EJ52-1998-1

Journal of the Chinese Chemical Society, **1998**, *45*, 1-12

Photochemistry of Substituted 4,4-Dimethoxy-2,5-Cyclohexadienones

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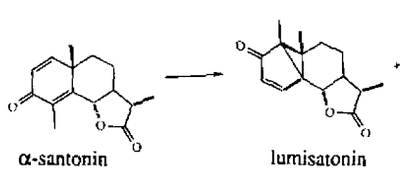
4,4-Dimethoxy-2,5-cyclohexadienones **9-14** were prepared from the corresponding hydroquinone monomethyl ethers by oxidation with thallium trinitrate in methanol. Irradiation of solutions of **9-13** in methanol with a broad band of UV light centered at 350 nm in a Rayonet reactor afforded 2-cyclopentenone derivatives **15-19** in moderate to excellent yields, whereas irradiation of **14** in methanol gave phenol **8** along with other unidentified products. Irradiation of **11-14** in benzene yielded substituted phenols. The plausible reaction pathways for the product formation are discussed.

INTRODUCTION

The photochemistry of 2,5-cyclohexadienones has been extensively investigated[1-3] since the discovery of the interesting transformation of α-santonin into lumisatonin and the related secondary products [Eq (1)].[4] Depending on the nature of substituents and the reaction conditions such as solvents and irradiation period, many 2,5-cyclohexadienones upon irradiation may yield bicyclo[3.1.0]hexenones or solvolytic products or other secondary photochemical products. In contrast to vast number of examples of other 4,4-disubstituted 2,5-cyclohexadienones, the photochemistry of masked *p*-benzoquinones, i.e., 4,4-dialkoxy-2,5-cyclohexadienones is little known; only four reports[5-8] have appeared prior to ours.[9] When the parent 4,4-dimethoxy-2,5-cyclohexadienone was irradiated in *tert*-butanol or benzene, a mixture of 4- and 5-carbonylmethoxy-2-cyclopentenones were obtained in low yields.[5] 2,6-Di-*tert*-butyl-4,4-dimethoxy-2,5-cyclohexadienone afforded *trans*-2,5-di-*tert*-butyl-4-carbonylmethoxy-2-cyclopentenone in 60% yield in benzene. In contrast, 2,5-di-*tert*-butyl-4,4-dimethoxy-2,5-cyclohexadienone gave no carbonylmethoxy-2-cyclopentenone. Instead, it produced 2,4-di-*tert*-butyl-4,5-dimethoxy-2,5-cyclohexadienone (28%) and 2,4-di-*tert*-butylcyclopentadienone (38%); the latter dimerized on standing at room temperature for 15 h.[6] A few examples of *p*-benzoquinone ethyene glycol monoketals were found to give 5-(carbonyl-2-hydroxyethoxy)-2-cyclopentenones in good yields when irradiated in glacial acetic acid.[7,8] We have been studying the chemistry, including the Diels-Alder reactions[10] and the photochemical reactions[11] of masked *o*-benzoquinones and their synthetic applications.[12] Our interests extend also to masked *p*-benzoquinones and other related systems.[13] We report here the photochemical reactions of various 4,4-dimethoxy-2,5-cyclohexadienones in methanol and in benzene in order to unravel the effect of the dimethoxy groups at C-4 as compared to other substitutents, the effect of alkyl groups at different positions, and the solvent effect on the reaction pathways.[9]



(1)

RESULTS AND DISCUSSION

Syntheses of 4,4-Dimethoxy-2,5-cyclohexadienones 9-14

4-Methoxyphenol (**1**) and 4-benzyloxphenol (**2**) were used as starting materials to prepare substituted 4-methoxyphenols **3-6** and **7-8** as shown in Eqs (2) and (3), respectively. These substituents were chosen because these compounds are easily prepared; the synthetic procedures were rather standard and routine. The conversions of **3-8** into the corresponding 4,4-dimethoxy-2,5-cyclohexadienones **9-14** were achieved by oxidation with thallium trinitrate (TTN)[14] in excellent yields [Eq (4)]. The assignments of the structures of **9-14** were based on their synthetic strategies and spectra. The pertinent infrared, ^{1}H and ^{13}C NMR spectral data of 2,5-cyclohexadienone moieties are given in Table 1.

The Results of the Photochemical Reactions of 9-14

Dilute solutions of **9-14** in methanol were irradiated with fluorescent lamps (350 nm) in a Rayonet reactor. A uranium-glass filter was used to minimize the secondary

Dedicated to Professor Hsien-Ju Tien on the occasion of his 65th birthday.

(2)

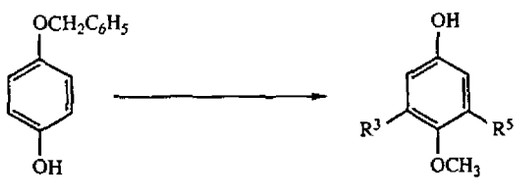
1 **3-6**

For **3** [$R^2 = CH_2CH{=}CH_2$, $R^6 = H$]:
(1) **1**, $CH_2{=}CHCH_2Br$, K_2CO_3, 2-butanone, reflux
(2) 185 °C

For **4** [$R^2 = CH_2CH(OCH_2)_2$, $R^6 = H$]:
(1) **3**, $C_6H_5CH_2Br$, K_2CO_3, 2-butanone, reflux
(2) O_3, CH_3OH-CH_2Cl_2, -78 °C; $(CH_3)_2S$
(3) $(HOCH_2)_2$, PTSA, C_6H_6, reflux
(4) H_2, Pd/C

For **5** [$R^2 = Pr$, $R^6 = H$]:
(1) **3**, H_2, Pd/C, EtOAc

For **6** [$R^2 = R^6 = Pr$]:
(1) **3**, $CH_2{=}CHCH_2Br$, K_2CO_3, 2-butanone, reflux
(2) 185 °C
(3) H_2, Pd/C

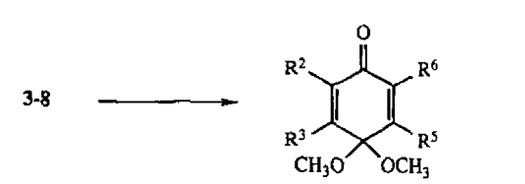


(3)

2 **7-8**

For **7** [$R^3 = Pr$, $R^5 = H$]:
(1) **2**, $CH_2{=}CHCH_2Br$, K_2CO_3, 2-butanone, reflux
(2) 185 °C
(3) $(CH_3)_2SO_4$, K_2CO_3, 2-butanone, reflux
(4) H_2, Pd/C

For **8** [$R^3 = R^5 = Pr$]:
(1) **2**, $CH_2{=}CHCH_2Br$, K_2CO_3, 2-butanone, reflux
(2) 185 °C
(3) $CH_2{=}CHCH_2Br$, K_2CO_3, 2-butanone, reflux
(4) 185 °C
(5) $(CH_3)_2SO_4$, K_2CO_3, 2-butanone, reflux
(6) H_2, Pd/C



(4)

3-8 **9-14**

9 : $R^2 = CH_2CH{=}CH_2$, $R^3 = R^5 = R^6 = H$
10 : $R^2 = CH_2CH(OCH_2)_2$, $R^3 = R^5 = R^6 = H$
11 : $R^2 = Pr$, $R^3 = R^5 = R^6 = H$
12 : $R^2 = R^6 = Pr$, $R^3 = R^5 = H$
13 : $R^3 = Pr$, $R^2 = R^5 = R^6 = H$
14 : $R^2 = R^6 = H$, $R^3 = R^5 = Pr$

photochemical reactions. The irradiated mixtures were quite complex as indicated by thin layer chromatography (TLC). The major products of moderate to excellent yields (Table 2) were isolated and purified by chromatographic methods. Masked *p*-benzoquinones, 4,4-dimethoxy-2,5-cyclohexadienones **9-11** and **13** produced 5-carbonylmethoxy-2-cyclopenetones **15-18**, respectively, and **12** afforded 4-carbonylmethoxy-2-cyclopenteone **19**. In contrast, **14** furnished no 2-cyclopentenone derivative but gave 4-methoxyphenol **8** in 23% yield instead. For comparison, the photochemical reactions of **11-14** were also carried out in benzene. Again, the irradiated mixtures were very complicated. Only phenolic products were isolated: **11** yielded **20**, **21** and **22**; **12** afforded **23**; **13** and **14** furnished **7** and **8**, respectively (Table 2). The assignments of the structures of the photochemical products were based on their spectral data; some of the pertinent infrared ^1H and ^{13}C NMR spectral data of 2-cyclopentenones are listed in Table 3. The structure of **19** is identical with that of the major product derived from irradiation of 6,6-dimethoxy-2,5-dipropyl-2,4-cyclohexadienone, a masked *o*-benzoquinone, in methanol;[11] the assignment of the stereochemistry was based on the assumption that *trans*-isomer is more stable and is generally formed preferentially.[8]

