J. Org. Chem. 1994, 59, 197-202

Photochemistry of Allylphenol Derivatives. Role of the Phenolic and Styrenic Excited States in the Behavior of Bichromophoric Cinnamylphenol

M. Consuelo Jiménez, Francisco Márquez, Miguel A. Miranda,* and Rosa Tormos

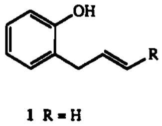
Departamento de Química/Instituto de Tecnología Química UPV-CSIC, Universidad Politécnica de Valencia, Camino de Vera s/n, Apartado 22012, E-46071-Valencia, Spain

Received October 22, 1993•

Irradiation of *trans*-2-cinnamylphenol (**2a**) in hexane, under argon, led to the *cis* isomer **2b**, 2-benzyl-2,3-dihyrobenzofuran (**3**), and 2-phenyl-3,4-dihydro-2*H*-benzopyran (**4**). The presence of oxygen produced a marked decrease of the **2b** yield, with a parallel enhancement of the pathway leading to **3** and **4**. In benzene, the cyclization process was enhanced, together with the **3**:**4** ratio. The latter was less favored in the presence of photosensitizers with lower singlet energies, such as toluene, methyl benzoate, or *p*-dichlorobenzene. In the acetone-photosensitized reaction, a clean and efficient isomerization to **2b** took place. These results, together with CNDO/S calculations, suggested involvement of the phenolic or the styrenic singlets in the cyclization to **3** or **4**, respectively, and the styrenic triplet (partially quenched by oxygen) in the double bond isomerization to **2b**. Addition of methanol to the benzene solutions of **2a** partially quenched the photocyclization. By contrast, the formation of **4** was markedly enhanced in the presence of trimethylamine or triethylamine, which were also efficient fluorescence quenchers. The above observations evidenced a new route to product **4** involving electron transfer from the tertiary amine to excited *trans*-2-cinnamylphenol (**2a**). The key step in the photocyclization must be intramolecular excited-state proton transfer (ESPT) and appears to involve π-complexes of the type **I**, **IIa**, and **IIb**. Accordingly, direct irradiation of the *o*-acetyl derivative **9a** resulted exclusively in isomerization to **9b**, owing to chelation of the hydroxy group, which should prevent formation of the π-complexes and facilitate deactivation of the phenolic singlet, *via* intramolecular proton exchange.

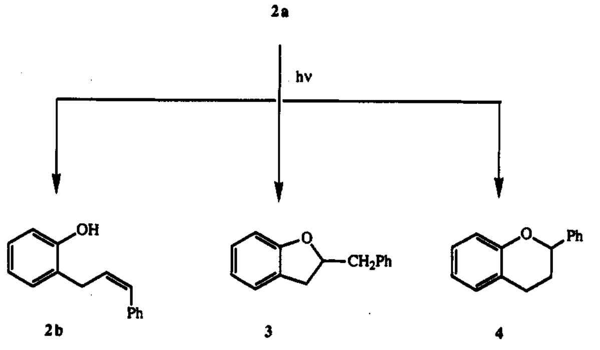
Introduction

A number of reports have appeared in the last 25 years on the photocyclization of allylphenol (**1**) and related compounds, due to the intriguing mechanistic aspects of this reaction.[1-9] According to the excited-state proton transfer (ESPT) model, the process takes place *via* intramolecular protonation of the ground-state olefin by the first excited singlet of phenol, which is the absorbing chromophore, followed by thermal cyclization of the resulting zwitterion. Intersystem crossing does not compete efficiently with ESPT from the phenolic singlet, thus preventing the photocyclization pathway involving protonation of the olefin triplet by ground-state phenol.[3]



1 R = H
2a R = Ph

With this background, we decided to examine the photochemistry of *trans*-2-cinnamylphenol (**2a**), a previously described compound[10] where the allylic double bond is part of a styrene chromophore. Extended conjugation of the latter might in principle allow an easy access to the olefin excited states upon direct irradiation, in competition with the usual excitation of the phenolic portion. Our results show that the only process occurring from the styrenic T_1 is E/Z isomerization. By contrast, photocyclization to **3** or **4** occurs from the phenolic or the styrenic singlets, respectively, through different intramolecular π-complexes. The relative ratios of the five- *versus* six-membered ring product are strongly dependent upon the reaction conditions and can be controlled by selective sensitization and/or quenching.



Results and Discussion

Irradiation of *trans*-2-cinnamylphenol (**2a**) was carried out under a variety of conditions. The results are

---

• Abstract published in *Advance ACS Abstracts*, December 1, 1993.

(1) Horspool, W. M.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1967**, 195-196.

(2) Fráter, G.; Schmid, H. *Helv. Chim. Acta* **1967**, *50*, 255-262.

(3) Kropp, P. J.; Krauss, H. J. *J. Am. Chem. Soc.* **1969**, *91*, 7466-7474.

(4) Shani, A.; Mechoulam, R. *Tetrahedron* **1971**, *27*, 601-606.

(5) Houri, S.; Geresh, S.; Shani, A. *Isr. J. Chem.* **1973**, *11*, 805-818.

