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# PHOTOCHEMICAL REACTIONS OF ALLYLPHENOXIDE ANIONS

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**Abstract**—Photochemical behaviour of sodium allylphenoxides **1a–3a** was compared with that of corresponding neutral allylphenols **1b–3b**, and a striking difference was found in reactivity as well as in course of the reaction. Remarkably higher photoreactivity of allylphenoxide anions, especially that of *o*-allylphenoxide **1a**, is ascribed to the efficiency of electron transfer. The characteristic reaction products derived only from the anions were as follows: (a) intramolecular cyclization products, indanols **9**, from **2a**, (b) rearranged reduction products **10** from both **2a** and **3a**, and (c) degradative methanol-adduct **11** from **3a**. Methanol-adducts **7** and photo-reduction products **6** were formed in either case. In addition cyclization products with the participation of O atom, **4** and **5**, were obtained from **1a** and **1b**. Occurrence of the di-$\pi$-methane rearrangement was restricted to the reaction of neutral species **1b–3b**. A mechanism based on electron transfer in the excited state is suggested for the course of the photoreaction.

The photo-induced reactions of phenols have been widely examined.[1] UV irradiation of simple phenols is known to give phenoxy radicals and solvated electrons from their excited states. Phenoxy radicals are generally accepted species in the chemistry of phenols, and combination of phenoxy radicals has been extensively studied because of their synthetic and, particularly, biosynthetic importante.[2] On UV irradiation phenol itself gives all five possible dimers derived from C–C and C–O coupling of phenoxy radical.[3] Both phenol and phenoxide anion have been recognized to produce phenoxy radical and solvated electron by irradiation.[1]

It is the purpose of the present study to establish the difference in the photochemical behaviour of phenol and phenoxide anion.[4] To the best of our knowledge the photochemistry of phenoxide anion has enjoyed only limited study,[5] although the photochemistry of allyl-substituted phenol,[6] anisoles,[7] and anilines[8] have been reported. In the present paper we wish to describe the results obtained during the investigation of the photochemical behaviour of sodium allylphenoxides **1a–3a** and neutral allylphenols **1b–3b**, in which a striking difference in reactivity and also in the reaction course became evident.

