Mechanistic Studies of Photocyclizations of Vicinal Allylnaphthols: The Duality of Excited-State Proton-Transfer Complexes

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Abstract: Photoexcitations of 2-allyl-1-naphthol and 1-allyl-2-naphthol caused cyclization, forming dihydrofuranyl and pyranyl ethers and the secondary photodehydrogenation of the dihydrofuranyl ethers. The quenching experiments of the product formations as well as fluorescence intensities of allylnaphthols by methanol, triethylamine, *N*-nitrosodimethylamine, and 1,3-dienes confirmed that the cyclization occurred from the singlet excited-state proton transfer (ESPT) of the phenolic group; i.e., kinetic acidity initiated photocyclization. The primary photoprocess is quenched mainly by a static quenching process arising from the ground-state hydrogen-bonding association between allylnaphthols and a quencher, as supported by IR spectroscopy, and to a minor extent by a dynamic quenching of the singlet excited state of the allylnaphthol intramolecular proton-transfer complexes. Kinetic analyses also reveal the presence of two identifiable intramolecular ESPT intermediates, probably conformers of the proton-transfer species; one is the precursor of the furanyl ethers and not quenchable in the dynamic process by Et_3N, and the other that of the pyranyl ethers and quenchable in the dynamic process by Et_3N. The IR absorption of intramolecular hydrogen bonds between the OH and olefin groups began to be replaced by that of intermolecular hydrogen bonds at tetrahydrofuran concentrations above 10^{-2} M; methanol, at about this concentration and above, also quenches the photocyclization.

Phenols carrying *o*-allyl groups have been shown to undergo light-promoted as well as acid-catalyzed cyclization to form a mixture of furanyl ethers and pyranyl ethers. The acid-catalyzed thermal process is more regioselective than the light-promoted process in generating furanyl ethers.[1] The former photoinitiated cyclic ether formation was originally interpreted as an acid-catalyzed cyclization with an excited-state proton transfer (ESPT) from the phenolic OH group.[2-4] An alternative mechanism by electron transfer also has been suggested.[5] Later works have shown that other substituted *o*-allylphenols[6] can undergo similar photoinitiated cyclization without adding new information to the reaction mechanism. While the net cyclization reaction can be achieved by an acid-catalyzed thermal process,[1] photoinitiated cyclization poses interesting questions with respect to the excited-state reactivities of phenolic compounds in vivo as well as in vitro. Enhanced acidity of excited-state phenols and naphthols is well established in the literature[6-13] and, recently, its proton-transfer processes have been studied with picosecond laser spectroscopy.[14] The use of time-constrained high acidity of excited phenolic derivatives to initiate chemical reactions is an attractive concept and worth developing because of the fact that high acidity is generated only momentarily in a confined local. We have shown an example of ESPT in photonitrosation of naphthols with *N*-nitrosodimethylamine.[15] Undoubtedly, such acid catalysis will be most facile in intramolecular reactions such as those which may occur in the singlet excited state of *o*-allylphenols.[1,6] We wish to describe the ESPT-initiated photocyclization of allylnaphthols and pertinent evidence to substantiate the ESPT mechanism.

Results

In this study, 2-allyl-1-naphthol (**1**, 1-NpOH-2A) and 1-allyl-2-naphthol (**2**, 2-NpOH-1A) were synthesized[16] and used for mechanistic studies. Irradiation of **1** in benzene under nitrogen above 300-nm absorption (see Figure 1) for 1.5 h gave furanyl ether **3** and pyranyl ether **4** in a 7:1 ratio (GC analysis) in addition to furanyl ether **5**, the amount of which depended on the concentration of **1**. Similar irradiation of **2** in benzene proceeded more sluggishly and yielded compounds **6**, **7**, **8**, and naphthalene (**9**) in the ratio 2.6:3.3:0.2:1. The products were isolated by repeated column chromatography for characterization, and their percentages were, in most cases, determined by GC analysis for mechanistic studies. The formation of naphthalene in this photolysis was unexpected but was confirmed beyond any doubt. These products were identified from their spectroscopic properties which agreed with those of published data.[17-19]

The relative efficiency of the photoconversion of **1** and the formation of **3** in various solvents decreased drastically in the order of benzene, methylene chloride, acetonitrile, tetrahydrofuran (or dioxane), and methanol. The relative efficiency for the former was calculated to be 1:0.47:0.17:0.04:0.0 under identical conditions of photolysis; no photocyclization was observed in methanol in a short irradiation period. The relative efficiency for the photoconversion of **2** similarly diminished in the same solvent order as shown above; in methanol, the formations of **6** and **7** were too small to be integrated in GC analysis.