It is interesting to note that, for the unsymmetrical masked *p*-benzoquinones **9-11** and **13**, the respective photorearrangements to 5-methoxycarbonyl-2-cyclopetenones **15-18** are of such high chemoselectivity that the more substituted alkene moieties remain. In contrast to our findings, the photochemical reactions of mono(ethylene glycol) ketals of *p*-benzoquinones in glacial acetic acid were reported to afford 4-methoxycarbonyl-2-cyclopentenones possessing fewer substituents on the alkene moieties.[7,8]

Photochemical Reaction Pathways

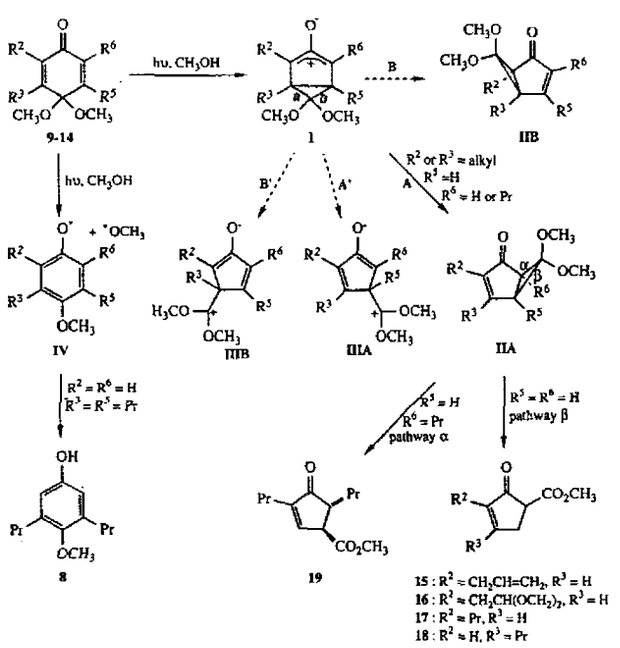
The photorearrangements of 4,4-disubstituted 2,5-cyclohexadienones have been extensively studied; the Zimmerman-Schuster mechanism[15] is generally accepted for these transformations. We did not investigate the mechanisms for the photochemical reactions of **9-14** in this work; however, the reactions may be rationalized in terms of the Zimmerman-Schuster mechanism. Accordingly the n,π* triplet states of **9-13** are presumably involved in methanol, followed by formation of bond between carbon atoms C(3) and C(5) and electron-remotion to generate zwitterions **I**. In principle, zwitterions **I** may undergo [1,4]-sigmatropic rearrangements (modes **A** and **B**) to form bicyclo[3.1.0]-hexenones (**IIA** and **IIB**, respectively) or bond cleavage (modes **A′** and **B′**) to yield zwitterions **IIIA** and **IIIB** (see Scheme I). However, retroanalysis of the formation of prod-

Table 1. The Yields and the Pertinent Spectral Data of 2,5-Cyclohexadienones **9-14**

Dienone	Yield	IR (ν)/cm^{-1})	^{1}H NMR (δ/ppm)	^{13}C NMR (δ/ppm)
9	88%	1681, 1650, 1629	6.20 (d, J = 10.3 Hz, 1H), 6.51 (d, J = 3.0 Hz, 1H), 6.75 (dd, J = 10.3, 3.0 Hz, 1H)	92.9 (C), 129.9 (CH), 138.5 (CH), 139.0 (C), 142.8 (CH), 184.9 (C)
10	94%	1682, 1650, 1629	6.14 (d, J = 10.2 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 6.69 (dd, J = 10.2, 3.0 Hz, 1H)	92.6 (C), 129.6 (CH), 134.9 (C), 141.0 (CH), 142.7(CH), 184.5 (C)
11	94%	1681, 1651, 1629	6.10 (d, J = 10.3 Hz, 1H), 6.41 (d, J = 3.6 Hz, 1H), 6.65 (dd, J = 10.3, 3.6 Hz, 1H)	92.8 (C), 129.9 (CH), 137.8 (CH), 140.2 (C), 142.4 (CH), 185.0 (C)
12	98%	1679, 1648, 1610	6.47 (s, 2H)	93.1 (C), 137.4 (CH × 2), 140.9 (C × 2), 185.6 (C)
13	99%	1681, 1644, 1621	6.19 (d, J = 2.1 Hz, 1H), 6.36 (dd, J = 10.3, 2.1 Hz, 1H), 6.71 (d, J = 10.3 Hz, 1H)	95.6 (C), 128.0 (CH), 132.1 (CH), 144.0 (CH), 159.0 (C), 185.2 (C)
14	97%	1680, 1635, 1621	6.27 (s, 2H)	98.5 (C), 129.6 (CH × 2), 159.0 (C × 2), 185.2 (C)

ucts **15-18** clearly indicates that, among the aforementioned four possibilities, the [1,4]-sigmatropic rearrangements of **I** to **IIA** followed by opening of the cyclopropane ring in **IIA** via pathway α seems most likely. This reaction pathway may also be responsible for the formation of **19** from **12**; however, an alternative pathway via **I** and **IIIA**, though less likely, cannot be ruled out.

Scheme I Irradiation of **9-14** in methanol



As described above, the unsymmetrical masked *p*-benzoquinones **9-11** and **13** underwent photorearragements to 2-cyclopetenones **15-18** in a highly chemoselective manner. In contrast to our findings, the photochemical reactions of mono(ethylene glycol) ketals of *p*-benzoquinones in glacial acetic acid yielded 4-carbonylmethoxy-2-cyclopentenones possessing fewer substituents on the alkene moieties.[7,8] In the latter cases, in acetic acid media the protonated intermediates **V** were proposed to undergo cleavage of bond **b** of the cyclopropane ring in **V** preferentially[7,8] (see Scheme II); the reason for the preference of cleavage of **b** bond to **a** bond was not given. It is interesting to note that the intermediates **I** and **V** (see Schemes I and II, respectively) show distinct types of reactions and chemoselectivities. The positive charge of protonated intermediate **V** and the high solvating power of acetic acid are presumably the main factors that facilitate the ring-opening of cyclopropane in **V**, whereas in the present study the neutral species **I**, although zwitterionic in nature, does not proceed with a similar ring-opening reaction but instead undergoes a [1,4]-sigmatropic rearrangement.

There are two possible [1,4]-sigmatropic rearrangements, pathways **IIA** and **IIB**, for **I** when it is unsymmetrical, however pathway **IIA** is predominant. This preference may be due to both electronic and steric effects. The double bond in **IIA** is more substituted than that in **IIB**, and the cy-

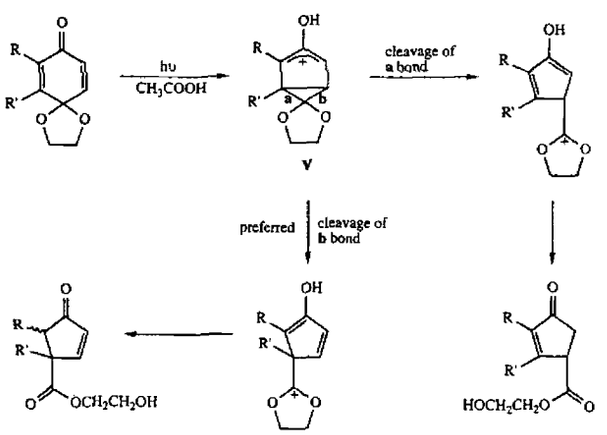
Table 2. The Yields of Photoproducts of **9-14** in Methanol and Benzene

Dienone	Solvent	Photoproduct (Yield)
9	CH_3OH	**15** (46%)
10	CH_3OH	**16** (53%)
11	CH_3OH	**17** (50%)
12	CH_3OH	**18** (51%)
13	CH_3OH	**19** (99%)
14	CH_3OH	**8** (23%)
11	C_6H_6	**20** (51%), **21** (22%), **22** (3%)
12	C_6H_6	**23** (34%)
13	C_6H_6	**7** (2.%)
14	C_6H_6	**8** (12%)

Table 3. The Pertinent Spectral Data of 2-Cyclopentenones **15-19**

Enone	IR (ν/cm^{-1})	^{1}H NMR (δ/ppm)	^{13}C NMR (δ/ppm)
15	1745, 1621	7.22 (m, 1H)	142.9 (C), 157.9 (CH), 201.7 (C); 169.4 (C)
16	1740, 1710, 1632	7.38 (m, 1H)	144.8 (C), 157.1 (CH), 202.7 (C); 169.7 (C)
17	1740, 1710, 1638	7.54 (m, 1H)	138.8 (C), 159.8 (CH), 201.7 (C); 169.2 (C)
18	1739, 1710, 1619	5.86 (br s, 1H)	127.3 (CH), 183.0 (C), 202.7 (C); 169.4 (C)
19	1741, 1718, 1635	7.08 (br s, 1H)	146.4 (C), 151.5 (CH), 209.1 (C); 172.3 (C)

Scheme II Photochemical reactions of monoethylene glycol ketals of *p*-benzoquinones