(6) Geresh, S.; Levy, O.; Markovits, Y.; Shani, A. *Tetrahedron* **1975**, *31*, 2803-2807.

(7) Kitamura, T.; Imagawa, T.; Kawanisi, M. *Tetrahedron* **1978**, *34*, 3451-3457.

(8) Chow, Y. L.; Zhou, X.-M.; Gaitan, T. J.; Wu, Z.-Z. *J. Am. Chem. Soc.* **1989**, *111*, 3813-3818.

(9) Morrison, H. *Org. Photochem.* **1979**, *4*, 143-188.

(10) Tarbell, D. S. The Claisen Rearrangement. In *Organic Reactions*; Adams, R., Ed.; John Wiley and Sons: New York, 1944; Vol. 2, p 28.

0022-3263/94/1959-0197$04.50/0

Table 1. Irradiations of *trans*-2-Cinnamylphenol (2a)

entry	solvent	condns	conversion	products (yield, %) 2b	3	4
1	hexane	Ar, λ > 200 nm	64	48	22	30
2	hexane	O_2, λ > 200 nm	73	20	32	48
3	benzene	Ar, λ > 200 nm	80	25	45	30
4	benzene	O_2, λ > 200 nm	87	15	62	23
5	toluene	O_2, λ > 200 nm	75	17	48	35
6	hexane	O_2, λ > 200 nm, $PhCOOCH_3$	76	8	40	52
7	hexane	O_2, λ > 200 nm, *p*-$Cl_2C_6H_4$	87	21	26	53
8	acetone	Ar, λ > 300 nm	69	100		
9	acetone	O_2, λ > 300 nm	57	100		

summarized in Table 1. When hexane was used as solvent, the major photoproduct under inert atmosphere was the *cis* isomer **2b**, although cyclization to 2-benzyl-2,3-dihydrobenzofuran (**3**)[11] and 2-phenyl-3,4-dihydro-2*H*-benzopyran (**4**)[12] was also observed. The presence of oxygen produced a marked decrease of the **2b** yield, with a parallel enhancement of the pathway leading to **3** and **4**. This suggested the possible involvement of excited states of different multiplicity: the phenolic or the styrenic singlets in the cyclization and the styrenic triplet (partially quenched by oxygen) in the double bond isomerization.

To gain further insight into the mechanism of the above processes, we performed a series of photosensitization experiments. Thus, benzene was used as solvent to attempt an enhanced generation of the phenolic singlet.[13] This led to higher conversions, together with a marked predominance of the cyclization and an enhanced **3**:**4** ratio. The use of photosensitizers with lower singlet energies, such as toluene and, especially, methyl benzoate or *p*-dichlorobenzene, favored the formation of **4**, thus suggesting that a styrenic singlet is actually involved in the photocyclization to the six-membered ring product **4**.[13]

On the other hand, when the photolysis was carried out in acetone to provide an easy access to the styrenic triplet,[13] using a Pyrex filter to prevent direct absorption by this chromophore, the photocyclization was completely suppressed and instead a clean and efficient *trans*/*cis* isomerization to **2b** took place. The conversion was slightly higher under inert atmosphere, as could be expected for an excited triplet state.

On the basis of the above results, the photochemistry of *trans*-2-cinnamylphenol can be justified as follows. Photocyclization to **3** and **4** appears to be initiated by promotion of the ground-state π-complex **I** to the excited singlet states of the phenolic or the styrenic chromophores, respectively. The corresponding conformations of the excited-state complexes, which would justify the observed regioselectivities, are **IIa** and **IIb**. These species would decay rapidly to the zwitterions **IIIa** and **IIIb** to afford the corresponding cyclization products after intramolecular nucleophilic attack. It is worth mentioning that the ground-state association is in good agreement with the FTIR spectrum of **2a** in the gas phase (Figure 1), which shows two different absorptions in the region of the O–H stretching at 3651 and 3581 cm^{-1}. The former can be assigned to the free hydroxyl band, while the latter must correspond to the intramolecularly hydrogen-bonded group.