In the irradiation of **1** in benzene at 0.012 M, the pattern of the formation and disappearance of materials were monitored at various time intervals (Figure 2). The formation pattern of furanyl ether **5** was studied with a merry-go-round in a low conversion range (<20%). In the initial concentration range of [**1**] < 0.005 M, the relative efficiency of the formation of **5** with respect to **3** and **4** increased to a maximum value as [**1**] decreased, but the efficiency dropped to nearly 0% in the region of [**1**] > 0.02 M. While this indicated that **5** was derived from a secondary photoreaction, irradiation of **3** (or **6** + **7**) in benzene under nitrogen

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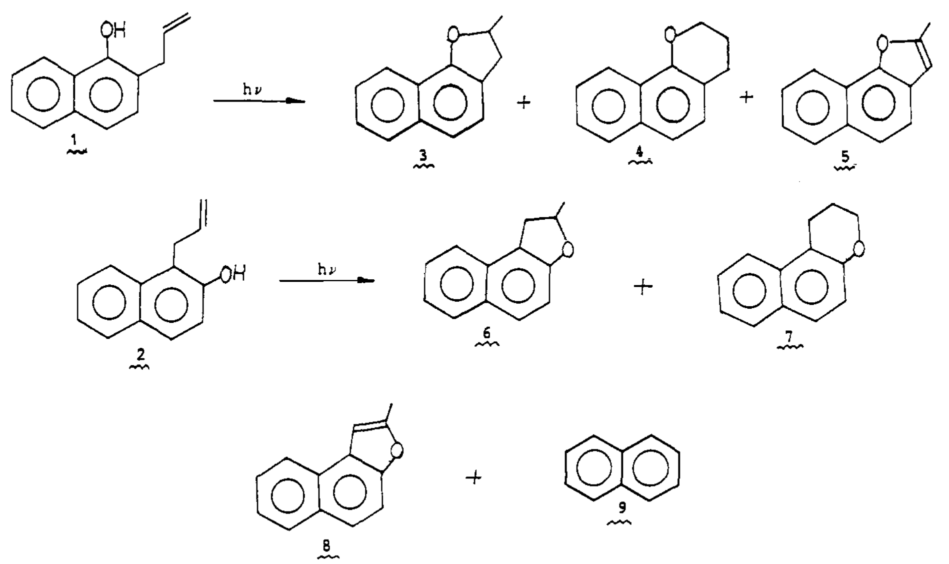
Scheme I



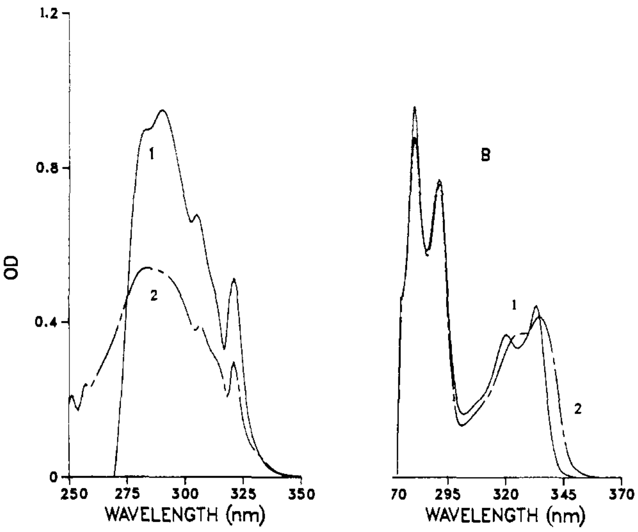


Figure 1. (A) Absorption spectra of allylnaphthol **1** in benzene (1) and in acetonitrile (2). (B) Absorption spectra of allylnaphthol **2** in benzene (1) and in benzene–2.4 M methanol (2).

gave no furanyl ether **5** (or **8**). Irradiation of **3** (or **6** + **7**) in the presence of **1** (or **2**) under comparable conditions gave **5** (or **8**) rapidly when the initial mole ratio of the former to the latter was about 0.5 or higher; if this mole ratio was in the range of <0.1, naturally, the incipient light was primarily absorbed by **1** (or **2**) leading to no formation of **5**. These results agreed with the concentration effects observed above.