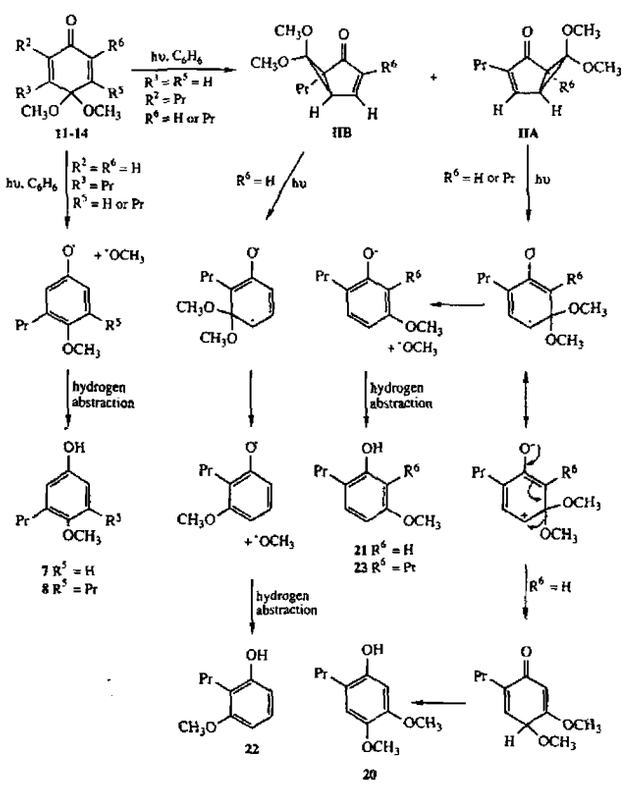


clopropane ring in **IIA** is less substituted than that in **IIB**, thus both the hyperconjugative and steric effects favor the production of **IIA**. Examples for the chemoselective [1,4]-sigmatropic photorearrangements of unsymmetrical 4,4-disubstituted 2,5-cyclohexadienones to lumiketones are known.[8,9,16,17] For instance, 3,4,4-trimethyl-2,5-cyclohexadienone, upon irradiation in methanol, resulted in the migration of the more substituted bond to afford 4,6,6-trimethylbicyclo[3.1.0]hexenone.[16]

Lumiketone **IIA**, having a cyclopropane ring with two electron-donating methoxy groups on one carbon and a fused cyclopentenone moiety on the other two carbons, is anticipated to undergo facile ring opening. There are in principle two possible pathways by which the ring can be opened, i.e. cleavage of the α or β bond leading to 4- or 5-carbonylmethoxy-2-cyclopentenone, respectively. It is interesting to note that pathway α prevails, when R^6 = H, to give 5-carbonylmethoxy-2-cyclopentenones **15-18**, whereas pathway β becomes predominant, when R^6 = Pr, to yield 4-carbonylmethoxy-2-cyclopentenones **19**. Similar results were obtained when masked *o*-benzoquinones were irradiated in methanol through intermediate bicyclo[3.1.0]-hexenones like **IIA**.[11]

When masked *p*-benzoquinones **11-14** were irradiated in benzene, the product mixtures were rather complex. The plausible mechanisms for the formation of the isolated phenolic products are depicted in Scheme III. For **11** and **12**, having $R^3 = R^5$ = H, the [1,4]-sigmatropic rearrangements prevailed. Masked *p*-benzoquinone **12** is symmetrical structurally. However, for the unsymmetrical **11**, the selectivity of the migratory aptitude is not so profound as that in methanol (cleavage of **a** bond of intermediate **I** being preferential as shown in Scheme I) and provided both **IIA** and **IIB**, which presumably are thermally quite stable in benzene but yielded, upon further photolysis, **20** and **21**, and **22**, respectively (Scheme III). In the case of masked *p*-benzoquinones **13** and **14**, due to steric hindrance, the propyl groups at the

Scheme III Irradiation of **11-14** in benzene



C(3) and C(5) positions decrease the bonding tendency between these two carbon atoms to form lumiketones that render the homolytic cleavage of the C-O bond at C(4) to give phenolic compounds **7** and **8**, respectively. For **14**, even in methanol, no 2-cyclopentenone derived from lumiketone was obtained; phenol **8** was isolated from a complex mixture of unidentified products.

CONCLUSION

Masked *p*-benzoquinones proceed chemoselective [1,4]-sigmatropic photorearrangements in methanol to lumiketones which undergo ring opening of fused dimethoxycyclopropanes to afford 4- or 5-carbonylmethoxy-2-cyclopentenones in moderate yields. This methodology provides a short and convenient entry to 2-cyclopentenones from easily available hydroquinone monomethyl ethers. The photolysis in benzene, although furnishing complex mixtures of no synthetic usefulness, give mechanistic information about the solvent effect on the reactivities of substituted masked *p*-benzoquinones as compared with those in methanol.

EXPERIMENTAL SECTION

General Remarks

Melting points were determined on a Büchi-512 apparatus and are uncorrected. Infrared (IR) spectra were obtained on a Perkin-Elmer 781 IR spectrophotometer as films on NaCl disks for liquid or KBr pellets for solid. Ultraviolet (UV) absorption spectra were acquired by a Perkin-Elmer Lambda-5 spectrophotometer using spectral-grade ethanol (95%) as solvent. Most ^{1}H and ^{13}C spectra were recorded on Bruker AM-400 and AM-300 (400 and 300 MHz for ^{1}H and 100 and 75.4 MHz for ^{13}C) spectrometers in $CDCl_3$ with tetramethylsilane (δ 0.00) as an internal standard. Some were recorded on a Varian EM-390 spectrometer. Chemical shifts (δ) are given in ppm, and coupling constants (*J*) are reported in Hz; multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Low-resolution mass spectra (MS) and High-resolution mass spectra (HRMS) were determined on a JEOL JMS-D-100 spectrometer and a JEOL-HX-100 spectrometer, respectively. Elemental analyses were performed on a Perkin-Elmer 240C spectrometer or Heracus CHN-O-RAPID spectrometer in the Tainan Instrumentation Center, National Science Council. Ordinary gravity column chromatography and flash column chromatography were executed on silica gel (E. Merck Art. 7734 Kieselgel 60, 70-230 mesh and E. Merck Art. 9385 Kieselgel 60, 230-400 mesh, respectively). Preparative thin-layer chromatography was carried out on silica gel (E. Merck 254 Kieselgel). Solvents as eluents were of industrial grade and purified by means of simple distillation. 2-Butanone was distilled from anhydrous potassium carbonate. Anhydrous methanol was obtained from distillation over magnesium. Acetonitrile was distilled from anhydrous calcium carbonate. All reactions were performed under an atmosphere of dry nitrogen unless specified.

1-Allyloxy-4-methoxybenzene

To a magnetically stirred solution of 4-methoxyphenol (12.44 g), allyl bromide (15.2 mL) and K_2CO_3 (24.88 g) in anhydrous 2-butanone (125 mL) were refluxed for 12 h until the reaction was completed as indicated by TLC analysis. The reaction mixture was allowed to cool and was filtered to remove salts which were then washed with ether. The organic phase was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried over magnesium sulfate, and concentrated in vacuo to give a pale yellow oil, 1-allyloxy-4-methoxybenzene (16.42 g, 100%): IR (neat) 3090, 3050, 3001, 1650, 1595, 1510, 1470, 1290, 1230, 1188, 1115, 1048, 1008, 935, 830, 765, 728 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 3.73 (s, 3H), 4.45 (br d, J = 6.3 Hz, 2H), 5.16-5.44 (m, 1H), 6,77 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 56.6 (CH_3), 69.4 (CH_2), 114.5 (CH × 2), 115.6 (CH × 2), 117.3 (CH_2), 133.6 (CH), 152.7 (C), 153.8 (C); MS (75 eV) *m/z* 164 (M^+, 27), 123 (100), 95 (15), 41 (16).

2-Allyl-4-methoxyphenol (3)

1-Allyloxy-4-methoxybenzene (16.42 g) placed in a round-bottomed flask equipped with a condenser was heated at 185 °C with stirring for 12 h until the complete disappearance of the starting material was indicated by TLC analysis. The red-brownish crude product was allowed to cool to room temperature. It was purified by column chromatography on silica gel (ethyl acetate : hexane = 1 : 5) and then distilled in vacuo (109 °C/0.34 torr) to give a colorless liquid **3** (14.02 g, 85%): IR (neat) 3418 (br), 3080, 3007, 1640, 1617, 1509, 1433, 1348, 1210, 1155, 1100, 1040, 1000, 920, 870, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.37 (d, J = 6.2 Hz, 2H), 3.74 (s, 3H), 5.10-5.15 (m, 2H), 5.22 (s, 1H), 5.96-6.02 (m, 1H), 6.64-6.74 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.0 (CH_2), 55.7 (CH_3), 112.5 (CH), 115.9 (CH), 116.3 (CH_2), 116.3, (CH), 126.7 (C), 136.1 (CH), 147.9 (C), 153.5 (C); MS (75 eV) *m/z* 164 (M^+, 100), 149 (73), 121 (20), 107 (14), 103 (15), 91 (25), 77 (36), 65 (14), 55 (17), 51 (15), 43 (21), 39 (23), 27 (12).