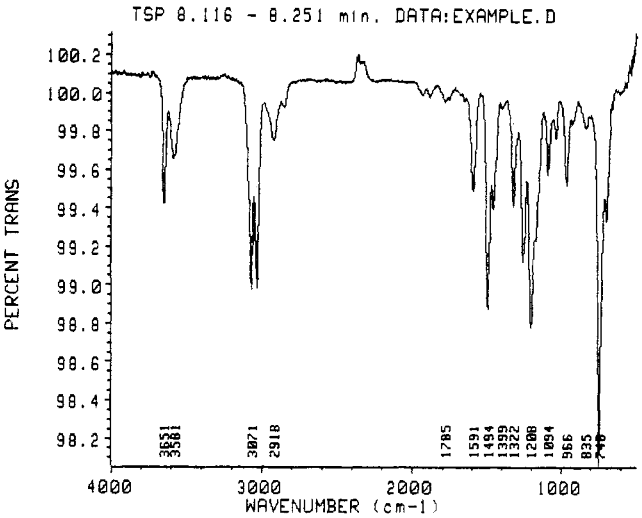
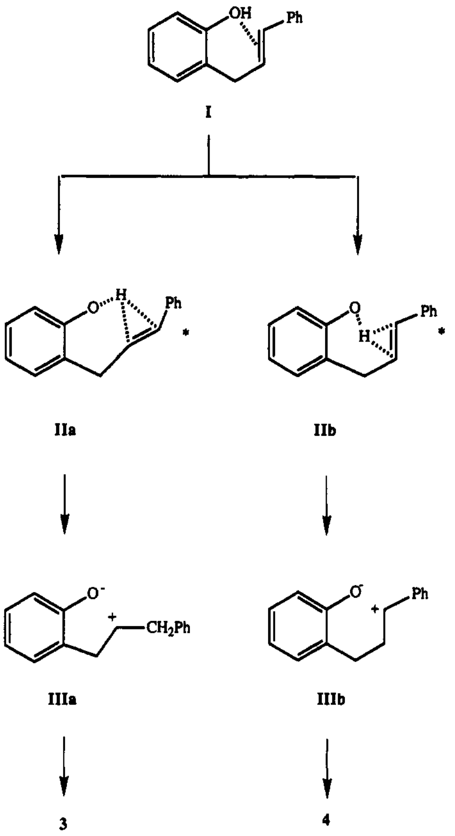


Figure 1. FTIR spectrum of **2a** in the gas phase, showing the O–H stretching bands corresponding to the free (3651 cm^{-1}) and intramolecularly hydrogen-bonded (3581 cm^{-1}) hydroxyl groups.



In view of the above rationalization, it was anticipated that bases capable of establishing hydrogen bonds with ground-state *trans*-2-cinnamylphenol might lead to chemical entities whose excitation would be followed by intermolecular proton transfer (static quenching).[8] Additionally, the bases could compete for the proton of excited-state π-complexes **IIa** or **IIb**, a process which would result in the formation of a noncyclizing species (dynamic quenching).[8] For this reason, the photochemistry of **2a** was examined in benzene containing variable

---

[11] Gripenberg, J.; Hase, T. *Acta Chem. Scand.* **1966**, *20*, 1561–1570.

[12] Yato, M.; Ohwada, T.; Shudo, K. *J. Am. Chem. Soc.* **1990**, *112*, 5341–5342.

[13] The singlet energies of benzene, phenol, toluene, methyl benzoate, *p*-dichlorobenzene, and styrene are 110, 103, 106, 102, 101, and 98 kcal/mol, respectively. The triplet energies of acetone and styrene are 80 and 62 kcal/mol, respectively. These data can be found in: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973.

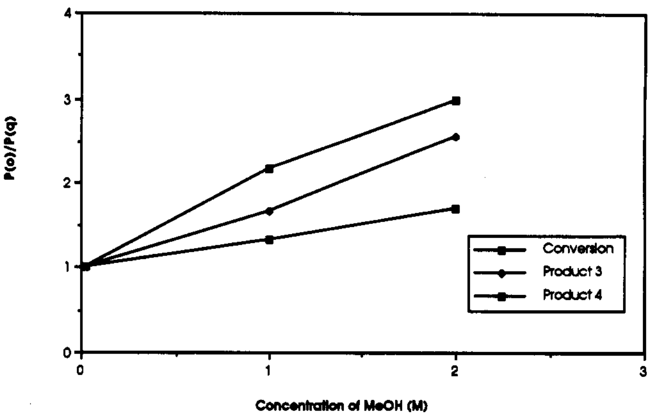


Figure 2. Quenching of the photocyclization of **2a** by methanol. The parameter $P(o)/P(q)$ is the ratio between the percentages (conversion or formation of **3** and **4**) in the absence and presence of quencher.

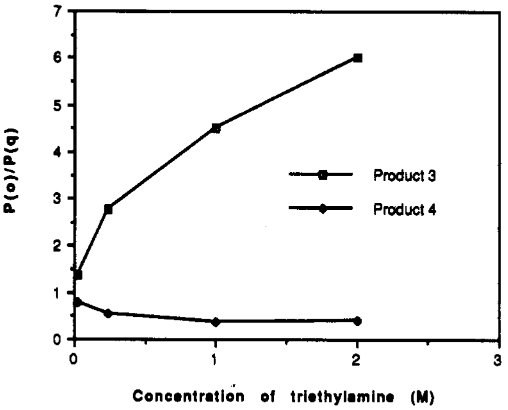
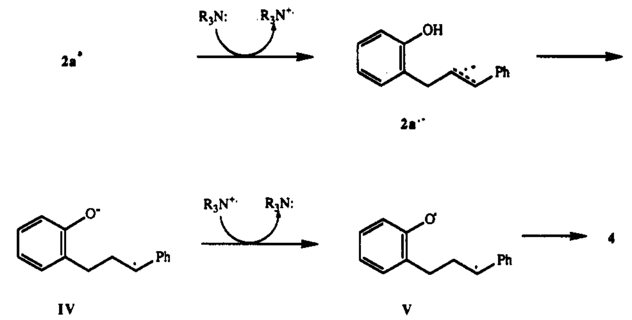


Figure 3. Influence of triethylamine (TEA) on the photocyclization of **2a**. The parameter $P(o)/P(q)$ is the ratio between the percentage yields of **3** and **4** in the absence and presence of TEA.

amounts of methanol, trimethylamine, and triethylamine. As expected, the percentages of cyclization products decreased with increasing concentrations of methanol, while the opposite was true for the amount of remaining **2a**. This effect was more pronounced in the case of the six-membered ring product **4**, probably due to the higher contribution of dynamic quenching (Figure 2).