Owing to the fact that the products from the present photolysis of **1** or **2** possessed similar absorption patterns to the starting naphthols, the true quantum yields could not be determined accurately. Maintaining low conversions under comparable conditions, meaningful but approximate quantum yields could be obtained. Using Rayonet 3000-Å lamps as the source, the quantum yields of **3** and **4** were shown to be nearly constant in the concentration range of [**1**] at 1×10^{-3} to $\sim 5 \times 10^{-2}$ M, but that of **5** decreased rapidly to nearly zero at [**1**] > 10^{-2} as described above. In benzene the quantum yields of **3** and **4** were 0.02 and 0.003 at the <15% conversion of **1**, and those of **6** and **7** were 0.0014 and 0.0016 under comparable conditions, respectively. In tetrahydrofuran, the quantum yields of **3** and **4** decreased to 7 × 10^{-3} and 8 × 10^{-4}, respectively.

The fluorescence spectra of naphthols **1** and **2** in 1 N HCl and 0.2 N NaOH, together with those in organic solvents, are given in Figure 3. From the 0–0 band wavelengths of the fluorescence spectra of the naphthols (spectrum 3) and naphtholates (spectrum 4) in Figure 3, the approximate excited-state dissociation constants (p*K**) were calculated according to the relation of the Förster cycle.[2-4] Together with the ground-state p*K* values, they are given in Table I. The corresponding data for 1-naphthol were also determined to be p*K* = 9.27 and p*K** = 2.1; the agreement with the previous determinations[2,3] supported the reliability of the determinations. Neither the fluorescence intensities of **1** and **2** nor the quantum yields of the furanyl ethers **3** and **6** and pyranyl ether **7** were affected within experimental errors in the presence of 1,3-pentadiene or 1,3-cyclohexadiene at $\sim 10^{-3}$–10^{-2} M in benzene. Owing to the uncertainty involved in the quantum yield determinations as described above, all quenching experiments were run at low conversions (<15%) in a merry-go-round.

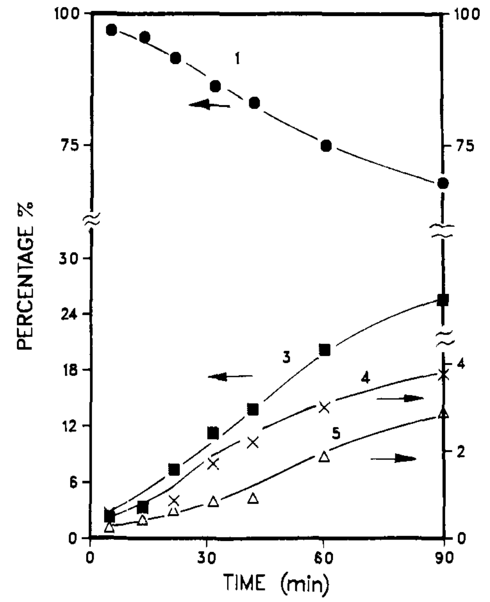


Figure 2. Percentage changes during photocyclization of allylnaphthol **1** (0.012 M) in benzene.

The photocyclization as well as fluorescence intensity of both **1** and **2** were quenched by *N*-nitrosodimethylamine (NND), a good singlet quencher.[20] Quantitative treatments of these quenchings were difficult because of overlaps in absorptions and emission (internal screen effects) of NND and the naphthols, and of the efficient formation of 2-allyl-1,4-napthoquinone-4-oxime (**10**) from **1**. The structure of oxime **10** was assigned on the basis

