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Notes

Chemical Evidence for Intramolecular Proton, Electron, and Energy Transfer in the Photochemistry of *o*-Allylphenol Derivatives

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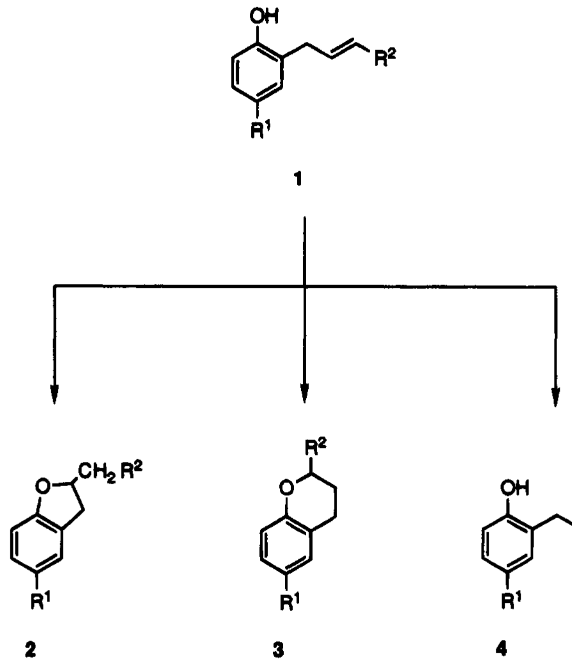
Introduction

The photochemistry of *o*-allylphenol (**1a**) and its derivatives has been extensively investigated.[1−10] In general, photocyclization to dihydrobenzofurans **2** and dihydrobenzopyrans **3** has been explained through intramolecular proton transfer from the excited phenol to the ground state olefin. However, an alternative mechanistic pathway might involve excited state electron transfer within the same donor−acceptor pair.[9] In this work, chemical evidence is provided for both mechanisms using suitably substituted cinnamylphenols (**1c**,**d**). Moreover, energy transfer is shown to take place in **1e** from the triplet phenol to the styrenic moiety. Processes of this type in bichromophoric *o*-allylphenol derivatives are unprecedented.

Results and Discussion

The required substrates **1c**−**e** were prepared by treatment of the corresponding phenols with cinnamyl chloride in a strong basic medium.[11] Irradiation experiments were carried out under an inert atmosphere in benzene or acetone solutions, using a Pyrex filter, since preliminary photolysis experiments with a shorter wavelength resulted in extensive degradation of these compounds. The results are presented in Table 1, together with those previously reported for the parent cinnamylphenol **1b**.[12]



a $R^1 = R^2 = H$
b $R^1 = H, R^2 = Ph$
c $R^1 = R^2 = Ph$
d $R^1 = OMe, R^2 = Ph$
e $R^1 = COMe, R^2 = Ph$

When the biphenyl derivative **1c** was irradiated using benzene as solvent, a mixture of the cyclization products **2c** and **3c** was obtained, together with the *cis* isomer **4c** (Table 1, entry 2). The ratio **2**/**3** was found to be 0.5, markedly lower than the value (1.5) obtained for the parent cinnamylphenol **1b** (Table 1, entry 1). This observation agrees with the involvement of the phenolic singlet in the formation of the five-membered ring products **2** since the population of this state is expected to be quantitatively less important in the case of the biphenyl derivative **1c**, owing to deactivation by intersystem crossing to the noncyclizing phenolic triplet.[13,14] Products **3c** and **4c** should arise from the styrenic excited states (singlet and triplet, respectively), and accordingly, the **3c**/**4c** ratio is not significantly affected by this structural change in the phenolic moiety. Further support in favor of this rationalization was obtained by the acetone-sensitized photolysis of **1c**, which resulted exclusively in *trans* to *cis* photoisomerization (Table 1, entry 3). A point of special interest was to determine whether excited state proton transfer was involved in the photocyclization of **1c** to the dihydrobenzofuran **2c** and/or the dihydrobenzopyran **3c**. This was achieved by adding 2