By contrast, the photocyclization to **4** was markedly enhanced in the presence of trimethylamine, in apparent contradiction with the efficient quenching of the formation of **3** produced by this additive. The same trend was observed for triethylamine (Figure 3). These observations strongly suggested that the employed tertiary amines were making available a new route to product **4** involving an electron-transfer mechanism, which would be in agreement with the reported formation of radical ion pairs upon photochemical excitation of styrene/amine mixtures.[14,15] The resulting radical anion $\mathbf{2a}^{\bullet-}$ would undergo intramolecular proton transfer to afford intermediate **IV**. Subsequent back-electron transfer to the amine radical cation, followed by collapse of the diradical **V**, would lead to the six-membered ring product **4**.



This hypothesis is supported by thermodynamic factors. Application of the Rehm–Weller equation,[16] using the known values of $E_{D^{\bullet+}/D}$ for trimethylamine (0.76–0.98 V vs SCE)[17] or triethylamine (0.69–1.00 V vs SCE),[17] $E_{A/A^{\bullet-}}$ for styrene (between −2.34 and −2.45 V vs SCE),[17] and the above-mentioned E_S of styrene (98 kcal/mol), allowed us to estimate a ΔG_{FIS} of approximately −20 kcal/mol. According to the Marcus theory,[18] this parameter would be associated to a low activation barrier and hence to a favorable kinetic behavior. Thus, electron transfer must occur from the ground-state amine to the excited singlet state of styrene. By contrast, the analogous process involving the styrene triplet[13] does not fulfill the thermodynamic requirements, since the associated ΔG_{FIS} value would be about +15 kcal/mol.

A further piece of evidence in favor of the above rationalization was provided by the emission spectrum of **2a** in hexane, upon excitation at 250 nm (Figure 4). It consisted of one fluorescence band, having maxima at approximately 300 and 309 nm. The latter was slightly more intense. The excitation spectra of both emissions were identical to each other (data not shown) and similar to the absorption spectrum (Figure 5), which suggested a common ground-state precursor. Nevertheless, both fluorescence maxima cannot be justified as vibrational transitions because of the different behavior observed upon addition of triethylamine. Table 2 shows the decrease in the fluorescence quantum yield of **2a** (long wavelength region) with increasing amounts of quencher and also with higher temperatures. The most plausible explanation of these results appears to be that each fluorescence maximum is associated to a different chromophore of the molecule. This would agree with the experimental results and will be justified from a theoretical point of view. In this context, MO calculations must be preceded by a knowledge of the molecular geometry. No structural data on *trans*-2-cinnamylphenol (**2a**) are avalaible from the literature. Thus, the geometry of the isolated molecule has been approximated by finding the minimum stationary point on each potential energy hypersurface. This aspect was fully optimized using the PM3 semiempirical method,[19] which indicated that the planar conformation (Figure 6) is preferred in the ground state (S_0). The energy of excited singlet states was computed using the complete neglect of differential overlap/spectroscopic parameterization (CNDO/S) method.[20–23] The results (Table 3)

---

[14] Lewis, F. D. Carbon–Carbon Multiple Bonds. In *Photoinduced Electron Transfer, Part C, Photoinduced Electron Transfer Reactions: Organic Substrates*; Fox, M. A., and Chanon, M., Eds.; Elsevier: Amsterdam, 1988; pp 1–69.

[15] Mai, J. C.; Lin, Y. C.; Hseu, T. M.; Ho, T. I. *J. Photochem. Photobiol. A: Chem.* 1993, *71*, 237–243.

[16] Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, *8*, 259–271.

[17] 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 and Sons: New York, 1975; Vol. 5, Part 2, pp 667–1056.

[18] Marcus, R. A. *Ann. Rev. Phys. Chem.* 1964, *15*, 155–196.

[19] Stewart, J. J. P. *J. Comput. Chem.* 1989, *10*, 221–264.

[20] Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* 1968, *48*, 1807–1813.

[21] Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* 1968, *48*, 4050–4055.