2-Allyl-1-benzyloxy-4-methoxybenzene

A magnetically stirred mixture of **3** (5.53 g), benzyl bromide (3.90 mL) and K_2CO_3 (8.30 g) in anhydrous 2-butanone (50 mL) was refluxed for 32 h until the complete disappearance of **3** was indicated by TLC analysis. The reaction mixture was allowed to cool and was filtered to remove salts which were then washed with ether (50 mL). The combined filtrate was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried, and concentrated in vacuo to give a pale yellowish oil, 2-allyl-1-benzyloxy-4-methoxybenzene (8.44 g, 99%): IR (neat) 3037, 3035, 3000, 1639, 1610, 1591, 1503, 1460, 1468, 1436, 1384, 1283, 1230, 1162, 1050, 1030, 1002, 918, 860, 806, 742, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.43 (d, J = 6.6 Hz, 2H), 3.75 (s, 3H), 5.02 (s, 2H), 5.04-5.10 (m, 2H), 5.59-6.06 (m, 1H), 6.69 (dd, J = 8.8, 3.0 Hz, 1H), 6.76 (d, J = 3.0 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H), 7.29-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 33.4 (CH_2), 55.6 (CH_3), 70.9 (CH_2), 111.4 (CH), 113.1 (CH), 115.7 (CH_2), 116.1 (CH), 127.2 (CH, × 2), 127.7 (CH), 128.4 (CH, × 2), 130.5 (C), 136.7 (CH), 137.6 (C), 150.6 (C), 153.8 (C); MS (12 eV) *m/z* 254 (M^+, 100), 164 (21), 163 (69), 92 (16), 91 (32).

2-(2-Benzyloxy-5-methoxyphenyl)acetaldehyde

Ozone was passed through a cooled (-78 °C) solution of 2-allyl-1-benzyloxy-4-methoxybenzene (2.27 g) and methanol (2 mL) in methylene chloride (30 mL) for 12 min until the disappearance of the starting material. Excess dimethylsulfide was added, and the solution was allowed to warm up to room temperature and was stirred for another 4 h. Water was then added, and the resulting mixture was extracted with ether (20 mL × 3). The combined organic phase was washed with brine, dried, and stripped of solvent. The residue was chromatographed (ethyl acetate : hexane = 1 : 15 as eluent) to give 2-(2-benzyloxy-5-methoxyphenyl)acetaldehyde (1.82 g, 71%): IR (neat) 3060, 3030, 3000, 2712, 1722, 1608, 1590, 1498, 1452, 1430, 1381, 1320, 1278, 1222, 1160, 1121, 1047, 851, 809, 740, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.59 (d, J = 1.9 Hz, 2H), 3.65 (s, 3H), 4.92 (s, 2H), 6.62-6.68 (m, 2H), 6.82 (d, J = 8.8 Hz, 1H), 7.22-7.36 (m, 5H), 9.62 (t, J = 1.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 45.6 (CH_2), 55.7 (CH_3), 70.8 (CH_2), 113.0 (CH), 113.1 (CH), 117.4 (CH), 122.9 (C), 127.2 (CH, × 2), 127.9 (CH), 128.6 (CH, × 2), 137.0 (C), 150.9 (C), 153.9 (C), 199.8 (C); MS (75 eV) *m/z* 256 (M^+, 100), 165 (24), 137 (28), 91 (7), 75 (10).

2-(2-Benzyloxy-5-methoxybenzyl)-1,3-dioxolane

A solution of 2-(2-benzyloxy-5-methoxyphenyl)acetaldehyde (10.5 g), *p*-toluenesulfonic acid (0.80 g) and ethylene glycol (2.5 mL) in benzene (100 mL) was refluxed with a Dean-Stark trap overnight. Water (50 mL) and ether (40 mL) were added to the cooled reaction mixture. The phases were separated, and the aqueous layer was extracted with ether (25 mL × 3). The combined organic solution was washed with brine, dried, and stripped of solvent. The residue was chromatographed (ethyl acetate : hexane = 1 : 10) to give 2-(2-benzyloxy-5-methoxybenzyl)-1,3-dioxolane (11.95 g, 97%): IR (neat) 3058, 3022, 1606, 1590, 1496, 1450, 1427, 1379, 1285, 1130, 1215, 1040, 946, 835, 804, 740, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.96 (d, J = 5.1 Hz, 2H), 3.69 (s, 3H), 3.75-3.78 (m, 2H), 3.89-3.93 (m, 2H), 4.96 (s, 2H), 5.09 (t, J = 5.1 Hz), 6.64 (dd, J = 8.9, 3.1 Hz, 1H), 6.76 (d, J = 8.9 Hz, 1H), 6.80 (d, J = 3.1 Hz, 1H), 7.28-7.36 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 35.3 (CH_2), 55.6 (CH_2), 64.8 (CH_2), 70.8 (CH_2), 103.7 (CH), 112.1 (CH), 113.1 (CH), 117.4 (CH), 126.5 (C), 127.1 (CH, × 2), 127.7 (CH), 128.5 (CH, × 2), 137.5 (C), 150.9 (C), 153.6 (C); MS (75 eV) *m/z* 300 (M^+, 16), 165 (3), 137 (6), 91 (25), 73 (100), 45 (11).

2-(1,3-Dioxolan-2-ylmethyl)-4-methoxyphenol (4)

A solution of 2-(2-benzyloxy-5-methoxybenzyl)-1,3-dioxolane (11.33 g) in ethyl acetate (35 mL) was hydrogenated over Pd/C (10%, 1.2 g) at room temperature under H_2 atmosphere (about 1 atm) for 6 h until no more H_2 was consumed. The catalyst was removed by filtration. The filtrate was stripped of solvent, and the residue was chromatographed (ethyl acetate : hexane = 1 : 15) to give **4** (6.99 g, 88%): IR (neat) 3396 (br), 3005, 1601, 1490, 1435, 1389, 1359, 1277, 1235, 1140, 1105, 1035, 941, 839, 815, 768 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.99 (d, J = 3.9 Hz, 2H), 3.73 (s, 3H), 3.86-3.96 (m, 4H), 4.20 (s, 1H), 5.10 (t, J = 3.9 Hz), 6.64 (d, J = 3.0 Hz, 1H), 6.69 (dd, J = 8.8, 3.0 Hz, 1H), 6.84 (d, J = 8.8 Hz, 1H),; ^{13}C NMR ($CDCl_3$, 100 Hz) δ 36.7 (CH_2), 55.7 (CH_3), 65.3 (CH_2), 104.7 (CH), 113.8 (CH), 117.5 (CH), 118.1 (CH), 123.1 (C), 149.4 (C), 153.4 (C); MS (12 eV) *m/z* 210 (M^+, 75), 176 (14), 87 (16), 91 (25), 73 (100).

4-Methoxy-2-propylphenol (5)

A solution of **3** (14.00 g) in ethyl acetate (50 mL) was hydrogenated over Pd/C (10%, 1.4 g) at room temperature under H_2 atmosphere (about latm) until no more H_2 was consumed. The catalyst was removed by filtration, and the solvent was stripped off. Purification by distillation of the pale yellow residue provided **5** (12.97 g, 94%) as a colorless oil: IR (neat) 3410 (br), 3038, 3005, 1615, 1510, 1345, 1290, 1208, 1180, 1155, 1120, 1075, 1040, 940, 858, 815, 725 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, J = 7.5 Hz, 3H),

1.63 (sextet, J = 7.5 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 3.75 (s, 3H), 4.76 (s, 1H), 6.62 (dd, J = 8.3, 3.0 Hz, 1H), 6.68 (d, J = 8.3 Hz, 1H), 6.69 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (CH_3), 22.9 (CH_2), 32.2 (CH_2), 55.7 (CH_3), 111.6 (CH), 115.8 (CH), 115.9 (CH), 129.7 (C), 147.5 (C), 153.5 (C); MS (12 eV) *m/z* 166 (M^+, 100), 137 (40).

2-Allyl-1-allyloxy-4-methoxybenzene

A magnetically stirred solution of **3** (14.0 g), benzyl bromide (10.9 g) and K_2CO_3 (12.44 g) in anhydrous 2-butanone (100 mL) was refluxed for 18 h until the complete disappearance of **3** was indicated by TLC analysis. The reaction mixture was allowed to cool and was filtered to remove salts which were then washed with ether (100 mL). The combined filtrate was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried, and concentrated in vacuo to give a pale yellowish oil, 2-allyl-1-allyloxy-4-methoxybenzene (17.31 g, 99%): IR (neat) 3075, 3000, 1639, 1610, 1590, 1496, 1455, 1425, 1280, 1220, 1160, 1047, 998, 918, 870, 800, 750, 717 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.39 (d, J = 6.6 Hz, 2H), 3.74 (s, 3H), 4.47 (dd, J = 5.0, 1.4 Hz, 2H), 5.05 (dt, J = 8.9, 1.4 Hz, 1H), 5.07 (dt, J = 17.5, 1.4 Hz, 1H), 5.24 (dd, J = 10.6, 1.4 Hz, 1H), 5.39 (dd, J = 17.0, 1.4 Hz, 1H), 5.94-6.04 (m, 2H), 6.67 (dd, J = 8.8, 3.0 Hz, 1H), 6.73 (d, J = 3.0 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H); ^{13}C NMR ($CDCl^3$, 100 Hz) δ 34.5 (CH_2), 55.6 (CH_3), 69.7 (CH_2), 111.3 (CH), 113.1 (CH), 115.6 (CH_2), 116.0 (CH), 116.8 (CH_2), 130.4 (C), 133.8 (CH), 136.7 (CH), 150.5 (C), 153.7 (C); MS (25 eV) *m/z* 204 (M^+, 53), 163 (100), 135 (25), 105 (12), 103 (16), 71 (36), 57 (15), 28 (16).