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(13) The singlet energies of *p*-phenylphenol,[14a] *p*-methoxyphenol,[14b] *p*-acetylphenol,[14c] and styrene[14d] are 91.5, 92.8, 82.6, and 98.2 kcal/mol, respectively. The triplet energies of *p*-phenylphenol,[14a] *p*-acetylphenol,[14c] and styrene[14d] are 63.6, 72.3, and 61.7 kcal/mol, respectively. The triplet energy of *p*-methoxyphenol is *ca.* 80 kcal/mol.[14e,f] The intersystem crossing quantum yield of biphenyl[14d] is 0.81. The phosphorescence quantum yield of *p*-acetylphenol[14d] is 0.55.

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Table 1. Irradiation of Cinnamylphenol Derivatives

entry	substrate	solvent	conversion (%)	product distribution (%) 2	3	4
1	**1b**	benzene	80	45	30	25
2	**1c**	benzene	100	20	40	40
3	**1c**	acetone	60	–	–	100
4	**1c**	benzene/dioxane	53	11	29	60
5	**1d**	benzene	94	10	86	4
6	**1d**	benzene/dioxane	96	5	90	5
7	**1d**	acetone	63	–	–	100
8	**1e**	benzene	47	–	–	100

M dioxane to the reaction media, which was found to quench the formation of both products (Table 1, entry 4).

The photochemical behavior of the related cinnamylphenol **1d**,[15] posessing an electron-donating methoxy substituent, was markedly different. Irradiation of this compound in benzene led to the six-membered ring product **3d**.[16] Only minor amounts of **2d** and **4d** were obtained in this case (Table 1, entry 5). In view of the lower oxidation potential of the phenolic nucleus in **1d**,[17] the preferred cyclization to **3d** must be associated with the operation of an excited state electron transfer mechanism. In fact, when the styrene radical anion is generated by intermolecular electron transfer from tertiary amines to **1b**, cyclization to dihydrobenzopyran **3b** is also the only observed process.[12] Hence, the photochemical conversion of **1d** into **3d** does not appear to involve the usual excited state proton transfer process. An unambiguous confirmation of this idea was obtained by performing the irradiation of **1d** in the presence of 2 M dioxane. By contrast with the results obtained in the experiments with the biphenyl derivative **1c**, no quenching associated with intermolecular proton transfer was observed for **3d** formation (Table 1, entry 6). Taking into account the oxidation potentials and the excitation energies of *p*-methoxyphenol and styrene,[13,14,17] the Rehm–Weller equation[18] predicts that electron transfer would be thermodynamically allowed upon excitation of either the donor or the acceptor substructures of **1d**.[19] This would explain the parallel decrease observed for both **2d** and **4d** yields, as compared with the unsubstituted compound **1b**.

The possible participation of the styrene triplet[19] in this process was safely ruled out in view of the lack of **3d** formation upon acetone-sensitized photolysis of **1d** (Table 1, entry 7), which led exclusively to the *cis* isomer **4d**. Thus, the phenolic and styrenic singlets must be the excited states involved in intramolecular electron transfer.

Finally, the acetyl derivative **1e** was irradiated as a model for favored intersystem crossing in the phenolic chromophore.[13,14] The result of this experiment is presented in Table 1 (entry 8). As photocyclization to the five-membered ring product **2e** should take place *via* the phenolic singlet, an efficient deactivation of this state to the corresponding triplet would result in a substantial decrease of **2e** yield. In fact, not even traces of this photoproduct were found in the reaction mixture. On the other hand, it was anticipated that intramolecular triplet–triplet energy transfer might contribute to enhancing the formation of the *cis* isomer **4e**. Actually, this was found to be the case. It is noteworthy that photocyclization to **3e**, which should involve the excited styrenic singlet, was not detected. In the parent cinnamylphenol **1b**, this process occurs, in competition with intersystem crossing to the styrenic triplet, which is responsible for *trans–cis* isomerization (Table 1, entry 1). This is compatible with the reported excited state energies of *p*-acetylphenol.[14c]