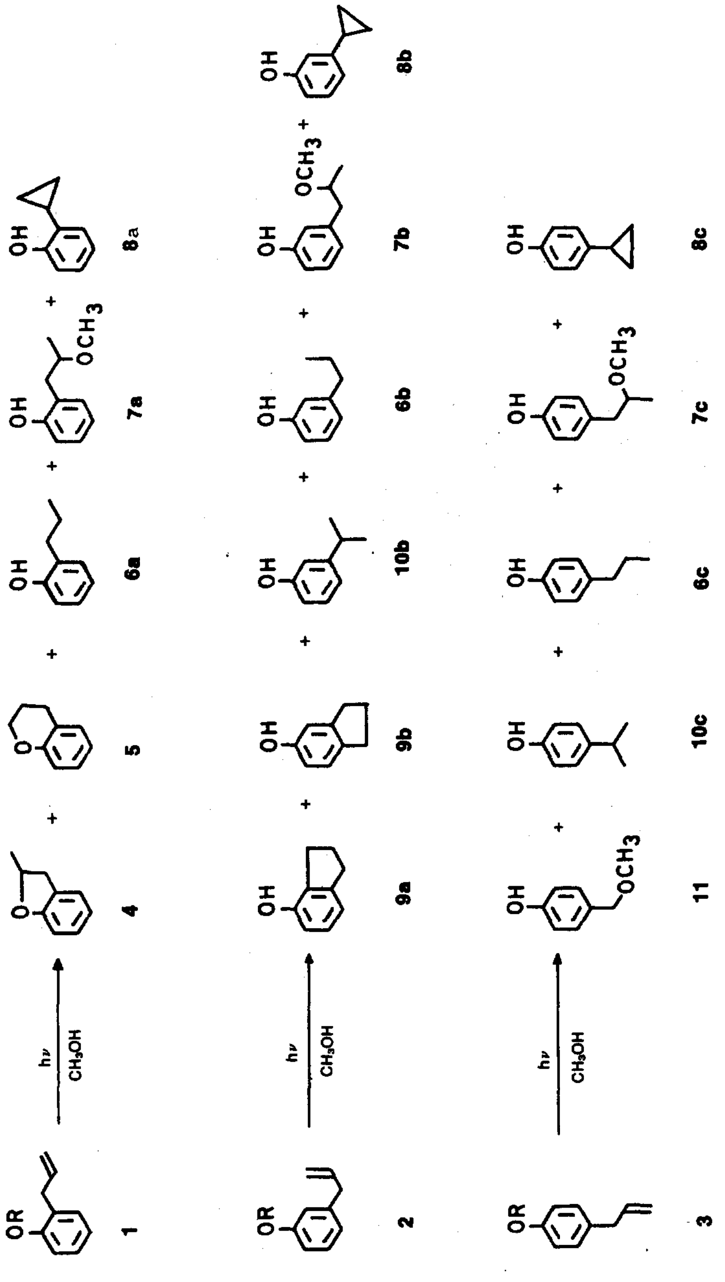
## RESULTS AND DISCUSSION

Sodium *o*-, *m*- and *p*-allylphenoxides **1a–3a** in methanol were irradiated with a high pressure mercury lamp (quartz). After acidification of the mixture with acetic acid, the products were secured by preparative glc. The irradiation of neutral *o*-, *m*- and *p*-allylphenols **1b–3b** was also carried out for the sake of comparison and the products were isolated in a similar manner. The structures of the products were readily derived via NMR, IR and mass spectral data. The results are summarized in Scheme 1 and Table 1.

It is notable that the results of irradiation of the allylphenoxide anion are strikingly different from those of *neutral* allylphenols, both in the reactivity of the substrates and in the nature of the products. The higher photo-reactivity of allylphenoxide anions, especially of *o*-substituted ones, than that of neutral allylphenols was recognized as judged from comparison of the conversion rates.

Table 1. Photo-products from allylphenols 1–3

| Starting material | Irradiation time (hr) | conv. (%) | Products (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | 4 | 5 | 6a | 7a | 8a | |
| 1a (R=Na) | 40 | 100 | 13 | 9 | 24 | 38 | - | |
| 1b (R=H) | 200 | 63 | 24 | 2 | - | 25 | 49 | |
| | | | 9a | 9b | 10b | 6b | 7b | 8b |
| 2a (R=Na) | 90 | 100 | 15 | 4 | 8 | 20 | 53 | - |
| 2b (R=H) | 115 | 53 | - | - | - | 9 | 11 | 80 |
| | | | 11 | 10c | 6c | 7c | 8c | |
| 3a (R=Na) | 86 | 97 | 64 | 7 | 13 | 7 | - | |
| 3b (R=H) | 92 | 35 | - | - | - | - | 100 | |


OR
1
2
3
hν
CH₃OH
OH
OCH₃
4
5
6a
7a
8a
9a
9b
10b
6b
7b
8b
11
10c
6c
7c
8c
a: R = Na
b: R = H

Scheme 1.

In the reaction of *o*-allylphenoxide anion **1a**, methanol-adduct **7a** and intramolecular cyclization products, 2-methylcoumaran **4** and chroman **5**, were obtained accompanied with a reduction product **6a**. On the other hand, photolysis of *o*-allylphenol **1b** gave *o*-cyclopropylphenol **8a** as a major product, in addition to **4**, **5**, and **7a**. Schmid[6] reported that photolysis of **1b** in benzene solution gave cyclization products, **4** and **5**, but no **8a**; this solvent effect for the formation of **8a** is remarkable.

The reaction of *m*-allylphenoxide anion **2a** showed a more distinct difference from the reaction of corresponding neutral **2b**. Irradiation of **2a** gave a methanol-adduct **7b** as a major product, in addition to reduction products **10b** and **6b** and cyclization produces **9a** and **9b**. The formation of 4-indanol **9a** and 5-indanol **9b** can be regarded as an intramolecular alkylation reaction. On the other hand, irradiation of **2b** gave *m*-cyclopropylphenol **8b** as a major product accompanied with a small amount of **6b** and **7b**.

In the reaction of *p*-allylphenoxide anion **3a**, the reaction modes were completely different from the result of *neutral p*-allylphenol **3b**. Irradiation of **3a** afforded also a methanol-adduct **7c** and reduction products **6c** and **10c**, but the major product was *p*-methoxymethylphenol **11**, which was apparently resulted from some kind of degradation. On the contrary, irradiation of **3b** gave *p*-cyclopropylphenol **6c** as a sole reaction product.