2,6-Diallyl-4-methoxyphenol

2-Allyl-1-allyloxy-4-methoxybenzene (17.31 g) was placed in a round-bottomed flask equipped with a condenser and was heated at 190 °C with stirring for 12 h until the complete disappearance of the starting material was indicated by TLC analysis. The red-brownish crude product then was cooled down and purified by chromatography (ethyl acetate : hexane = 1 : 20) and then by vacuum distillation (114 °C/0.59 torr) to give a colorless liquid 2,6-diallyl-4-methoxyphenol (12.11 g, 70%): IR (neat) 3525 (br), 3080, 3005, 1638, 1608, 1480, 1440, 1340, 1318, 1240, 1196, 1147, 1052, 999, 917, 855 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.36 (d, J = 6.6 Hz, 4H), 3.74 (s, 3H), 4.77 (s, 1H), 5.13 (dd, J = 9.7, 1.3 Hz, 2H), 5.14 (dd, J = 16, 1.3 Hz, 2H), 5.96-6.04 (m, 2H), 6.58 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.4 (CH_2, × 2), 55.6 (CH_3), 113.8 (CH, × 2), 116.4 (CH_2, × 2), 126.9 (C, × 2), 136.4 (CH, × 2), 146.4 (C), 153.4 (C); MS (12 eV) *m/z* 204 (M^+, 100), 189 (6).

4-Methoxy-2,6-dipropylphenol (6)

A solution of 2,6-diallyl-4-methoxyphenol (14.03 g) in ethyl acetate (30 mL) was hydrogenated with vigorous stirring over Pd/C (10%, 2.81 g) at room temperature under H_2 atmosphere (about 1atm) until no more H_2 was consumed. The catalyst was removed by filtration, and the filtrate was stripped of solvent. Recrystalization of the residue from ethyl acetate-hexane afforded white needles **6** (14.02 g, 98%): mp 33-34 °C; IR (KBr) 3490 (br), 1604, 1471, 1380, 1240, 1347, 1195, 1150, 1097, 1042, 949, 851, 770 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.97 (t, J = 7.3 Hz, 6H), 1.63 (sextet, J = 7.3 Hz, 4H), 2.53 (t, J = 7.3 Hz, 4H), 3.73 (s, 3H), 4.25 (s, 1H), 6.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (CH_3 × 2), 22.9 (CH_2 × 2), 32.5 (CH_2 × 2), 55.6 (CH_3), 112.9 (CH × 2), 129.0 (C × 2), 145.4 (C), 153.1 (C); MS (12 eV) *m/z* 208 (M^+, 100), 204 (9), 189 (9).

1-Allyloxy-4-benzyloxybenzene

A magnetically stirred solution of 4-benzyloxyphenol (10.00 g), allyl bromide (7.7 mL) and K_2CO_3 (15.0 g) in anhydrous 2-butanone (125 mL) was refluxed for 12 h until the reaction was completed as indicated by TLC analysis. The reaction mixture was allowed to cool and was then filtered to remove salts which were washed with ether (200 mL). The combined organic phase was washed with saturated ammonium chloride solution and brine, dried, and stripped of solvent to give a pale yellow solid (12.02 g, 100%) which was recrystallized from ethyl acetate-hexane to afford white platelet 1-allyloxy-4-benzyloxybenzene: mp 57.5-58 °C; IR (KBr) 3080, 3065, 3040, 3010, 1640, 1510, 1465, 1452, 1429, 1383, 1289, 1240, 1117, 1028, 996, 935, 830, 788, 740, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.64 (d, J = 5.0 Hz, 2H), 5.00 (s, 2H), 5.26 (dd, J = 10.2, 1.1 Hz, 1H), 5.39 (dd, J = 16.8, 1.1 Hz, 1H), 6.00-6.09 (m, 1H), 6.66 & 6.69 (AA'BB', J_{AB} = 6.8 Hz, 4H), 7.31-7.41 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 69.4 (CH_2), 70.7 (CH_2), 115.7 (CH × 2), 115.8 (CH × 2), 117.5 (CH_2), 127.5 (CH × 2), 127.9 (CH), 128.5 (CH, × 2), 133.6 (CH), 137.3 (C), 153.0 (C), 153.1 (C); MS (12 eV) *m/z* 240 (M^+, 100), 199 (7), 149 (12), 92 (10), 91 (79).

2-Allyl-4-benzyloxyphenol

1-Allyloxy-4-benzyloxybenzene (11.82 g) was placed in a round-bottomed flask equipped with a condenser and was heated at 186 °C with stirring for 26 h until the complete disappearance of the starting material was indicated by TLC analysis. The red-brownish crude product was allowed to cool and was purified by flash column chromatography (hexane : ethyl acetate = 15 : 1) to give a colorless liquid 2-allyl-4-benzyloxyphenol (9.81 g, 83%): IR (neat) 3430 (br),

3077, 3040, 1640, 1612, 1511, 1447, 1385, 1290, 1260, 1225, 1196, 1162, 1080, 1028, 1005, 920, 811, 745 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.38 (d, J = 6.4 Hz, 2H), 4.96 (s, 1H), 5.00 (s, 2H), 5.12-5.18 (m, 2H), 5.97-6.04 (m, 1H), 6.71-6.80 (m, 3H), 7.34-7.44 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 34.9 (CH_2), 70.5 (CH_2), 113.5 (CH), 116.2 (CH), 116.3 (CH_2), 116.9 (CH), 126 (C), 127.4 (CH × 2), 127.7 (CH), 128.3 (CH × 2), 136.0 (CH), 137.1 (CH), 148.0 (C), 152.8 (C); MS (12 eV) *m/z* 240 (M^+, 30), 92 (9), 91 (100).

2-Allyl-4-benzyloxy-1-methoxybenzene

A magnetically stirred solution of 2-allyl-4-benzyloxyphenol (3.87 g), dimethyl sulfate (2.78 mL) and K_2CO_3 (4.0 g) in anhydrous 2-butanone (100 mL) was refluxed for 8 h until the complete disappearance of 2-allyl-4-benzyloxyphenol was indicated by TLC analysis. The reaction mixture was allowed to cool and was filtered to remove salts which were then washed with ether (50 mL). The combined filtrate was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried, and concentrated in vacuo to give a pale yellowish oil, 2-allyl-4-benzyloxy-1-methoxybenzene (3.89 g, 96%): IR (neat) 3061, 3030, 3000, 1638, 1605, 1590, 1462, 1380, 1280, 1225, 1180, 1162, 1125, 1085, 1045, 1030, 998, 913, 875, 850, 800, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.37 (d, J = 6.4 Hz, 2H), 3.78 (s, 3H), 5.00 (s, 2H), 5.04-5.09 (m, 2H), 5.94-6.01 (m, 1H), 6.75-6.83 (m, 3H), 7.31-7.45 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 34.2 (CH_2), 56.1 (CH_3), 70.6 (CH_2), 111.3 (CH), 112.4 (CH), 115.6 (CH_2), 117.3 (CH), 127.5 (CH × 2), 127.6 (CH), 128.5 (CH × 2), 129.9 (C), 136.7 (CH), 137.4 (C), 151.7 (C), 152.8 (C); MS (12 eV) *m/z* 254 (M^+, 100), 163 (19), 91 (27).

4-Methoxy-3-propylphenol (7)

A solution of 3-allyl-4-methoxyphenol (3.80 g) in ethyl acetate (40 mL) was hydrogenated over Pd/C (10%, 0.38 g) at room temperature under H_2 atmosphere (1 atm) until no more H_2 was consumed. The catalyst was removed by filtration. The filtrate was stripped of solvent and then distilled in vacuo (102 °C/0.1 torr) to afford a white solid **7** (3.42 g, 90%) which was recrystallized from ethyl acetate-hexane: mp 41.5-42 °C; IR (neat) 3340 (br), 3022, 1599, 1500, 1460, 1438, 1380, 1340, 1288, 1240, 1180, 1156, 1125, 1075, 1035, 961, 859, 808, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J = 7.3 Hz, 3H), 1.52-1.59 (m, 2H), 2.52 (t, J = 7.7 Hz, 2H), 3.76 (s, 3H), 5.32-5.61 (br, 1H), 6.62 (dd, J = 8.4, 3.0 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 6.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (CH_3), 22.9 (CH_2), 32.1 (CH_2), 56.1 (CH_3), 111.7 (CH), 112.6 (CH), 117.1 (CH), 132.6 (C), 149.1 (C), 151.7 (C); MS (12 eV) *m/z* 166 (M^+, 100), 137 (26).