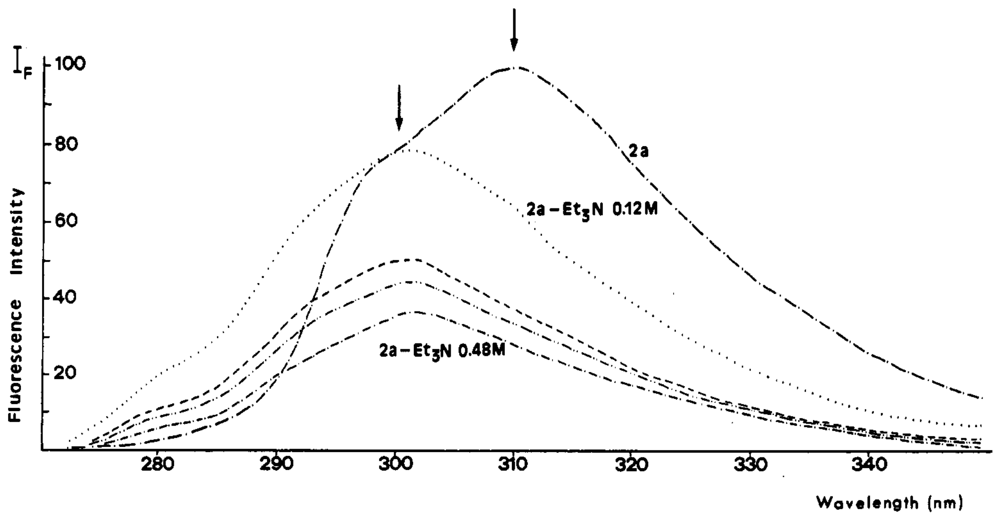


Figure 4. Fluorescence spectrum of **2a** in hexane (5 × 10^{-5} M) showing two maxima at 300 and 309 nm. The latter is more efficiently quenched by addition of increasing amounts of triethylamine (see Table 2).

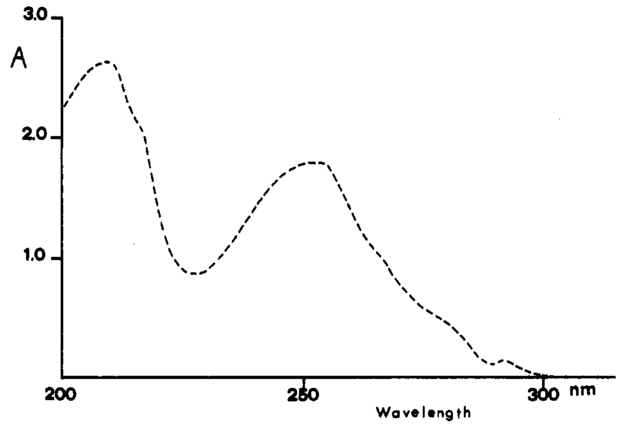


Figure 5. Absorption spectrum of **2a** in hexane (10^{-4} M).

Table 2. Fluorescence Quantum Yield Φ_F of 2a (309 nm) at Different Temperatures, in the Presence of Increasing Amounts of Triethylamine (TEA)

[TEA][a]	$T = 278$ K	$T = 293$ K	d$T = 308$ K
0	0.0140 (Φ_{F°)	0.0101 (Φ_{F°)	0.0091 (Φ_{F°)
0.12	0.0101	0.0081	0.0072
0.24	0.0082	0.0053	0.0050
0.36	0.0045	0.0040	0.0041
0.48	0.0028	0.0030	0.0030

[a] mol/L.

indicated that the styrenic chromophore is involved in the transition to the first and second singlet excited states, whereas the phenolic chromophore is involved in the transition to the third singlet excited state. Accordingly, the fluorescence maximum observed at 309 nm could be associated to the styrenic chromophore (by excitation to the S_1 and S_2 states), and the shoulder at 300 nm could be generated from the emission of the phenolic group (by excitation to the S_3 state).

Although intramolecular excited-state electron transfer (ESET) has been suggested to explain the photochemistry of allylphenols,[9] intermolecular amine-mediated cyclizations *via* electron transfer have not been previously reported. In the case of allylnaphthols, the role of tertiary amines appears to be limited to its involvement as efficient quenchers of the reaction.[8] This is compatible with our observations, since isolated double bonds absorb at a very short wavelength and their excited singlet states cannot be reached through direct irradiation under standard conditions. On the other hand, their excitation energies are too high to allow intramolecular energy transfer from the excited naphthol chromophores.

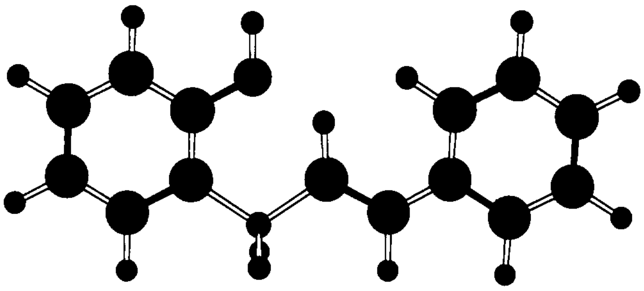


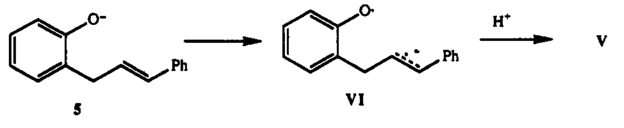
Figure 6. Ground-state conformation of **2a** optimized using the PM3 semiempirical method.