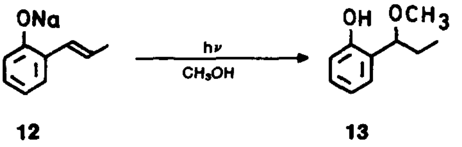
The photochemical transformation of allylbenzene derivatives into their cyclopropyl isomers have been described,[8] and rationalized as an outcome of di-$\pi$-methane rearrangement.

It is interesting that methanol can add readily to such a simple olefin as an allylic double bond. The photochemical addition of alcohols to C–C double bond is classified as photo-polar addition.[9] Generally, however, photochemical polar addition has been restricted to those cases where the double bond is either contained within the ring or conjugated to a phenyl group,[10] and the addition reaction often requires the presence of added acid or BTX sensitizer. We investigated the role of phenoxide anion in this photochemical transformation, since photochemical formation of methanol-adducts has no precedent in the case of allylphenol and its derivatives, and might be thought to be formed by the participation of phenoxide anion.

With regard to the formation of methanol-adducts **7a**–**7c**, the role of efficient sensitization by the phenoxide anion attracted our attention. When allylbenzene and an excess of sodium phenoxide were irradiated in methanol, none of the methanol-adduct as well as phenol-adduct was detected and only phenol and allylbenzene were recovered unchanged. This result rules out the role of phenoxide as sensitizer.

Secondly, the route of photochemical isomerization of allylphenoxide anion to propenylphenoxide anion was considered. When sodium *o*-propenylphenoxide **12** was irradiated under similar conditions, only *o*-(1-methoxypropyl)phenol **13** was obtained but no *o*-(2-methoxypropyl)phenol **7a** was formed (Scheme 2). From this result, the intermediacy of propenylphenoxide was also excluded.

Cyclopropylphenols **8a**–**8c** were obtained on irradiation of *neutral* allylphenols **1b**–**3b** but not at all on irradiation of sodium allylphenoxides **1a**–**3a**. Cyclopropylphenoxides might be exist as intermediates of irradiation of allylphenoxides **1a**–**3a**. However, only cyclopropylphenols were recovered when *o*-, *m*-, and *p*-cyclopropylphenoxides were irradiated under similar conditions. From these results, the intermediacy of cyclopropylphenoxide anion was also improbable.



Scheme 2.

A mechanism which accommodates these results is one similar to that postulated for the photochemical methanol addition to allylanilines reported by Schmid,[7] and is outlined in Scheme 3. The reaction is initiated by transfer of an electron from the excited phenoxide anion to the double bond of the allyl group.

Production of the anion radicals **14a** by electron capture is followed by proton transfer from the solvent methanol giving biradicals **15a** and **16a**. Intramolecular radical coupling of **15a** yields **5**, and that of **16a** yields **4** and a spiro-substituted cyclohexadienone **17a**.[11] Addition of methanol to **17a** results in the formation of **7a**. The reduction product **6a** formally originates from hydrogen abstraction of the biradicals **15a** and **16a** from the solvent methanol. However, the photo-reduction accompanied with photochemical addition of alcohol has some precedents and is explained as the results of radical reaction[12] or hydride abstraction by the cationic intermediate.[13]