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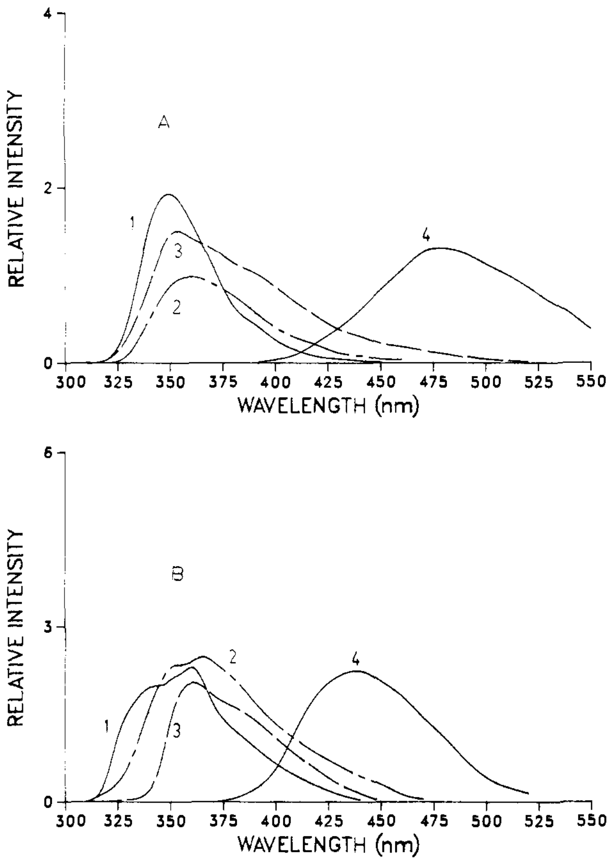


Figure 3. (A) Fluorescence spectra of allylnaphthol **1** in benzene (1), benzene–3 M methanol (2), 1 N HCl in methanol–water (9:1 v/v) (3), and 0.2 N NaOH in methanol–water (9:1 v/v) (4). (B) Fluorescence spectra of allylnaphthol **2** in benzene (1), benzene–0.80 M methanol (2), 1 N HCl in methanol–water (9:1 v/v) (3), and 0.2 N NaOH in methanol–water (9:1 v/v) (4).

Table I. Quenching Parameters and Dissociation Constants

	2-allyl-1-naphthol	1-allyl-2-naphthol
pK^a	9.88	10.01
fluorescence 0–0 band (E_a)^b		
in benzene	330 nm (87 kcal/mol)	322 nm (89 kcal/mol)
in 0.25 N NaOH	410 nm (69 kcal/mol)	393 nm (72 kcal/mol)
pK^{*a}	1.7	2.2
$K_q\tau^0$ for NEt$_3$ quenching^c		
slope of I^0/I plot	26^d (1.01)	70^e (0.92)
slope of Φ^0/Φ (furanyl ether formation)	24^f (0.96)	70^f (0.99)
$K_q\tau^0$ MeOH quenching^c		
slope of I^0/I plot	1.2^g (0.97)	
slope of Φ^0/Φ (furanyl ether formation)	2.7^h (0.98)	6.7^h (1.2)

[a] These values were determined in a methanol–water mixture (9:1 v/v); see Experimental Section for the calculation. [b] The estimated 0–0 band from fluorescence spectra in benzene or in 0.25 N NaOH solution in methanol–water (9:1). [c] The figures in the parentheses are the intercept at [Q] = 0 obtained from a least-squares analysis. [d] λ_{ex} 325 nm, $\lambda_{monitor}$ 350 nm, [NEt$_3$] = 0.0075~0.048 M, and [**1**] = 2.1×10^{-4} M. [e] λ_{ex} 325 nm, $\lambda_{monitor}$ 354 nm, [NEt$_3$] = 0.0046~0.036 M, and [**2**] = 2.2×10^{-4} M. [f] [NEt$_3$] = 0.004~0.08 M, [allylnaphthols] = 1.2×10^{-2} M. [g] [MeOH] = 0.05~0.3 M λ_{ex} 325 nm, $\lambda_{monitor}$ 350 nm, and [**1**] = 2.6×10^{-4} M. [h] [MeOH] = 0.04~2.0 M, [allylnaphthols] = 1.2×10^{-2} M.

of its physical data and in analogy to the similar self-photonitrosation of 1-naphthol promoted by the enhanced acidity of its singlet excited state.[15] The quenching of the photoreaction of **2** with NND leads to simultaneous photodecomposition of NND without the formation of a new product.