Table 3. Energy of the Excited Singlet States of 2a Calculated by the CNDO/S Method

CI[a]	λ[b]	f[c]	symmetry	transitions	contribution to CI (%)
1	246	0.1171	$\pi\pi^*$	40–41	28
				40–44	52
				38–41	18
2	244	0.3279	$\pi\pi^*$	40–41	69
				40–44	18
				38–41	12
3	206	0.0192	$\pi\pi^*$	40–42	99

[a] Configuration interaction. [b] Excitation wavelength corresponding to a vertical transition. [c] Oscillator strength.

It is also noteworthy that irradiation of the phenolate **5** in methanol led to the benzopyran derivative **4** (50% yield, based on reacted **5**). Lower amounts of 2-(3-phenylpropyl)phenol (**6**),[24] 2-(methoxymethyl)phenol (**7**),[25]



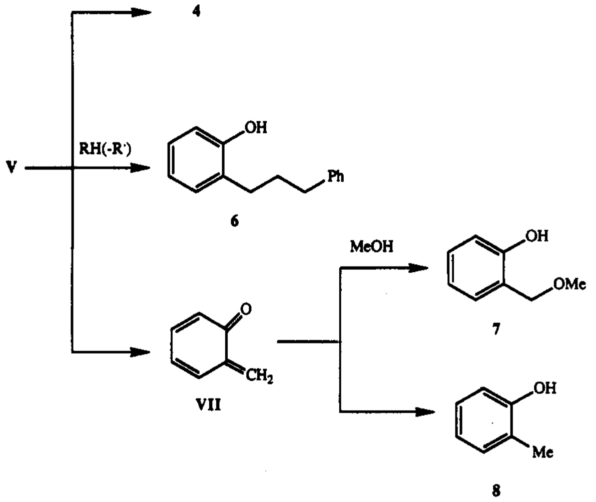
---

(22) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *49*, 1221–1229.

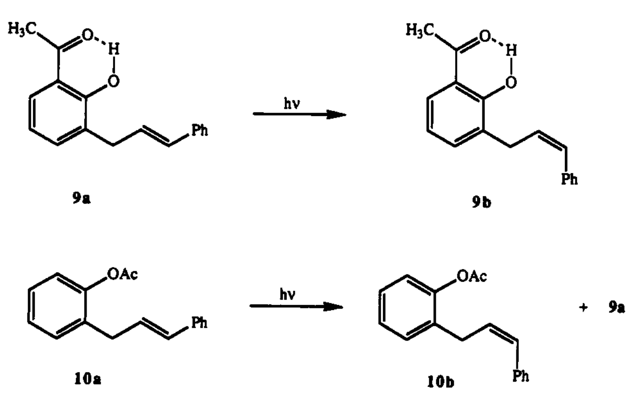
(23) Del Bene, J.; Jaffe, H. H. *J. Chem. Phys.* **1969**, *50*, 1126–1129.

(24) Bird, T. G. C.; Brown, B. R.; Stuart, I. A.; Tyrrell, A. W. R. *J. Chem. Soc., Perkin. Trans. 1* **1983**, *8*, 1831–1846.

and *o*-cresol (**8**) were obtained as byproducts (ca. 15% of each compound). Not even traces of the benzofuran derivative **3** were detected. These results can be explained by intramolecular excited state electron transfer to **VI**, followed by protonation. The diradical **V** would cyclize to **4** or undergo hydrogen abstraction from the medium to give **6**. Alternative carbon–carbon bond cleavage to the *o*-quinone methide **VII**, followed by methanol addition or hydrogen abstraction, would explain the formation of products **7** and **8**, respectively. It is rather significant that irradiation of the sultone derived from *o*-hydroxytoluene-α-sulfonic acid in methanol also produces a mixture of **7** and **8**, *via* the proposed intermediate **VII**.[25] Again, photocyclization initiated by electron transfer with formation of the styrene radical anion leads preferentially to **4**, as observed during the irradiation of **2a** in the presence of triethylamine.



It has been stated above that the key step in the photocyclization of *trans*-2-cinnamylphenol (**2a**) must be intramolecular excited-state proton transfer (ESPT) and appears to involve π-complexes of the type **I**, **IIa**, and **IIb**. To check the consistency of this hypothesis, we decided to prepare the *o*-acetyl derivative **9a**, where the phenolic hydroxyl was expected to be strongly chelated with the adjacent carbonyl group. This structural feature should prevent formation of a π-complex of the type **I** and, on the other hand, would facilitate an efficient, energy-wasting, deactivation of the phenolic singlet *via* proton exchange between both oxygen atoms, followed by thermal tautomerization.[26] Synthesis of the required substrate **9a** was first attempted by photo-Fries rearrangement[27] of the acetate **10a** in benzene, but the yield was very low, owing to preferential formation of the *cis* isomer **10b**. Using acetone as solvent, **10b** was the only photoproduct obtained. This result showed that in the case of the acetate **10a** isomerization of the double bond from the styrene triplet prevailed over rearrangement from the phenyl ester singlet. A more convenient preparation of the acetyl derivative **9a** was achieved by treatment of the sodium salt of *o*-hydroxyacetophenone with cinnamyl chloride.



As expected, the only process observed upon irradiation of **9a** was *trans*/*cis* isomerization, either in benzene or in acetone. The efficiency was markedly higher in the latter solvent, thus confirming that the styrenic triplet was involved in this transformation.