Experimental Section

Melting points were determined with a Büchi 510 apparatus and are uncorrected. IR spectra were obtained with a GC-FTIR Hewlett-Packard 5965 spectrophotometer; ν_{max} (cm^{-1}) is given for the main absorption bands. ^{1}H NMR spectra were measured in CDCl$_3$ with a 400-MHz Varian VXR-400 S instrument; chemical shifts are reported in δ (ppm) values, using TMS as the internal standard. Mass spectra were obtained under electron impact using a Hewlett-Packard 5988 A spectrometer; the ratios *m/z* and the relative intensities are reported. Combustion analyses were performed at the Instituto de Química Bio-Orgánica of the CSIC in Barcelona. Isolation and purification were done by conventional column chromatography on silica gel Merck 60 (0.063–0.200 mm), by preparative layer chromatography on silica gel Merck 60 PF$_{254}$, using methylene chloride or mixtures of hexane/methylene chloride as eluent, or by means of isocratic HPLC equipment provided with a semipreparative microporasil column, using hexane/ethyl acetate as eluent.

General Irradiation Procedures. Solutions of 0.02 g of the substrates in 20 mL of the indicated solvents were placed into Pyrex tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium-pressure Hg lamp and irradiated for 1 h. The reaction mixtures were analyzed by GC and GC–MS.

Preparation of Compounds 1c–e. The sodium salt obtained from 40.0 mmol of *p*-phenyl-, *p*-methoxy-, or *p*-acetylphenol was added to *trans*-cinnamyl chloride (6.10 g, 40.0 mmol) in 100 mL of benzene. After the mixture was refluxed for 5 h (12 h in the case of **1e**), the solvent was distilled and the residue was treated with 100 mL of Claisen's alkali (35.00 g of potassium hydroxide in 25 mL of water and methanol up to 100 mL). The alkaline solution was washed with hexane, acidified with HCl, and extracted with methylene chloride. Evaporation of the solvent gave a residue which was submitted to column chromatography.

***trans*-2-Cinnamyl-4-phenylphenol (1c)** (40%): mp 127–128 °C; FTIR 3651 (OH), 3576 (OH), 3070, 3034, 1603, 1487, 1259, 1196, 1103, 966, 759, 697; ^{1}H NMR 7.58–7.18 (m, 12H, Ar*H*), 6.89 (d, *J* = 8 Hz, 1H, 6-Ar*H*), 6.56 (d, *J* = 16 Hz, 1H, CH$_2$CH=C*H*), 6.43 (dt, J_1 = 16 Hz, J_2 = 6 Hz, 1H, CH$_2$C*H*=CH), 4.98 (s, 1H, O*H*), 3.63 (d, *J* = 6 Hz, 2H, C*H*$_2$); MS 286 (M$^+$, 94), 207 (18), 195 (45), 194 (25), 182 (100), 181 (37), 167 (44), 165 (37), 154 (52), 153 (48), 115 (40), 91 (44). Anal. Calcd for C$_{21}$H$_{18}$O: C, 88.08; H, 6.34. Found: C, 88.07; H, 6.35.

***trans*-2-Cinnamyl-4-methoxyphenol (1d)**[15] (60%): FTIR 3656 (OH), 3585 (OH), 3070, 3032, 1601, 1500, 1232, 1173, 1044, 965; ^{1}H NMR 7.40–7.18 (m, 5H, C$_6$*H*$_5$), 6.84–6.66 (m, 3H, Ar*H*), 6.51 (d, *J* = 16 Hz, 1H, CH$_2$CH=C*H*), 6.28 (dt, J_1 = 16 Hz, J_2 = 6 Hz, 1H, CH$_2$C*H*=CH), 5.30 (s, 1H, O*H*), 3.77 (s, 3H, OC*H*$_3$), 3.54 (d, *J* = 6 Hz, 2H, C*H*$_2$); MS 240 (M$^+$, 54), 209 (4), 149 (31), 136 (100), 121 (18), 115 (22), 108 (34), 91 (50), 65 (15).

