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Photocyclization of Cinnamylnaphthols

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Abstract: The naphtholic chromophore is responsible for the photophysical and photochemical properties of cinnamylnaphthols 1e, f. Both fluorescence emission and photocyclization occur from the naphtholic singlet excited states. The formation of five- and six- membered ring products (2e and 3e, f) is shown to involve a proton transfer mechanism. The low efficiency of *trans* to *cis* isomerization is explained as the result of deactivation of the styrenic triplet *via* intramolecualr energy transfer. The resulting naphtholic triplets behave as energy sinks. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Phenols and naphthols possessing an o-allyl group (1a-c) have been shown to cyclize upon light excitation.¹⁻⁹ In such compounds, light is exclusively absorbed by the phenol or naphthol chromophore under the usual irradiation conditions ($\lambda > 200$ nm). Attachment of a phenyl group at the remote position of the allylic double bond leads to a new absorbing chromophore. Extended conjugation in the styrenic system allows an easy access to its excited states upon direct irradiation, in competition with phenol excitation. In the case of *trans*-2-cinnamylphenol (1d), both the phenolic and styrenic chromophores are involved in the photocyclization process.¹⁰ On the other hand, substitution at the styrenic ring of 1d is a tool to enhance the contribution of the styrenic chromophore.¹¹ In the literature, no previous report has dealt with the photochemical behaviour of *trans*-2-cinnamyl-1-naphthol (1e) and *trans*-1-cinnamyl-2-naphthol (1f). Taking into account the singlet energies of 1-naphthol, 2-naphthol and styrene (89, 87 and 98 kcal/mol, respectively)¹², in the case of 1e, f the naphtholic portion should determine the photoreactivity, by contrast with the previously reported *o*-cinnamylphenols substituted at the styrenic ring.¹¹

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RESULTS AND DISCUSSION

The required cinnamylnaphthols 1e, f were prepared by reaction of the corresponding naphtholates (obtained by previous treatment of 1- or 2-naphthol with sodium) with *trans*-cinnamyl chloride in benzene. Their photophysical and photochemical behaviour are reported below.

Photophysical properties

In order to obtain information about the nature of the excited states of 1e, f, their absorption and fluorescence emission spectra were recorded in cyclohexane at room temperature (Figure 1). The results showed that, while the UV-absorption spectra display the absorption bands of both chromophores present in the molecules, the fluorescence spectra can be attributed to the naphtholic portion. This is supported by i) the similarity of the fluorescence spectra of 1e, f with those of 1-naphthol and 2-naphthol (not shown), respectively, ii) the singlet energies derived for 1e (89 kcal/mol) and 1f (85 kcal/mol), which are very close to those reported for 1-naphthol and 2-naphthol and 2-naphthol and far from that of styrene¹² and iii) the fact that hydrogenation of the styrenic double bond in 1f (to give compound 1f-H) produces no significant change in the shape and position of the fluorescence emission bands.

From the quantitative point of view, the most interesting observation was the markedly lower fluorescence quantum yields of 1e, f, as compared with the parent 1- and 2-naphthol. Thus, for example, in the case of 1f, ϕ_F was *ca*. 0.08, while the value reported for 2-naphthol is 0.27.¹² This indicates that the naphtholic singlets are partially quenched by the styrenic moiety; the main result is formation of photocyclization products (see below). Accordingly, when the possibility of such interchromophoric interaction was suppressed (as in the case of the dihydro derivative 1f-H) the fluorescence quantum yields underwent a dramatic increase, becoming of the same order than the unsubstituted naphthols.

Product studies

Although the absorption spectra of both compounds showed their most intense maxima below 300 nm, irradiation using quartz-filtered light gave rise to a high degree of polymerization. In order to prevent this



problem, a Pyrex filter was used for the photolysis experiments. The results are shown in Table 1, together with those previously reported for 1a-d, to facilitate discussion.

Figure 1. Absorption (up) and fluorescence emission (down) spectra of the cinnamylnaphthols 1e,f and the dihydro derivative 1f-H in cyclohexane, at 10⁻⁴ M concentration.

Irradiation of 1e in benzene led to the dihydrobenzofuran 2e, together with the dihydrobenzopyran 3e (Table 1, entry 5). No significant *trans* to *cis* isomerization of the styrenic double bond was observed. When compound 1f was irradiated under the same conditions, the six membered ring cyclic ether 3f was found to be the major product. In this case, small amounts of the *cis* isomer 4b were also detected (Table 1, entry 6).