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; 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; chemical shifts are reported in δ (ppm) values, using TMS as 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 dichloromethane as eluent, or by means of isocratic HPLC equipment provided with a semipreparative Microporasil column, using hexane/ethyl acetate as eluent. Corrected fluorescence emission spectra were obtained in the usual manner, with a Perkin-Elmer LS-5b luminescence spectrometer. Temperature-dependent studies were obtained using a Haake F3 thermostat. A slit width corresponding to a wavelength of 2.5 nm was chosen for both the incident and emitted light. All measurements were made on dilute solutions. Concentration of **2a** was usually in the range of 5 × 10^{-5} M, but no significant changes were observed on dilution to 10^{-5} or to 5 × 10^{-6} M.

General Irradiation Procedures. Procedure A. Solutions of 1.00 g of the substrate in 400 mL of freshly distilled solvent were irradiated at room temperature with a 125-W medium-pressure mercury lamp inside a quartz immersion well. The photoproducts were isolated after removal of the solvent with silica gel column chromatography and subsequently by HPLC. **Procedure B.** Solutions of 0.02 g of the substrates in 7 mL of the indicated solvents were placed into Pyrex or quartz 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.

***trans*-2-Cinnamylphenol (2a).** FTIR: 3651 (OH), 3581 (OH), 3071, 2918, 1591, 1494, 1399, 1322, 1208, 1094, 966, 748. ^{1}H NMR: 7.40–7.10 (m, 7H, Ar*H*), 6.89 (t, J = 8 Hz, 1H, 4-Ar*H*), 6.79 (d, J = 8 Hz, 1H, 6-Ar*H*), 6.49 (d, J = 16 Hz, 1H, CH$_2$-CH=C*H*), 6.37 (dt, J_1 = 16 Hz, J_2 = 6 Hz, 1H, CH$_2$C*H*=CH), 5.11 (s, 1H, O*H*), 3.55 (d, J = 6 Hz, 2H, C*H*$_2$). MS: 210 (M$^+$, 85), 209 (29), 165 (23), 119 (24), 116 (27), 115 (67), 104 (35), 94 (20), 91 (91), 77 (100), 51 (71).

***cis*-2-Cinnamylphenol (2b).** Oil. Anal. Found: C, 85.74; H, 6.85. Calcd for C$_{15}$H$_{14}$O: C, 85.68; H, 6.71. FTIR: 3650 (OH), 3595 (OH), 3028, 2916, 1590, 1492, 1456, 1322, 1258, 1206, 1092,

---

(25) Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc., Chem. Commun.* 1971, 383–384.

(26) Catalán, J.; Fabero, F.; Guijarro, M. S.; Claramunt, R. M.; Santamaría, M. D.; Foces-Foces, M. L.; Hernández-Cano, F.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1990**, *112*, 747–759. In addition, photocyclization of **9a** should be prevented by rapid intersystem crossing.

(27) Miranda, M. A.; García, H. Rearrangements. In *The Chemistry of Functional Groups, Suppl. B, The Chemistry of Acid Derivatives*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1992; Vol. 2, pp 1271–1394.

749, 702. ^{1}H NMR: 7.40–7.24 (m, 5H, C_6H_5), 7.17 (d, *J* = 8 Hz, 3-Ar*H*), 7.12 (t, *J* = 8 Hz, 1H, 5-Ar*H*), 6.88 (t, *J* = 8 Hz, 1H, 4-Ar*H*), 6.79 (d, *J* = 8 Hz, 1H, 6-Ar*H*), 6.65 (d, *J* = 12 Hz, 1H, $CH_2CH{=}CH$), 5.84 (dt, J_1 = 12 Hz, J_2 = 7 Hz, 1H, $CH_2CH{=}CH$), 4.88 (s, 1H, OH), 3.67 (d, *J* = 7 Hz, 2H, CH_2). MS: 210 (M^+, 85) 209 (36), 165 (21), 131 (26), 119 (60), 116 (22), 115 (55), 104 (80), 92 (18), 91 (100), 77 (31).

Preparation of *trans*-6-Acetyl-2-cinnamylphenol (9a). The sodium salt obtained from 5.00 g (37.0 mmol) of 2-hydroxyacetophenone was added to *trans*-cinnamyl chloride (5.60 g, 37.0 mmol) in 100 mL of benzene. After the solution was refluxed for 5 h, 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 acidified with HCl and extracted with dichloromethane. Evaporation of the solvent gave a residue which was submitted to column chromatography, affording 1.65 g of *trans*–6–acetyl–2–cinnamylphenol. An analytical sample was obtained by preparative layer chromatography. Oil. Anal. Found: C, 81.05; H, 6.40. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. FTIR: 3069 (OH), 3025 (OH), 1652 (C=O), 1436, 1368, 1306, 1244, 750, 700, 618. ^{1}H NMR: 7.62 (d, *J* = 8 Hz, 1H, 5-Ar*H*), 7.40 (d, *J* = 8 Hz, 1H, 3-Ar*H*), 7.36–7.16 (m, 5H, C_6H_5), 6.84 (t, *J* = 8 Hz, 1 H, 4 Ar*H*), 6.47 (d, *J* = 16 Hz, 1H, $CH_2CH{=}CH$), 6.39 (dt, J_1 = 16 Hz, J_2 = 6 Hz, 1H, $CH_2CH{=}CH$), 3.57 (d, *J* = 6 Hz, 2H, CH_2), 2.63 (s, 3H, CH_3). MS: 252 (M^+, 25), 209 (10), 161 (100), 133 (24), 115 (20), 91 (31), 43 (14).