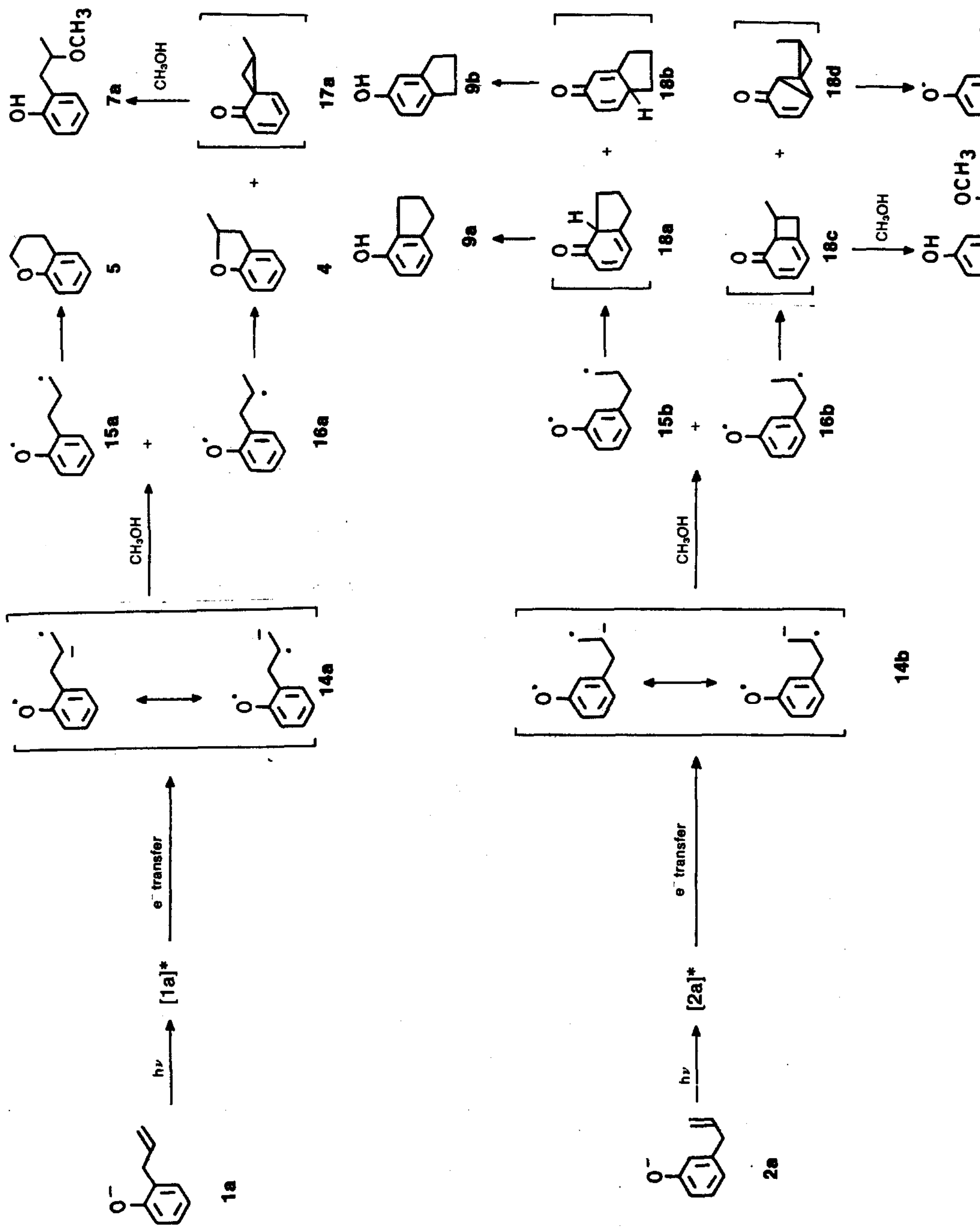
In the case of *m*-allylphenoxide anion **2a**, a similar mechanism of electron capture from phenoxide anion can interpret the formation of the products. Intramolecular coupling of the biradical **15b** gives cyclopentanocyclohexadienones **18a** and **18b**, and biradical **16b** gives cyclobutanocyclohexadienone **18c**[11] or **18d**.[11] Aromatization by 1,3-H shift of **18a** and **18b** gives **9a** and **9b** respectively, and addition of methanol to **18c** affords **7b**. Transformation of **18d** to **16d'** followed by hydrogen abstraction gives **10b**. The other reduction product **6b** is formed similarly to **6a**.