2-Allyl-1-allyloxy-4-benzyloxybenzene

A magnetically stirred mixture of 2-allyl-4-benzyloxyphenol (9.8 g), allyl bromide (7.5 mL) and K_2CO_3 (12.2 g) in anhydrous 2-butanone (125 mL) was refluxed for 20 h until the complete disappearance of 2-allyl-4-benzyloxyphenol was indicated by TLC analysis, allowed to cool and filtered of salts which were then washed with ether (150 mL). The combined filtrate was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried, and concentrated in vacuo to give a pale yellowish oil, 2-allyl-1-allyloxy-4-benzyloxybenzene (11.15 g, 96%): IR (neat) 3080, 3040, 1642, 1610, 1591, 1498, 1458, 1429, 1385, 1286, 1227, 1170, 1033, 1002, 921, 802, 741, 702 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.49 (d, J = 6.5 Hz, 2H), 4.52 (d, J = 4.9 Hz, 2H), 4.56 (s, 2H), 5.14 (dd, J = 9.1, 1.2 Hz, 1H), 5.17 (dd, J = 15.1, 1.2 Hz, 1H), 5.34 (dd, J = 10.3, 1.2 Hz, 1H), 5.49 (dd, J = 17.3, 1.2 Hz, 1H), 6.04-6.12 (m, 2H), 6.93 (s, 1H), 6.65 (s, 2H), 7.33-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 Hz) δ 34.4 (CH_2), 69.6 (CH_2), 70.5 (CH_2), 112.4 (CH), 112.9 (CH), 115.9 (CH_2), 116.8 (CH_2), 117.1 (CH), 127.5 (CH × 2), 127.8 (CH), 128.5 (CH × 2), 130.5 (C), 133.7 (CH), 136.7 (CH), 150.6 (C), 152.9 (C); MS (12 eV) *m/z* 208 (M^+, 80), 239 (12), 92 (9), 91 (100), 71 (64), 65 (84).

2,6-Diallyl-4-benzyloxyphenol

2-Allyl-1-allyloxy-4-benzyloxybenzene (11.00 g) was placed in a round-bottomed flask equipped with a condenser and heated at 186 °C with magnetic stirring for 14 h until the complete disappearance of the starting material was indicated by TLC analysis. The red-brownish crude product was allowed to cool and was purified by chromatography (ethyl acetate : hexane = 1 : 15) to give liquid 2,6-diallyl-4-benzyloxyphenol (8.47 g, 77%): IR (neat) 3520 (br), 3075, 3030, 3000, 1635, 1605, 1479, 1380, 1338, 1312, 1238, 1182, 1147, 1041, 1030, 997, 917, 862, 843, 740, 697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.38 (d, J = 6.4 Hz, 4H), 4.99 (s, 2H), 5.15 (dd, J = 9.8, 1.4 Hz, 2H), 5.16 (dd, J = 15.8, 1.4 Hz, 2H), 5.92-6.05 (m, 2H), 6.68 (s, 2H), 7.30-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.4 (CH_2 × 2), 70.5 (CH_2), 114.9 (CH × 2), 116.4 (CH_2 × 2), 126.7 (C, × 2), 127.5 (CH × 2), 127.6 (CH), 128.5 (CH × 2), 136.3 (CH × 2), 137.3 (C), 146.5 (C), 152.6 (C); MS (75 eV) *m/z* 280 (M^+, 59), 189 45), 91 (100), 85 (34), 71 (37), 57 (38).

2,6-Diallyl-4-benzyloxy-1-methoxybenzene

A magnetically stirred mixture of 2,6-diallyl-4-benzyloxyphenol (13.79 g), dimethyl sulfate (4.65 mL) and K_2CO_3 (12.2 g) in anhydrous 2-butanone (125 mL) was re-

fluxed for 18 h until the complete disappearance of the starting material was indicated by TLC analysis. The reaction mixture was cooled and filtered to remove salts which were then washed with ether (200 mL). The combined filtrate was washed with saturated ammonium chloride solution (50 mL × 2) and brine, dried, and concentrated in vacuo to give liquid 2,6-diallyl-4-benzyloxy-1-methoxybenzene (14.25 g, 99%): IR (neat) 3075, 3024, 3005, 1637, 1605, 1599, 1495, 1480, 1431, 1380, 1325, 1228, 1172, 1142, 1042, 1013, 915, 863, 848, 739, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 3.42 (d, J = 6.5 Hz, 4H), 3.69 (s, 3H), 4.99 (s, 2H), 5.09 (dd, J = 12, 1.4 Hz, 2H), 5.10 (dd, J = 16, 1.4 Hz, 2H), 5.93-6.03 (m, 2H), 6.70 (s, 2H), 7.32-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.1 (CH_2 × 2), 61.5 (CH_3), 70.2 (CH_2), 114.4 (CH × 2), 115.9 (CH_2 × 2), 127.6 (CH × 2), 127.7 (CH), 128.5 (CH × 2), 133.9 (C × 2), 137.0 (CH × 2), 137.1 (C), 150.2 (C), 154.8 (C); MS (25 eV) *m/z* 294 (M^+, 100), 203 (68), 91 (100).

4-Methoxy-3,5-dipropylphenol (8)

A solution of 2,6-diallyl-4-benzyloxy-1-methoxybenzene (14.11 g) in ethyl acetate (30 mL) was hydrogenated with vigorous stirring over Pd/C (10%, 1.41 g) at room temperature under H_2 atmosphere (1 atm) until no more H_2 was consumed. The catalyst was removed by filtration, and the filtrate was stripped of solvent and distilled in vacuo (133 °C/0.1 torr) to give liquid **8** (10.90 g, 77%): IR (neat) 3380 (br), 1600, 1462, 1430, 1379, 1345, 1318, 1233, 1209, 1176, 1142, 1097, 1018, 990, 855, 750 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.98 (t, J = 7.4 Hz, 6H), 1.63 (sextet, J = 7.4 Hz, 4H), 2.55 (t, J = 7.4 Hz, 4H), 3.67 (s, 3H), 4.49 (br, 1H), 6.50 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (CH_3 × 2), 23.7 (CH_2 × 2), 31.8 (CH_2 × 2), 61.3 (CH_3), 113.9 (CH × 2), 136.6 (C × 2), 150.2 (C), 151.4 (C); MS (25 eV) *m/z* 208 (M^+, 100), 193(23), 179 (10), 165 (13), 164 (8), 151 (13), 71 (13).

2-Allyl-4,4-dimethoxy-2,5-cyclohexadienone (9)

To a cooled (ice-salt bath) solution of **3** (164 mg) in anhydrous methanol (7 mL) suspended with anhydrous potassium bicarbonate (0.4 g) was added dropwise a solution of thallium trinitrate (TTN, 0.45 g) in anhydrous methanol (7 mL) over a period of 5 min. The resulting mixture was stirred for 10 more min and quenched with saturated aqueous sodium bicarbonate (10 mL). Ether was subsequently added. The milky mixture was filtered through basic alumina (4 cm in length). The layers of the filtrate were separated, and the organic phase was washed with saturated aqueous sodium bicarbonate and brine, dried, and stripped of solvent to afford **9** (171 mg, 88%): IR (neat) 3080, 1681, 1650, 1629, 1378, 1310, 1125, 1070, 1041, 970, 921, 832 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.06 (br d, J = 6.1 Hz, 2H), 3.33 (s, 6H), 5.00-5.14 (m, 2H), 5.52-5.97 (m, 1H), 6.20 (d, J = 10.3 Hz, 1H), 6.51 (d, J = 3.0 Hz, 1H), 6.75 (dd, J = 10.3, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.7 (CH_2), 50.1 (CH_3 × 2), 92.9 (C), 117.6 (CH_2), 129.9 (CH), 134.2 (CH), 138.5 (CH), 139.0 (C), 142.8 (CH), 184.9 (C); MS (25 eV) *m/z* 194 (M^+, 14), 179 (18), 168 (34), 153 (100), 135 (23), 103 (25), 99 (20), 91 (30).

2-(1,3-Dioxolan-2-ylmethyl)-4,4-dimethoxy-2,5-cyclohexadienone (10)

The preparation of **10** (112 mg, 92%) from **4** (105 mg) was done in a manner similar to that of **9**. The spectral data of **10**: UV (95% EtOH) λ_{max} (ε/M^{-1} cm^{-1}) 218 (6.0×10^3), 312 (1.3×10^3) nm; IR (neat) 3040, 1682, 1650, 1629, 1490, 1468, 1396, 1370, 1315, 1248, 1200, 1125, 1080, 1040, 967, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.55 (d, J = 4.4 Hz, 2H), 3.24 (s, 6H), 3.69-3.84 (m, 4H), 4.88 (t, J = 4.4 Hz), 6.14 (d, J = 10.2 Hz, 1H), 6.64 (d, J = 3.0 Hz, 1H), 6.69 (dd, J = 10.2, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 35.1 (CH_2), 50.1 (CH_3 × 2), 64.6 (CH_2 × 2), 92.6 (C), 102.1 (CH), 129.6 (CH), 134.9 (C), 141.0 (CH), 142.7(CH), 184.5 (C); MS (12 eV) *m/z* 209 (M^+-OCH_3, 52), 136 (29), 37 (100).