It has been proposed that proton transfer in the excited state is the predominating pathway in the photocyclization of the allylnaphthols 1b,c.⁸ In order to check this possibility in the case of cinnamylnaphthols

1e,f, their irradiation was performed in the presence of different amounts of dioxane as guencher. Under these conditions, a progressive decrease in the yield of photocyclization products was observed with increasing

Table 1. Irradiation of compounds 1a-f							
		Compound	Conversion (%)	Products yield (%)			
	Entry			2	3	4	Others
•	1	1a ^a	34	91	9	-	-
	2	1b ⁶	37	81	11	-	8°
	3	1c ^b	29	38	45	-	17 ^d
	4	1d°	80	45	30	25	-
	5	1e	71	55	44	tracesf	-

^aRef. 4 :^b Ref. 8: ^c2-methylnaphtho[1,2-b]furan was also isolated: methylnaphtho[2,1-b]furan and naphthalene were also isolated; Ref. 10; Ref. 13.

90

0

traces

92

7

1f

1g

concentrations of dioxane (Figure 2). The fact that the slope of the straight line obtained for 1e is smaller than that of 1f (which shows an upward curvature) suggests that in the former case a mechanism different from proton transfer is also contributing to photocyclization.¹⁴



6

7

Figure 2. Influence of dioxane on the photocyclization of 1e, f. The parameter p(0)/p(q) is the ratio between the percentage yields (2+3) in absence and presence of quencher.

The predominance of proton transfer is also in agreement with the ground state preassociation¹⁵ between the naphtholic OH and the styrenic double bonds observed by GC-FTIR, where the free and associated OH groups gave rise to two different stretching bands (see Experimental Section). Moreover, although the acidity of 1e, f in the ground state is only moderate, it is dramatically increased in the excited states, becoming ca. 8 orders of magnitude higher.¹⁶ This would greatly enhance the feasibility of protonation of the styrenic double bond by the excited naphthol.

The observed product distributions deserve some comments in two respects: i) the different 2e,f/3e,f ratios and ii) the low amounts of 4e, f formed.

In connection with the selectivity of photocyclization, it is noteworthy that irradiation of 2-cinnamyl-1naphthol (1e) gave rise to comparable yields of dihydrobenzofuran 2e and dihydrobenzopyran 3e, as previously reported for the analogous cinnamylphenol 1d (Table 1, entries 4 and 5). The lack of significant differences between the behaviour of 1d and 1e agrees well with the results obtained in the case of the corresponding allyl derivatives 1a,b (Table 1, entries 1 and 2). Obviously, the enhanced formation of six membered ring products in the photolysis of 1d, e has to be attributed to the relative stability of the carbocations (benzylic *versus* primary) generated upon intramolecular protonation of the double bond.

Besides, the ratio 2e/3e was much higher than 2f/3f. This is because in the photocyclization of 1cinnamyl-2-naphthol (1f), the dihydrobenzopyran 3f is strongly favoured, what follows the same trend previously found in the allyl derivatives of 1- and 2-naphthol (Table 1, entries 2 and 3). Again, the formation of six membered ring products is enhanced in the cinnamylnaphthols.

The second interesting point was the low efficiency of *trans* to cis isomerization of the styrenic double bond (traces of 4e and only 7% of 4f obtained). This must be related with the fact that the triplet energies of 1-naphthol and 2-naphthol (58 and 60 kcal/mol, respectively)¹² are lower than that of styrene (62 kcal/mol)¹². This is illustrated in Figure 3. In both cases, the triplets can be deactivated through an energy transfer process to afford the naphtholic triplets. This is especially favoured in the case of 1e.



Figure 3. Relative position of the excited states in 1e, f, g.

Thus, the naphtholic triplets behave as energy sinks, leading to no reaction. As, on the other hand, the naphtholic singlets are also lower in energy than the styrenic singlets (Figure 3), the reactions occur overwhelmingly from the former. In order to check the validity of this picture, the acetyl derivative 1g was synthesized. Being this compound an aromatic ketone, the efficiency of intersystem crossing must be very close to 1. This way, the excitation energy should be entirely used to populate the naphtholic triplet and hence no reaction should take place. The experimental results (Table 1, entry 7) confirmed these expectations.

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EXPERIMENTAL SECTION

General

UV spectra were recorded in cyclohexane in a Shimadzu UV-160A; λ_{max} (nm) and log ε values (in brackets) are given for each absorption band. IR spectra were obtained with a GC-FTIR Hewlett-Packard 5965; ν_{max} (cm⁻¹) is given for all the absorption bands. ¹H-NMR spectra were measured in CDCl₃ with a 300-MHz Varian Gemini-300, 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 indicated for the significant peaks. Fluorescence spectra were recorded with a Perkin -Elmer LS50 instrument. High-resolution mass spectra were conducted on a VG Autospec instrument.