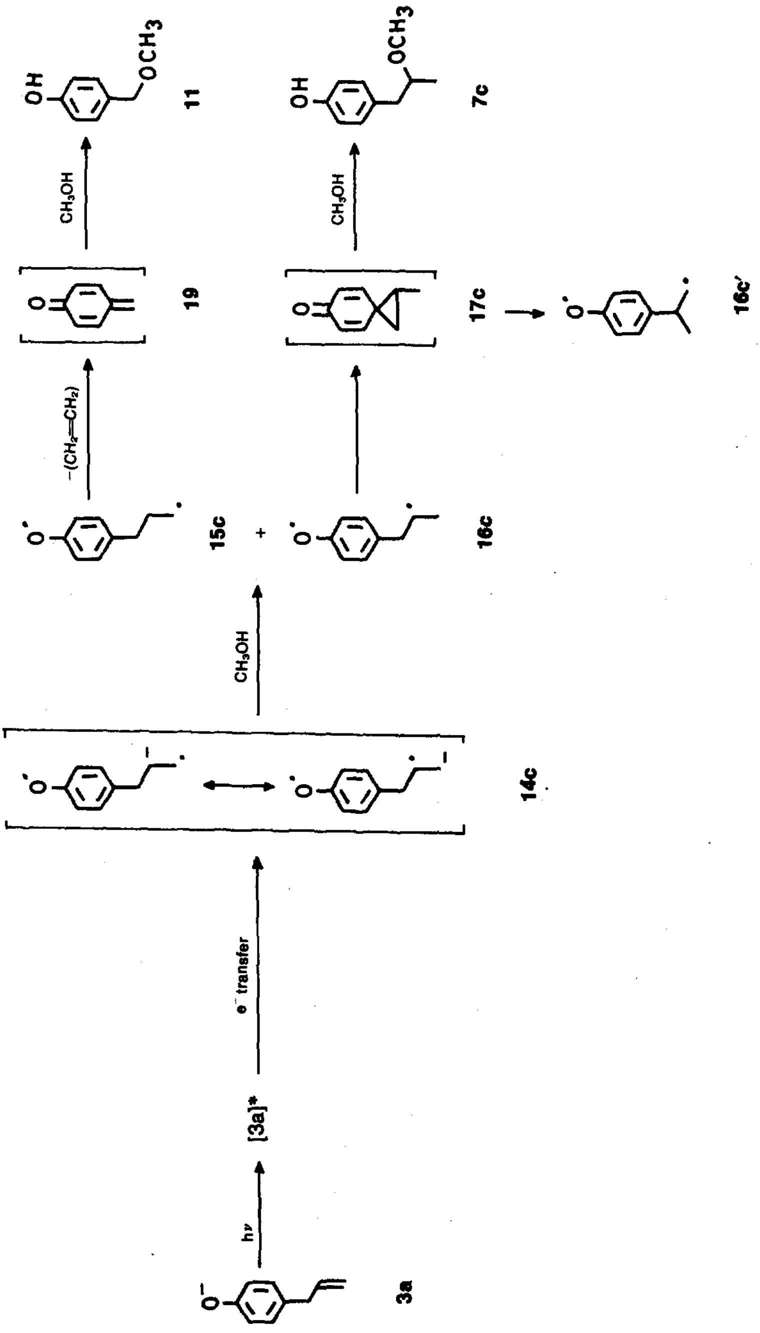
Likewise *p*-allylphenoxide **3a** gives two biradicals **15c** and **16c**. Elimination of ethylene from **15c** gives quinone methide **19**, addition of methanol to which gives **11**. On the other hand **16c** couples intramolecularly into **17c**,[11] and addition of methanol to **16c** gives **7c**. *p*-Isopropylphenol **10c** is formed through transformation of **17c** to **16c'**.

The most discriminating factor between the behaviour of allylphenoxide anion and corresponding *neutral* phenol is the efficiency of electron transfer. The present results are compatible with the conclusion of Jortner[14] who claims that solvated electrons are formed photochemically in aqueous solution of the phenoxide anion, but not formed or at most formed with very low quantum yields in neutral or acid solutions.[3]

In connection with this, the variation of the ratios of cyclopropylphenols (**8a**, 49%; **8b**, 79%; and **8c**, 100%) on irradiation of the neutral solution is ascribable to the order of the facility of electron transfer; in the case of *o*-allylphenol **1b**, the O atom and the double bond of allyl group are juxtaposed to cause efficient electron capture. In the case of *p*-allylphenol **3b** the situation is quite different.

