3·3(m) | 4·98(m) | 4·15(t) | 1·35(d) | 0·50(7%) | Found: C, 75·08; H, 6·75 |

*See Table 4.

*2-Allyl-3(and 5) acetyl phenol.* Thermal rearrangement in dichlorobenzene for 1·5 hr (60% yield). Ratio 3-acetyl:5-acetyl 1:5. $R_f$ in 35% ether–pet. ether is 0·32 for 3-acetyl, 0·43 for 5 acetyl, m.p. 75–6° (CHCl$_3$) (Found: C, 24·82; H, 6·66. Calc. for $C_{11}H_{12}O_2$: C, 75·00; H, 6·82%).

*2-Allyl-3(and 5) nitrophenol.* Thermal rearrangement in dichlorobenzene for 1 hr. Very low yield because of decomposition. Ratio 3-nitro:5-nitro 1:5. $R_f$ in 20% ether-pet. ether is 0·43 for 3-nitro (yellow liquid), 0·54 for 5-nitro, m.p. 49–50° (ether-petroleum ether) (Found: C, 60·08; H, 5·25. Calc. for $C_9H_9NO_3$: C, 60·33; H, 5·02%).

*Substituted chromans and methyl coumarans.* All compounds do not show the OH group in IR and instead strong band appeared at ~1230 cm$^{-1}$. In the NMR the olefinic hydrogens disappeared and peaks at higher field appeared. No change was found in the aromatic region. The data is collected in Table 5.

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