***cis*-6-Acetyl-2-cinnamylphenol (9b).** Oil. Anal. Found: C, 80.96; H, 6.56. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. FTIR: 3070 (OH), 3033 (OH), 1655, 1435, 1367, 1303, 1244, 967, 748, 617. ^{1}H NMR: 7.64 (d, 1H, *J* = 8 Hz, 5-Ar*H*), 7.40 (d, *J* = 8 Hz, 1H, 3-Ar*H*), 7.37–7.23 (m, 5H, C_6H_5), 6.86 (t, *J* = 8 Hz, 1H, 1H, 4-Ar*H*), 6.62 (d, *J* = 12 Hz, $CH_2CH{=}CH$), 5.86 (dt, J_1 = 12 Hz, J_2 = 8 Hz, 1H, $CH_2CH{=}CH$), 3.70 (d, *J* = 8 Hz, 2H, CH_2), 2.65 (s, 3H, CH_3). MS: 252 (M^+, 20), 209 (10), 161 (100), 133 (25), 115 (25), 91 (38), 43 (42).

Preparation of *trans*-2-Cinnamylphenyl Acetate (10a). To a solution of *trans*-2-cinnamylphenol (2.00 g, 9.5 mmol) in pyridine (10 mL) was added acetic anhydride (2.00 g, 21.0 mmol), and the mixture was refluxed for 1 h. After cooling, the resulting solution was poured into concentrated hydrochloric acid (10 mL) and ice (50 g) and then extracted with dichloromethane. The extract was washed with aqueous sodium hydroxide (10% w/w) and water, dried, and evaporated to give pure **10a** in nearly quantitative yield. An analytical sample was obtained by preparative-layer chromatography. Mp: 64–65 °C. Anal. Found: C, 80.93; H, 6.35. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. FTIR: 3072, 1784 (C=O), 1492, 1372, 1207, 1100, 743. ^{1}H NMR: 7.40–7.00 (m, 9H, Ar*H*), 6.42 (d, *J* = 16 Hz, 1H, $CH_2CH{=}CH$), 6.25 (dt, J_1 = 16 Hz, J_2 = 7 Hz, 1H, $CH_2CH{=}CH$), 3.44 (d, *J* = 7 Hz, 2H, CH_2), 2.24 (s, 3H, CH_3). MS: 252 (M^+,3), 210 (36), 209 (100), 119 (19), 115 (22), 91 (35), 43 (13).

***cis*-2-Cinnamylphenyl Acetate (10b).** Oil. Exact mass 252.1160, calcd for $C_{17}H_{16}O_2$ 252.1150. FTIR: 3071, 1783 (C=O), 1492, 1373, 1206, 1098, 748. ^{1}H NMR: 7.40–7.00 (m, 9H, Ar*H*), 6.57 (d, *J* = 12 Hz, 1H, $CH_2CH{=}CH$), 5.73 (dt, J_1 = 12 Hz, J_2 = 7Hz, 1H, $CH_2CH{=}CH$), 3.58 (d, *J* = 7 Hz, 2H, CH_2), 2.09 (s, 3H, CH_3). MS: 252 (M^+, 2), 210 (40), 209 (100), 119 (38), 115 (36), 91 (71), 43 (24).

Calculations. The ground-state geometry and heat of formation of *trans*-2-cinnamylphenol (**2a**) were calculated by using the semiempirical parametrized Model 3 (PM3) method, as implemented in version 6.00 of the MOPAC program,[28] which has proven to be very effective in studies on molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

The energy of excited singlet states was computed using the complete neglect of differential overlap/spectroscopic parameterizacion (CNDO/S) method.[20–23] The Nishimoto–Mataga approach[29] was employed to calculate the Coulomb integrals of the singlet states. The configuration interaction (CI) involved the 99 lowest energy monoexcited configurations in all cases. These calculations were performed by using the GEOMOS program.[30]

Acknowledgment. Financial support by the DGICYT (Grant No. PB-88 0494) is gratefully acknowledged. We also thank Mr. Manuel Adelantado for his excellent technical assistance in the mass spectral measurements and the CIUV (Centro de Informática de la Universidad de Valencia) for the computing facilities.

---

(28) Stewart, J. J. P. MOPAC (6.00). *Quantum Chemistry Program Exchange*; QCPE 455; Indiana University: Bloomington, IN, 1990.

(29) Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* **1957**, *13*, 140–157.

(30) Rinaldi, D.; Hoggan, P. E.; Cartier, A.; GEOMOS. *Quantum Chemistry Program Exchange*; QCPE 584; Indiana University: Bloomington, IN, 1992.