Lastly, the types of the products merit noting. Cyclopropylphenols, the products of di-$\pi$-methane rear-


1a
hν
[1a]*
e⁻ transfer
14a
CH3OH
15a
16a
5
4
17a
CH3OH
7a
OH
OCH3
2a
hν
[2a]*
e⁻ transfer
14b
CH3OH
15b
16b
18a
18b
18c
18d
9a
9b
OH
CH3OH
7b
OH
OCH3
16b'


3a
hν
[3a]*
e⁻ transfer
14c
CH₃OH
15c
+
16c
−(CH₂=CH₂)
19
CH₃OH
11
OH
OCH₃
17c
CH₃OH
7c
OH
OCH₃
16c′

Scheme 3.

rangement, **8** are formed only in the reaction of neutral phenols. Methanol-adducts **7** and photo-reduction products without rearrangement **6** are formed in the reaction of both neutral and anionic state. Intramolecular cyclization products with the participation of the phenolic O atom **4** and **5** serive from both neutral and anionic states of only *o*-substituted phenol. The products resulting only from the reaction of the anionic state are (a) intramolecular cyclization products (cyclopentane rings) **9** which are obtained only in the case of *m*-substituted phenol, (b) rearranged reduction product **10** formed in the cases of both *m*- and *p*-substituted phenols, and (c) degradative methanol-adducts **11** formed only in *p*-substituted phenol.

## EXPERIMENTAL

NMR spectra were recorded for the $CCl_4$ soln on a Varian EM 360 spectrometer with TMS as an internal standard. IR spectra were determined using a Shimadzu IR-27 spectrophotometer. Mass spectra were obtained using a Hitachi RMS-4 mass spectrometer with a nominal ionizing energy of 70 eV. Analytical glc was accomplished on a shimadzu GC-4BPT using 3 mm × 1.5 m columns [10% HVSG or 10% PEG 20M on Chromosorb W-AW (80–100 mesh)]; preparative work was conducted on a Varian associate Model 920 using a 6 mm × 1 m column [10% PEG 20M on Chromosorb W-AW (80–100 mesh)]. Elemental analyses were carried out at the Elemental Analyses Center of Kyoto University.

o-*Allylphenol* **1b** and o-*propenylphenol* **12** were prepared by reported methods.[15]

m-*Allylphenol* **2b**. A soln of 1.00 g of *m*-allylanisole,[16] 6 ml of dry 2,4,6-collidine, and 2.36 g of LiI (dried at 300° under $N_2$) was heated to reflux under $N_2$ for 19 hr.[17] After the mixture was acidified with HCl aq and extracted with $Et_2O$. The extract was washed with water, dried over $Na_2SO_4$, and evaporated. The crude product was purified by preparative glc, which gave 550 mg of **2b**;[18] NMR: $\delta$ 3.38 (d, 2H, $CH_2$), 3.65 (s, 1H, OH), 4.95 (m, 2H, $CH_2$=), 5.5–6.3 (m, 1H, CH=) and 6.4–7.3 (m, 4H, ArH); MS: *m/e* 134 ($M^+$, 100%).

p-*Allylphenol* **3b**. To a cooled soln of 3.3 g of Na in 50 ml abs. MeOH, 24.8 g of *p*-bromophenol in 100 ml MeOH was added. The temp. of the soln was maintained at 0° while 12.5 g of chloromethyl methyl ether was added dropwise under $N_2$. The successive addition of 3.3 g of Na and 12.5 g chloromethyl methyl ether was carried out in the manner described above. The resulting soln was stirred overnight at room temp. The precipitated NaCl was filtered off and the solvent was evaporated *in vacuo*. The residue, dissolved in ether, was washed with 10% NaOH aq, dried ($Na_2SO_4$), and evaporated. Distillation gave 20.0 g *p*-bromophenyl methoxymethyl ether, b.p. 114–115° (25 mm).

A soln of 10 g of the above ether in 20 ml dry THF was added dropwise to 1.35 g Mg and 5 ml THF at such a rate as to maintain gentle reflux. After 2 hr reflux, 13 g allyl bromide in 10 ml THF was added and refluxed for 2 hr. After cooling, ice-water was added. Extraction with $Et_2O$ and drying followed by distillation gave 6.7 g of *p*-allylphenyl methoxymethyl ether, b.p. 92–114° (18 mm).