4,4-Dimethoxy-2-propyl-2,5-cyclohexadienone (11)

The preparation of **11** (184 mg, 94%) from **5** (166 mg) was done in a manner similar to that of **9**. The spectral data of **11**: UV (95% EtOH) λ_{max} (ε/M^{-1} cm^{-1}) 221 (8.7×10^3), 312 (1.0×10^3) nm; IR (neat) 3050, 1681, 1651, 1629, 1463, 1380, 1310, 1295, 1200, 1123, 1100, 1068, 1041, 962 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.79 (t, J = 7.3 Hz, 3H), 1.35 (sextet, J = 7.3 Hz, 2H), 2.14 (t, J = 7.3 Hz, 2H), 3.22 (s, 6H), 6.10 (d, J = 10.3 Hz, 1H), 6.41 (d, J = 3.6 Hz, 1H), 6.65 (dd, J = 10.3, 3.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.4 (CH_3), 21.0 (CH_2), 30.7 (CH_3), 49.9 (CH_3 × 2), 92.8 (C), 129.9 (CH), 137.8 (CH), 140.2 (C), 142.4 (CH), 185.0 (C); MS (12 eV) *m/z* 196 ((M^+, 52), 181 (47), 168 (34), 166 (33), 165 (100), 154 (37), 153 (31), 137 (73).

4,4-Dimethoxy-2,6-dipropyl-2,5-cyclohexadienone (12)

The preparation of **12** (1.26 g, 92%) from **6** (1.04 mg, 0.50 mmol) was done in a manner similar to that of **9**. The spectral data of **12**: UV (95% EtOH) λ_{max} (ε/M^{-1} cm^{-1}) 234 (9.3×10^3), 252 (sh, 6.5×10^3), 280 (sh, 6.9×10^2) nm; IR (neat) 3030, 1679, 1648, 1610, 1462, 1380, 1360, 1300, 1230, 1209, 1185, 1150, 1100, 1083, 1045, 965, 890, 879, 796, 776, 728 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, J = 7.4 Hz, 6H), 1.45 (sextet, J = 7.6 Hz, 4H), 2.53 (t, J = 7.6 Hz, 4H), 3.31 (s, 6H), 6.47 (s, 2H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ 13.8 ($CH_3 \times 2$), 21.7 ($CH_2 \times 2$), 31.2 ($CH_2 \times 2$), 50.3 ($CH_3 \times 2$), 93.1 (C), 137.4 (CH × 2), 140.9 (C × 2), 185.6 (C); MS (75 eV) *m/z* 238 (40), 223 (60), 207 (100), 195 (31),179 (45), 137 (28), 121 (40), 91 (36), 77 (26).

4,4-Dimethoxy-3-propyl-2,5-cyclohexadienone (13)

The preparation of **13** (166 mg, 98%) from **7** (142 mg, 0.86 mmol) was done in a manner similar to that of **9**. The spectral data of **13**: UV (95% EtOH) λ_{max} (ε/M^{-1} cm^{-1}) 233 (6.5×10^3), 263 (sh, 8.0×10^2) nm; IR (neat) 3055, 1681, 1644, 1621, 1469, 1390, 1300, 1229, 1220, 1109, 1068, 1015, 977, 919, 868, 810, 780 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, *J* = 7.3 Hz, 3H), 1.54 (sextet, *J* = 7.3 Hz, 2H), 2.23 (t, *J* = 7.3 Hz, 2H), 3.17 (s, 6H), 6.19 (d, *J* = 2.1 Hz, 1H), 6.36 (dd, *J* = 10.3, 2.1 Hz, 1H), 6.71 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9 (CH_3), 19.4 (CH_2), 30.6 (CH_2), 51.0 ($CH_3 \times 2$), 95.6 (C), 128.0 (CH), 132.1 (CH), 144.0 (CH), 159.0 (C), 185.2 (C); MS (12 eV) *m/z* 196 (M^+, 15), 181 (9), 166 (100), 154 (11), 137 (13).

4,4-Dimethoxy-3,5-dipropyl-2,5-cyclohexadienone (14)

The oxidation of **8** (208 mg) was carried out in a manner similar to that of **9** to give a white solid (0.232 g, 97%) which was recrystallized from ethyl acetate-hexane to afford white crystals **14**: mp 60-61 °C; UV (95% EtOH) λ_{max} (ε/M^{-1} cm^{-1}) 229 (1.83×10^4), 268 (2.9×10^3) nm; IR (KBr) 3041, 1680, 1635, 1621, 1465, 1455, 1420, 1385, 1309, 1275, 1225, 1185, 1142, 1073, 929, 897, 875, 869, 720 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.96 (t, *J* = 7.3 Hz, 6H), 1.54 (sextet, *J* = 7.3 Hz, 4H), 2.19 (t, *J* = 7.3 Hz, 4H), 2.95 (s, 6H), 6.27 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 ($CH_3 \times 2$), 19.2 ($CH_2 \times 2$), 30.2 ($CH_2 \times 2$), 50.8 ($CH_3 \times 2$), 98.5 (C), 129.6 (CH × 2), 159.0 (C × 2), 185.2 (C); MS (75 eV) *m/z* 238 (M^+, 78), 223 (28), 209 (100), 207 (41), 195 (37), 181 (16), 179 (20), 155 (38), 71 (46), 57 (36), 55 (42); HRMS Calcd for $C_{14}H_{22}O_3$: 238.1569, Found: 238.1541; Anal Calcd for $C_{14}H_{22}O_3$: C, 70.56, H, 9.30; Found: C, 70.62, H, 9.59.

General Procedure for the Irradiation of Substituted 4,4-Dimethoxy-2,5-cyclohexadienones 9-14 in Methanol

A solution of appropriately substituted 4,4-dimethoxy-2,5-cyclohexadienone (**9-14**) in methanol (spectral grade) was placed in a Pyrex tube, bubbled with nitrogen for 45 min, stoppered and irradiated with fluorescent (350 nm) lamps in a Rayonet reactor through a uranium filter until the starting material disappeared as shown by TLC analysis. The irradiated solution was stripped of solvent and chromatographed on preparative TLC plates (ethyl acetate : hexane = 1 : 5 as eluent) to isolate and purify the products.

Methyl 3-Allyl-2-oxo-3-cyclopenten-1-carboxylate (15)

Compound **9** (171 mg) in methanol (30 mL) was irradiated for 2 h to give, after isolation and purification, **15** (72.8 mg, 46%): oil; IR (neat) 3037, 2974, 1745, 1621, 1508, 1377, 1310, 1255 ,1228, 1160, 1000, 962 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.57-2.59 (m, 1H), 2.75-2.80 (m, 1H), 2.92 (br d, *J* = 6.7 Hz, 2H), 3.42 (dd, *J* = 7.1, 2.3 Hz, 1H), 3.72 (s, 3H), 5.04-5.09 (m, 2H), 5.76-5.92 (m, 1H), 7.22 (m, 1H); ^{13}C NMR ($CDCl^3$, 100 MHz) δ 30.8 (CH_2), 37.4 (CH_2), 51.2 (CH), 52.6 (CH_3), 117.1 (CH_2), 133.8 (CH), 142.9 (C), 157.9 (CH), 169.4 (C), 201.7 (C); MS (25 eV) *m/z* 180 (M^+, 82), 148 (57), 121 (100), 91 (64), 77 (57).

Methyl 2-Oxo-3-propyl-3-cyclopenten-1-carboxylate (16)

Compound **10** (173 mg) in methanol (30 mL) was irradiated for 2 h to give, after isolation and purification, **16** (84.5 mg, 53%): oil; IR (neat) 1740, 1710, 1632, 1510, 1455, 1435, 1380, 1330, 1300, 1257, 1225, 1210, 1156, 1099, 1049, 1002, 970 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.53 (apparent sextet, 2H), 2.16 (m, 2H), 2.80 (br d, *J* = 17.6 Hz, 1H), 2.96 (br d, *J* = 17.6 Hz, 1H), 3.44 (dd, *J* = 6.9, 2.6 Hz, 1H), 3.76 (s, 3H), 7.38 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7 (CH_3), 20.8 (CH_2), 26.9 (CH_2), 30.8 (CH_2), 51.3 (C), 52.6 (CH_3), 144.8 (C), 157.1 (CH), 169.7 (C), 202.7 (C); MS (12 eV) *m/z* 224 (M^+, 20), 192 (72), 182 (100), 150 (17); HRMS Calcd for $C_{10}H_{14}O_3$: 182.0943. Found: 182.0937.