General irradiation procedure. Solutions of 0.02 g of the substrate in 20 ml of benzene or benzene/dioxane were placed into Pyrex tubes surrounding a centrally positioned quartz cooling jacket containing a 125 W medium-pressure Hg lamp and irradiated under argon for 1h. The reaction mixtures were analyzed by GC-MS and ¹H-NMR. Then, they were submitted to chromatographic separation, in order to obtain the pure photoproducts. This was done by conventional column chromatography on silica gel Merck 60 (0.063-0.200 mm) using dichloromethane as eluent, or by means of isocratic HPLC equipment provided with a semipreparative Microporasil column, using hexane/ethyl acetate as eluent. The spectral data reported below correspond to the isolated compounds. In ¹H-NMR, the main difference between the *cis* and *trans*-cinnamylnaphtols was the chemical shift of the olefinic protons (lower in the case of the *cis* isomers), while the diagnostically important difference between dihydrobenzofurans and dihydrobenzopyrans was the presence of a more shielded methylene group in the latter at *ca*. 2.2 ppm.

Synthesis of the substrates 1e,f, g.

Compounds 1e, 1f and 1g were prepared as previously described in the literature for 1d.¹⁰ The sodium salt obtained from the corresponding naphthol (37.0 mmol) was added to *trans*-cinnamyl chloride (5.60 g, 37.0 mmol) in 100 ml of benzene. After the solution was refluxed for 5h, 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, using dichloromethane or mixtures hexane/methylene chloride as eluent.

Spectral data of the new compounds

trans-2-Cinnamyl-1-naphthol (1e). 20%. Viscous oil. UV: 231 (4.4); FTIR: 3648 (OH), 3569 (OH), 3066, 3031, 2910, 2363, 1576, 1499, 1439, 1392, 1237, 1084, 802, 739; ¹H-NMR: 3.73 (d, J = 6 Hz, 2H, CH₂), 5.55 (s, 1H, OH), 6.44 (dt, $J_1 = 16$ Hz, $J_2 = 6$ Hz, 1H, CH₂C<u>H</u>=CH), 6.59 (d, J = 16 Hz, 1H, CH₂CH=C<u>H</u>), 7.22-7.49 (m, 9H, ArH), 7.79, 8.16 (m+m, 2H, 5,8-ArH); MS: 260, (M⁺, 42), 169 (12), 156 (100), 141 (13), 128 (45), 115 (20), 104 (13), 91 (20), 77 (9); Anal.: Calcd. for C₁₉H₁₆O: C: 87.65 %, H: 6.19%. Found: C: 87.22 %, H: 6.43 %; HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1202.

trans-1-Cinnamyl-2-naphthol (1f). 35 %. Viscous oil. UV: 238 (4.2), 334 (3.5); FTIR: 3652 (OH), 3585 (OH), 3068, 3031, 1935, 1624, 1599, 1515, 1468, 1390, 1350, 1255, 1203, 1145, 1062, 965, 804, 739; ¹H-NMR: 3.96 (d, J = 4 Hz, 2H, CH₂), 6.41 (m, 2H, CH₂C<u>H</u>=C<u>H</u>), 7.07 (d, J = 8 Hz, 1H, 3-Ar<u>H</u>), 7.14-7.28 (m, 5H, ArH), 7.33, 7.47 (m+m, 2H, 6,7-ArH), 7.65, 7.77, 7.95 (d+d+d, J = 8 Hz, 4,5,8-ArH); MS: 260, (M⁴, 66), 181 (18), 169 (88), 168 (25), 156 (60), 128 (63), 117 (47), 115 (43), 104 (100), 91 (83), 77 (19); HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1217.

trans-4-Acetyl-2-cinnamyl-1-naphthol (1g). 20 %. Viscous oil. UV: 243 (4.1), 318 (3.4); FTIR: 3647 (OH), 1695, 1582, 1514, 1355, 1240, 1053. ¹H-NMR: 3.71 (s, 3H, COCH₃), 3.76 (d, J = 6 Hz, 2H, CH₂), 6.37 (dt, $J_1 = 16$ Hz, $J_2 = 6$ Hz, 1H, CH₂CH=CH), 6.42 (s, 1H, OH), 6.61 (d, J = 16 Hz, 1H, CH₂CH=CH), 7.21-7.40 (m, 5H, ArH), 7.50-7.65 (m, 2H, 6,7-ArH), 7.88 (s, 1H, 3-ArH), 8.21, 8.97 (d+d, J = 8 Hz, 2H, 6,8-ArH); MS: 302, (M⁺, 64), 300 (13), 299 (13), 287 (21), 198 (46), 183 (100), 155 (35), 127 (30), 115 (24), 91 (53), 77 (17); Anal.: Calcd. for C₂₁H₁₈O₂: C: 83.10 %, H: 5.98 %. Found: C: 82.52 %, H: 5.99 %. HRMS Calcd. for C₂₁H₁₈O₂: 302.1307. Found: 302.1297.