***trans*-4-Acetyl-2-cinnamylphenol (1e)** (30%): mp 135–137 °C; FTIR 3646 (OH), 3556 (OH), 3071, 3033, 1701 (C=O), 1601, 1498, 1360, 1270, 1197, 1108, 965; ^{1}H NMR 7.81 (d, *J* = 2 Hz, 1H, 3-Ar*H*), 7.76 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H, 5-Ar*H*), 7.35–7.10 (m, 5H, C$_6$*H*$_5$), 6.86 (d, *J* = 8 Hz, 6-Ar*H*), 6.42 (m, 2H, C*H*=C*H*), 4.90 (s, 1H, O*H*), 3.52 (d, *J* = 5 Hz, C*H*$_2$), 2.50 (s, 3H,

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[17] The oxidation potential of *p*-methoxyphenol is 0.4 V *vs* SCE. The reduction potential of styrene is −2.4 V *vs* SCE. These data can be found: Siegerman, H. Oxidation and Reduction Half-wave Potentials of Organic Compounds. In *Techniques of Chemistry: Technique of Electroorganic Synthesis*; Weinberg, N. L., Ed.; John Wiley & Sons: New York, 1975; Vol. 5, Part 2, pp 667–1056.

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[19] The values estimated for ΔG_{FIS} involving the phenolic or styrenic singlet excited states are about −28 or −33 kcal/mol, respectively. By contrast, the analogous process involving the styrenic triplet would give a ΔG_{FIS} value of about +4 kcal/mol.

COCH_3); MS 252 (M^+, 56), 237 (86), 209 (83), 133 (86), 131 (24), 115 (49), 104 (47), 91 (100), 77 (47), 43 (38). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.02; H, 6.39.

2-Benzyl-5-phenyl-2,3-dihydrobenzofuran (2c): oil; FTIR 3071, 3037, 2957, 1607, 1481, 1285, 1231, 1114, 983, 750, 699; ^{1}H NMR 7.58–7.26 (m, 12H, Ar-*H*), 6.87 (d, *J* = 8 Hz, 1H, 7-Ar*H*), 5.09 (m, 1H, C*H*), 3.27 (m, 2H, CH_2), 3.01 (m, 2H, CH_2); MS 286 (M^+, 70), 195 (100), 194 (48), 167 (92), 165 (64), 152 (42), 115 (18), 91 (30), 77 (8). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.83; H, 6.43.

2-Benzyl-5-methoxy-2,3-dihydrobenzofuran (2d): oil; FTIR 3073, 3036, 2948, 1604, 1488, 1204, 1137, 1033, 986, 744; ^{1}H NMR: 7.44–7.22 (m, 5H, C_6H_5), 6.76–6.64 (m, 3H, Ar*H*), 5.00 (m, 1H, C*H*), 3.75 (s, 3H, OCH_3), 3.17 (m, 2H, CH_2), 2.93 (m, 2H, CH_2); MS 240 (M^+, 56), 209 (2), 149 (100), 136 (29), 121 (49), 108 (14), 91 (58), 78 (17), 77 (16), 65 (17). Exact mass calcd for $C_{16}H_{16}O_2$ 240.1150. Found: 240.1150.

2,6-Diphenyl-3,4-dihydro-2*H*-benzopyran (3c): mp: 127–128 °C; FTIR 3071, 2960, 1585, 1485, 1299, 1272, 1238, 1126, 1071, 755, 698; ^{1}H NMR: 7.58–7.22 (m, 12H, Ar*H*), 6.99 (d, *J* = 9 Hz, 1H, 8-Ar*H*), 5.10 (d, *J* = 10 Hz, 1H, C*H*), 2.95 (m, 2H, CH_2CH_2CH), 2.18 (m, 2H, CH_2CH_2CH); MS 286 (M^+, 86), 195 (46), 182 (100), 181 (41), 167 (39), 165 (29), 154 (61), 153 (67), 152 (49), 115 (24), 91 (21). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H 6.34. Found: C, 88.08; H, 6.33.