Methyl 3-(1,3-Dioxolan-2-ylmethyl)-2-oxo-3-cyclopenten-1-carboxylate (17)

Compound **11** (112 mg) in methanol (25 mL) was irradiated for 1.75 h to give, after isolation and purification, **17** (52.9 mg, 50%): oil; IR (neat) 1740, 1710, 1638, 1439, 1405, 1370, 1348, 1329, 1300, 1265, 1210, 1160, 1140, 1050, 1030, 1015, 995, 969, 950, 820, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43-2.53 (m, 2H), 2.78 (br d, *J* = 19.0 Hz, 1H), 2.93 (br d, *J* = 19.0 Hz, 1H), 3.38 (dd, *J* = 6.9, 2.7 Hz, 1H), 3.68 (s, 3H), 3.76-3.80 (m, 2H), 3.87-3.91 (m, 2H), 4.95 (t, *J* = 5.1 Hz, 1H), 7.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.5 (CH_2), 31.0 (CH_2), 50.6 (CH), 52.4 (CH_3), 64.8 ($CH_2 \times 2$), 102.0 (CH), 138.8 (C), 159.8 (CH), 169.2 (C), 201.7 (C); MS (12 eV) *m/z* 226 (M^+, 20), 195 (17), 180 (33), 122 (15), 86 (22), 84 (27), 74 (40), 73 (100); HRMS Calcd for $C_{11}H_{14}O_5$: 226.0842, Found: 226.0837.

Methyl 2-Oxo-4-propyl-3-cyclopenten-1-carboxylate (18)

Compound **13** (167 mg) in methanol (40 mL) was irradiated for 2 h to give **13** (16.3 mg) and **18** (70.4 mg, 51%

based on the consumed **13**) after isolation and purification. The data of **18**: oil; IR (neat) 3080, 1739, 1710, 1619, 1468, 1458, 1439, 1382, 1330, 1261, 1213, 1152, 1092, 1030, 1000, 969, 890, 850, 830, 770 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.95 (t, J = 7.4 Hz, 3H), 1.6 (apparent sextet, 2H), 2.39 (t, J = 7.6 Hz, 2H), 2.73 (dd, J = 18.5, 6.9 Hz, 1H), 2.95 (br d, J = 18.5 Hz, 1H), 3.44 (dd, J = 6.9, 2.6 Hz, 1H), 3.71 (s, 3H), 5.86 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.7 (CH_3), 20.2 (CH_2), 35.3 (CH_2), 35.4 (CH_2), 52.0 (CH), 52.6 (CH_3), 127.3 (CH), 169.4 (C), 183.0 (C), 202.7 (C); MS (12 eV) *m/z* 182 (100), 154 (43), 150 (50), 122 (27), 94 (13); HRMS Calcd for $C_{10}H_{14}O_3$: 182.0943, Found: 182.0941.

Methyl (1*R,5*S**)-2-oxo-3,5-dipropyl-2-cyclopenten-1-carboxylate (19)**

Compound **12** (249 mg) in methanol (30 mL) was irradiated for 1.5 h to give **19** (231 mg, 99%) after isolation and purification. **19**: oil; IR (neat) 1741, 1718, 1635, 1470, 1440, 1385, 1355, 1341, 1265, 1222, 1200, 1182, 1105, 1055, 1020, 960, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.814 (t, J = 7.3 Hz, 3H), 0.822 (t, J = 7.3 Hz, 3H), 1.26-1.34 (m, 3H), 1.65-1.77 (m, 1H), 2.06 (apparent t), 2.58-2.63 (m, 1H), 2.67-2.73 (m, 1H), 3.30-3.33 (m, 1H), 3.65 (s, 3H), 7.08 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.6 (CH_3), 19.9 (CH_2), 20.5 (CH_2), 26.6 (CH_2), 32.7 (CH_2), 48.5 (CH), 50.5 (CH), 52.2 (CH_3), 146.4 (C), 151.5 (CH), 172.3 (C), 209.1 (C); MS (12 eV) *m/z* 224 (M^+, 20), 192 (72), 182 (100), 150 (17); HRMS Calcd for $C_{13}H_{20}O_3$: 224.1412, Found: 224.1408.

Irradiation of 14 in Methanol and Benzene

A solution of **14** (181 mg) in methanol (20 mL) was irradiated for 4 h to give, after isolation and purification, **8** (58.3 mg, 37%) which showed identical ^1H NMR, IR and mass spectra with those of an authentic sample. Similarly a solution of **14** (213 mg) in benzene (25 mL) was irradiated for 6.5 h to give **8** (22.4 mg, 12%) after isolation and purification.

Irradiation of 11 in Benzene

A solution of **11** (180 mg) in benzene (30 mL) was irradiated for 2 h to yield **20** (91.6 mg, 51%), **21** (33.1 mg, 22%), and **22** (4.5 mg, 3%).

4,5-Dimethoxy-2-propylphenol (20): mp 73.5-74 °C (recrystallized from ethyl acetate-hexane, white needles); IR (KBr) 3440 (br), 1620, 1520, 1468, 1452, 1411, 1360, 1285, 1245, 1202, 1118, 1035, 1000, 850 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.93 (t, J = 7.4 Hz, 3H), 1.59 (apparent sextet, 2H), 2.49 (t, J = 7.7 Hz, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 5.47 (br s, 1H), 6.40 (s, 1H), 6.62 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8 (CH_3), 23.2 (CH_2), 31.5 (CH_2), 55.8 (CH_3), 56.6 (CH_3), 101.0 (CH), 114.0 (CH), 119.4 (C), 142.7 (C), 147.6 (C), 147.9 (C); MS (12 eV) *m/z* 196 (M^+, 100), 167 (38); HRMS Calcd for $C_{11}H_{16}O_3$ 196.1099. Found 196.1095. Anal Calcd for $C_{11}H_{16}O_3$ C, 67.26; H, 8.16, Found C, 67.31; H, 8.22.

5-Methoxy-2-propylphenol (21): IR (neat) 3420 (br), 3010, 1625, 1599, 1520, 1505, 1470, 1450, 1432, 1380, 1290, 1210, 1170, 1130, 1048, 960, 840 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, J = 7.3 Hz, 3H), 1.59 (apparent sextet, 2H), 2.50 (t, J = 7.6 Hz, 2H), 3.74 (s, 3H), 3.90 (s, 1H), 6.36 (d, J = 2.3 Hz, 1H), 6.43 (dd, J = 8.6, 2.3 Hz, 1H), 6.99 (d, J = 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.9 (CH_3), 23.1 (CH_2), 31.3 (CH_2), 55.3 (CH_3), 101.6 (CH), 105.7 (CH), 120.5 (C), 130.6 (CH), 154.2 (C), 158.6 (C); MS (12 eV) *m/z* 166 (M^+, 100), 137 (99); HRMS Calcd for $C_{10}H_{14}O_2$: 166.0994, Found: 166.0989.

3-Methoxy-2-propylphenol (22): IR (neat) 3420 (br), 3001, 1677, 1645, 1599, 1520, 1472, 1442, 1335, 1275, 1225, 1119, 1060, 960, 942, 780, 730 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.94 (t, J = 7.7 Hz, 3H), 1.49-1.56 (m, 2H), 2.58 (t, J = 7.7 Hz, 2H), 3.78 (s, 3H), 4.72 (s, 1H), 6.41 (d, J = 8.2 Hz, 1H), 6.45 (d, J = 8.2 Hz, 1H), 7.00 (t, J = 8.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2 (CH_3), 22.3 (CH_2), 25.0 (CH_2), 55.6 (CH_3), 103.2 (CH), 108.2 (CH), 117.2 (C), 126.6 (CH), 1154.3 (C), 158.6 (C); MS (12 eV) *m/z* 166 (M^+, 100), 137 (99); HRMS Calcd for $C_{10}H_{14}O_2$: 166.0994, Found: 166.0991.

Irradiation of 12 in Benzene

A solution of **12** (119 mg) in benzene (15 mL) was irradiated for 2 h to yield, after isolation and purification by preparative TLC plates (ethyl acetate : hexane = 1 : 80), 3-methoxy-2,6-dipropylphenol (**23**, 34 mg, 34%): IR (KBr) 3560 (br), 1613, 1593, 1492, 1464, 1444, 1378, 1325, 1267, 1223, 1196, 1163, 1119, 1061, 965, 920, 885, 853, 792 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.97 (t, J = 7.3 Hz, 6H), 1.51-1.64 (m, 4H), 2.51 (t, J = 7.7 Hz, 2H), 2.59 (t, J = 7.7 Hz, 2H), 3.78 (s, 3H), 4.70 (s, 1H), 6.49 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.0 (CH_3), 14.2 (CH_3), 22.3 (CH_2), 23.0 (CH_2), 25.5 (CH_2), 31.8 (CH_2), 55.5 (CH_3), 102.5 (CH), 116.3 (CH), 120,4 (C), 126,8 (CH), 152.0 (C), 156.5 (C); MS (75 eV) *m/z* 208 (M^+, 20), 180 (12), 179 (100), 149 (3), 121 (4), 91 (8).

Irradiation of 13 in Benzene

A solution of **13** (159 mg) in benzene (25 mL) was irradiated for 2 h to yield, after isolation and purification by preparative TLC plates (ethyl acetate : hexane = 1 : 5), **7** (28.5 mg, 21%), which showed identical ^1H NMR, IR and

mass spectra with those of an authentic sample.

ACKNOWLEDGEMENT

We thank the National Science Council of the Republic of China for the financial support.

Received August 14, 1997.

Key Words

Masked p-benzoquinones; 4,4-Dimethoxy-2,5-cyclohexadienones; Photochemical reactions; 2-Cyclopentenones; Solvent effects.

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