To a soln of 2.0 g of the above ether in 15 ml AcOH, a soln of 0.1 ml conc $H_2SO_4$ in 25 ml water was added and refluxed for 5 min. The mixture was extracted with $Et_2O$. The extract was washed with 5% NaOH aq and acidified with 5% HCl aq. Extraction with $Et_2O$, drying and solvent removal gave 1.1 g (38% based on *p*-bromophenol) of **3b** after distillation;[19] NMR: $\delta$ 3.27 (d, 2H, $CH_2$), 5.0 (m, 2H, =$CH_2$), 5.30 (bs, 1H, OH), 5.5–6.3 (m, 1H, =CH) and 6.83 (AA'BB', 4H, ArH).

*General procedure for the photoreaction.* Each soln of allylphenoxides in MeOH was prepared from allylphenols and equimolar NaOMe in MeOH. The respective soln was flushed with $N_2$ for at least 30 min prior to irradiation. Irradiation was carried out using a 350-W high-pressure Hg lamp through quartz filter. After irradiation the soln was neutralized with AcOH and concentrated under reduced pressure. The residue was taken up in $Et_2O$, washed with water, dried ($Na_2SO_4$), and concentrated. The crude products were separated by preparative glc.

A neutral soln of allylphenol was also irradiated and the mixture was treated similarly.

*Phororeaction of* o-*allylphenoxide anion* **1a**. A soln of **1a** (4.24 mmol) in MeOH (40 ml) was irradiated for 40 hr (conv. 100%) and acidified with AcOH and extracted with $Et_2O$ to give 522 mg of crude products. Glc analysis showed that the mixture consisted of **4**, **5**, **6a**, **7a**, and a mixture of unidentified products in thre ratio of 13:9:24:38:16. The products were purified by preparative glc. 2-Methylcoumaran **4** was identical in all respects with an authentic sample.[6] Chroman **5**: IR, NMR, and mass spectral data were identical with those reported.[6] *o*-Propylphenol **6a**: see Ref. 20. *o*-(2-Methoxypropyl)phenol **7a**; NMR: $\delta$ 1.21 (d, 3H, $CH_3$), 2.77 (d, 2H, $C\underline{H}_2CH_3$), 3.43 (s, 3H, $OCH_3$), 3.68 (m, 1H, CH), 6.5–7.3 (m, 4H, ArH); MS: *m/e* 166 ($M^+$, 19%) and 59 ($CH_3CH^+OCH_3$, 100%); IR (film): 3300 $cm^{-1}$. (Found: C, 72.37; H, 8.43. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%).

*Photoreaction of* o-*allylphenol* **1b**. A soln of **1b** (400 mg) in MeOH (40 ml) was irradiated for 200 hr. Evaporation of the solvent followed by short-path distillation gave 376 mg of a mixture. Glc analysis showed that the mixture was composed of **4**, **5**, **7a** and **8a** in the ratio of 24:2:25:49, along with the strating material **1b** (conversion 63%). *o*-Cyclopropylphenol **8a**; NMR: $\delta$ 0.4–1.1 (m, 4H, $CH_2$), 1.5–2.1 (m, 1H, CH), and 6.5–7.2 (m, 4H, ArH); MS: *m/e* 134 ($M^+$, 100%).[21]

*Photoreaction of* m-*allylphenoxide anion* **2a**. A soln of **2a** (5.43 mmol) in MeOH (60 ml) was irradiated for 90 hr (conv. 100%). The soln was acidified with AcOH and extracted with $Et_2O$ to give 578 mg of crude products. Glc analysis showed the mixture to consist of **9a**, **9b**, **10b**, **6b** and **7b** in the ratio of 15:4:8:20:53. Pure products were obtained by preparative glc. 4- and 5-Indanol **9a** and **9b** and *m*-isopropylphenol **10**: see Ref. [20] *m*-Propylphenol **6b**: NMR $\delta$ 0.95 (t, 3H, $CH_3$), 1.53 (m, 2H, $C\underline{H}_2CH_3$), 2.50 (t, 2H, $PHC\underline{H}_2$) and 6.2–7.3 (m, 4H, ArH); MS: *m/e* 136 ($M^+$, 49%), 107 ($M^+$-$CH_2CH_3$, 100%).[22] *m*-(2-Methoxypropyl)phenol **7b**; NMR: $\delta$ 1.10 (d, 3H, $CH_3$), 2.64 (m, 2H, $CH_2$), 3.30 (s, 3H, $OCH_3$), 3.40 (m, 1H, CH) and 6.4–7.2 (m, 4H, ArH); MS: *m/e* 166 ($M^+$, 32%) and 59 ($CH_3CH^+OCH_3$, 100%); IR (film): 3300 and 1075 $cm^{-1}$. (Found: C, 72.00; H, 8.42. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%).