6-Methoxy-2-phenyl-3,4-dihydro-2*H*-benzopyran (3d):[15] FTIR 3072, 3038, 2944, 1607, 1496, 1432, 1268, 1221, 1051; ^{1}H NMR 7.44–7.28 (m, 5H, C_6H_5), 6.84 (d, *J* = 9 Hz, 1H, 8-Ar*H*), 6.71 (dd, J_1 = 9 Hz, J_2 = 3 Hz, 1H, 7-Ar*H*), 6.63 (d, *J* = 3 Hz, 1H, 5-Ar*H*), 4.99 (dd, J_1 = 10 Hz, J_2 = 2 Hz, 1H, C*H*), 3.76 (s, 3H, OCH_3), 2.85 (m, 2H, CH_2CH_2CH), 2.18 (m, 2H, CH_2CH_2CH); MS 240 (M^+, 52), 149 (28), 136 (100), 108 (33), 91 (28), 78 (23), 77 (17), 65 (22).

***cis*-2-Cinnamyl-4-phenylphenol (4c):** oil; FTIR 3650 (OH), 3592 (OH), 3069, 3030, 1603, 1487, 1259, 1192, 1102, 759, 699; ^{1}H NMR 7.56–7.20 (m, 12H, Ar*H*), 6.85 (d, *J* = 8 Hz, 1H, 6-Ar*H*), 6.68 (d, *J* = 12 Hz, 1H, $CH_2CH{=}CH$), 5.88 (dt, J_1 = 12 Hz, J_2 = 7 Hz, 1H, $CH_2CH{=}CH$), 4.85 (s, 1H, O*H*), 3.72 (d, *J* = 7 Hz, 2H, CH_2); MS 286 (M^+, 80), 207 (13), 195 (41), 194 (23), 182 (100), 181 (39), 167 (44), 165 (38), 154 (55), 153 (45), 115 (40), 91 (42). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.12; H, 6.36.

***cis*-2-Cinnamyl-4-methoxyphenol (4d):** mp 68–69 °C; FTIR 3656 (OH), 3599 (OH), 3070, 3027, 1604, 1500, 1431, 1286, 1232, 1174, 1046, 807, 758, 701; ^{1}H NMR 7.40–7.20 (m, 5H, C_6H_5), 6.76–6.58 (m, 4H, Ar*H* + $CH_2CH{=}CH$), 5.81 (dt, J_1 = 12 Hz, J_2 = 7 Hz, 1H, $CH_2CH{=}CH$), 4.52 (s, 1H, O*H*), 3.75 (s, 3H, OCH_3), 3.63 (d, *J* = 7 Hz, 2H, CH_2); MS 240 (M^+, 57), 209 (4), 149 (32), 136 (100), 121 (17), 115 (20), 108 (31), 91 (45), 65 (13). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.92; H, 6.66.

***cis*-4-Acetyl-2-cinnamylphenol (4e):** oil; FTIR 3645 (OH), 3581 (OH), 3069, 3026, 1700 (C=O), 1602, 1498, 1360, 1270, 1194, 1107, 816, 759, 701; ^{1}H NMR 7.76 (m, 2H, 3,5-Ar*H*), 7.50–7.15 (m, 5H, C_6H_5), 6.85 (d, *J* = 9 Hz, 1H, 6-Ar*H*), 6.60 (d, *J* = 12 Hz, 1H, $CH_2CH{=}CH$), 5.88 (dt, J_1 = 12 Hz, J_2 = 7 Hz, 1H, $CH_2CH{=}CH$), 3.62 (d, *J* = 7 Hz, 2H, CH_2), 2.48 (s, 3H, COCH_3); MS 252 (M^+, 53), 237 (94), 209 (99), 133 (99), 131 (28), 115 (52), 104 (47), 91 (100), 77 (51), 43 (41). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.46; H, 6.39.

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