2-Benzyl-2,3-dihydro-2H-naphtho[1,2-b]furan (2e). FTIR:3066, 2948, 1576, 1444, 1399, 1373, 1277, 1170, 1069, 1008, 879, 799, 740, 699; ¹H-NMR: 3.08 (m, 2H, CH₂), 3.35 (m, 2H, CH₂), 5.27 (m, 1H, CH), 7.20-7.60 (m, 9H, ArH), 7.84 y 7.92 (m+m, 2H, 5,8-ArH); MS: 260 (M⁺, 100), 168 (82), 167 (30), 156 (65), 141 (37), 128 (21), 115 (15), 91 (23); HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1196.

2-Phenyl-3, 4-dihydro-2H-naphtho-[1,2-b]pyran (3e). FTIR: 3061, 2937, 1577, 1395, 1344, 1314, 1264, 1218, 1188, 1149, 1098, 1027, 976, 919, 797, 740. ¹H-NMR: 2.18 (m, 2H, CH₂CH₂CH), 2.91 (m, 2H, CH₂CH₂CH), 5.21 (br s, 1H, CH), 7.10-7.37 (m, 9H, ArH), 7.75, 8.10 (m+m, 2H, 5,8-ArH); MS: 260 (M⁺, 80), 169 (15), 156 (100), 141 (5), 128 (32), 115 (6), 104 (14), 91 (12), 78 (6), 77 (5); HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1208.

3-Phenyl-1,2-dihydro-3H-naphtho-[2, 1-b] pyran (3f). FTIR: 3073, 2958, 1624, 1599, 1513, 1467, 1437, 1396, 1347, 1238, 1181, 1083, 1030, 978, 807, 741, 696. ¹H-NMR: 2.25 (m, 2H, CH₂CH₂CH), 3.10 (m, 2H, CH₂CH₂CH), 5.05 (dd, $J_1 = 10$ Hz, $J_2 = 2$ Hz, 1H, CH), 7.07 (d, J = 9 Hz, 1H, 3-ArH), 7.16-7.42 (m, 7H, ArH), 7.57 (d, J = 8 Hz, 1H, 6-ArH); MS: 260 (M⁴, 66), 169 (63), 168 (18), 156 (57), 128 (83), 117 (28), 115 (20), 104 (100), 103 (20), 91 (33), 78 (20), 77 (19); HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1195.

cis-1-Cinnamyl-2-naphthol (4f). UV: 234 (4.3), 319 (3.4); FTIR: 3651 (OH), 3600 (OH), 3069, 1599, 1514, 1391, 1255, 1204, 1144, 965, 804, 739; ¹H-NMR: 4.08 (d, J = 7 Hz , 2H, CH₂), 4.97 (s, 1H, OH), 5.73 (dt, $J_1 = 11$ Hz, $J_2 = 7$ Hz, 1H, CH₂CH=CH), 6.59 (d, J = 11 Hz, 1H, CH₂CH=CH), 7.04 (d, 1H, $J_1 = 9$ Hz, 3-ArH), 7.25-7.50 (m, 7H, ArH), 7.63 (d, J = 9 Hz, 1H, 4-ArH), 7.73-7.77 (m, 2H, 6,8-ArH); MS: 260 (M⁺, 60), 181 (21), 169 (89), 168 (26), 156 (58), 128 (72), 117 (51), 115 (51), 104 (100), 91 (96), 77 (27); HRMS Calcd. for C₁₉H₁₆O: 260.1201. Found: 260.1200.

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- 14. Photocyclization of 1e could be partially occurring via electron transfer, which has also been proposed as a possible mechanism for this type of reaction (see Ref. 9). It is worth mentioning that the oxidation potential of 1-naphthol is slightly lower (0.1 V) than that of 2-naphthol: Weinberg, N. L. Techniques of Electroorganic Synthesis Part II. In Techniques of Chemistry Vol. V; John Wiley & Sons: New York 1975, p. 740.
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- 16. The pK_a values of 1e,f in the ground state were found to be 9.9 and 10.0, respectively. On the other hand, in MeOH:H₂O (9:1, v/v), the emission maximum of 1e shifted from 353 nm (in the presence of HCl 1 M) to 475 (in the presence of NaOH 0.2 N), while in the case of 1f, the corresponding maximum changed from 362 nm to 425 nm for the same media. Taking into account the singlet energies derived from the 0-0 transitions, the estimated pK_a*values are 1.8 (for 1e) and 2.4 (for 1f).

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