*Photoreaction of* m-*allylphenol* **2b**. A soln of **2b** (147 mg) in MeOH (30 ml) was irradiated for 115 hr. Evaporation of the solvent followed by short-path distillation gave 133 mg of a mixture. Glc analysis showed that the mixture contained **6b**, **7b** and **8b** in the ratio of 9:11:80, in addition to the starting **2b** (conv. 53%). *m*-Cyclopropylphenol **8b**; NMR: $\delta$ 0.3–1.1 (m, 4H, $CH_2$), 1.5–2.0 (m, 1H, CH), and 6.3–7.2 (m, 4H, ArH); MS: *m/e* 134 ($M^+$, 100%) and 133 (99%).[23]

*Photoreaction o* p-*allylphenoxide anion* **3a**. A soln of **3a** (5.43 mmol) in MeOH (60 ml) was irradiated for 86 hr. The soln was acidified with AcOH and extracted with $Et_2O$ to give 578 mg of crude products. Glc analysis showed that the mixture contained **11**, **10c**, **6c**, **7c**, and unidentified minor products in the ratio of 64:7:13:7:9, along with small amount of **3b** (conv. 97%). *p*-Methoxymethyphenol **11**; NMR: $\delta$ 3.30 (s, 3H, $CH_3$), 4.30 (s, 2H, $CH_2$), and 6.80 (AA'BB', 4H, ArH); MS: *m/e* 138 ($M^+$; 54%) and 107 ($M^+$-$OCH_3$, 100%); IR (film): 3300 $cm^{-1}$. (Found: C, 69.36; H, 7.28. $C_8H_{10}O_2$ requires: C, 69.54; H, 7.30%). *p*-Propylphenol **6c** and *p*-isopropylphenol **10c**; see Ref. 20. *p*-(2-Methoxypropyl)phenol **7c**; NMR: $\delta$ 1.10 (d, 3H, $CH_3$), 2.26 (m, 2H, $CH_2$), 3.30 (m, 1H, CH), 7.80 (AA'BB', 4H, ArH); MS: *m/e* 166 ($M^+$, 6%) and 59 ($CH_3CH^+OCH_3$, 100%); IR (film): 3300 $cm^{-1}$. (Found: C, 72.19; H, 8.46. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%).

*Photoreaction of* p-*allylphenol* **3b**. A soln of **3b** (212 mg) in MeOH (40 ml) was irradiated for 92 hr. Evaporation of the solvent followed by short-path distillation gave 207 mg of a mixture. Glc analysis showed that the mixture contained only **8c** in addition to the starting material (conv. 35%). *p*-Cyclopropylphenol **8c**; m.p. 68–72° (lit.[23] 65–66°); NMR: $\delta$ 0.3–1.1 (m, 4H, $CH_2$), 1.5–2.0 (m, 1H, CH), 6.80 (AA'BB', 4H, ArH); MS: *m/e* 134 ($M^+$, 100%) and 133 (91%).

*Photoreaction of* o-*propenylphenoxide anion* **12**. A soln of **12** (3.82 mmol) in MeOH (40 ml) was irradiated for 16 hr. The soln was acidified with AcOH and extracted with $Et_2O$. Short-path distillation of the crude product gave 365 mg (58%) of *o*-(1-methoxypropyl)phenol **13**; b.p. 113–116° (bath)/22 mm; NMR: $\delta$ 0.91 (t, 3H, $CH_3$), 1.76 (m, 2H, $CH_2$), 3.36 (s, 3H, $OCH_3$), 4.07 (t, 1H, CH), 6.5–7.2 (m, 4H, ArH); MS: $m/e$ 166 ($M^+$, 30%), 137 ($M^+$-$CH_2CH_3$, 100%), and 134 ($M^+$-$CH_3OH$, 80%); IR (film): 3350 $cm^{-1}$. (Found: C, 72.11; H, 8.54. $C_{10}H_{14}O_2$ requires: C, 72.26; H, 8.49%).

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