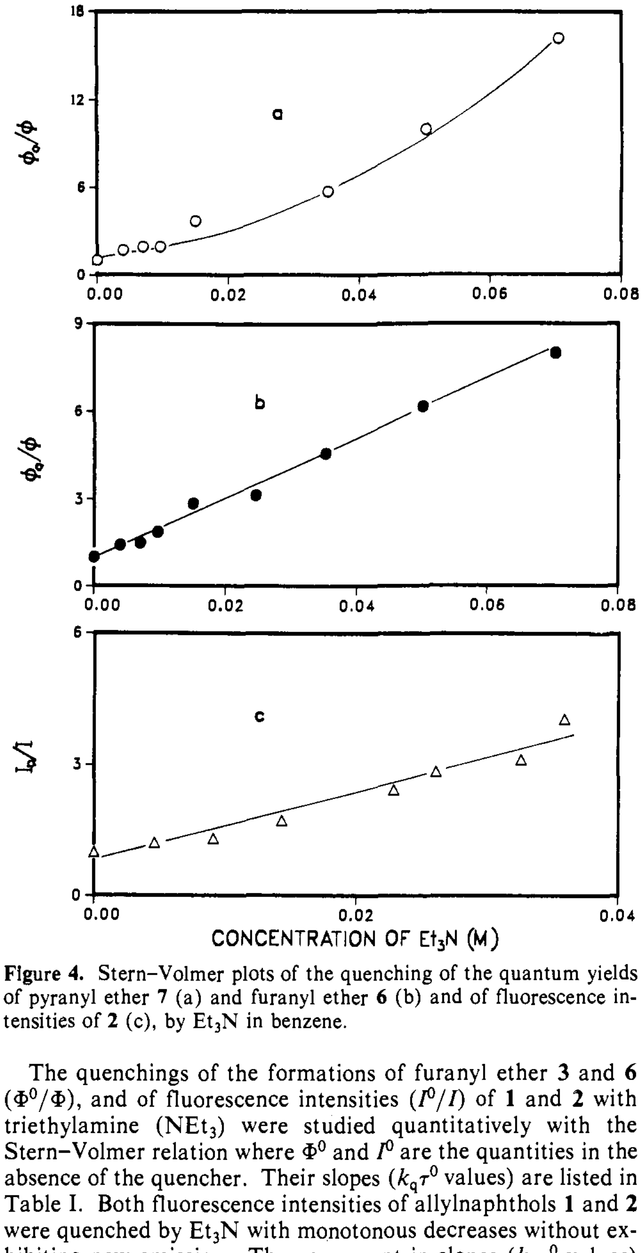


Figure 4. Stern–Volmer plots of the quenching of the quantum yields of pyranyl ether **7** (a) and furanyl ether **6** (b) and of fluorescence intensities of **2** (c), by Et$_3$N in benzene.

The quenchings of the formations of furanyl ether **3** and **6** (Φ^0/Φ), and of fluorescence intensities (I^0/I) of **1** and **2** with triethylamine (NEt$_3$) were studied quantitatively with the Stern–Volmer relation where Φ^0 and I^0 are the quantities in the absence of the quencher. Their slopes ($k_q\tau^0$ values) are listed in Table I. Both fluorescence intensities of allylnaphthols **1** and **2** were quenched by Et$_3$N with monotonous decreases without exhibiting new emission. The agreement in slopes ($k_q\tau^0$ values) between the two types of quenching experiments for both cases are good, indicating that the photocyclization occurs from the lowest singlet excited state of the naphthols. However, similar Stern–Volmer treatments of the quantum yields of the formations of pyranyl ethers **4** and **7** showed upward curvature which became steeper at [NEt$_3$] > 3×10^{-2} M (for example, see Figure 4a); the approximate slopes estimated from the low [NEt$_3$] range were 55 and 100, respectively.

The emission intensity of allylnaphthol **1** in benzene was reduced in the presence of methanol up to 1.0 M, but the maximum shifted to longer wavelengths (357 nm) and the intensities increased at [MeOH] > 1 M. The Stern–Volmer analysis of the intensity quenching by methanol up to the 1 M range gave slope ($k_q\tau^0$) = 1.2; this value was obviously too low owing to intensity contributions of a new emission emerging at a longer wavelength (see Figure 3A). The emission spectrum of **2** in benzene became more intense, and its maximum shifted to 365 nm on addition of methanol (Figure 3b). It was obvious that both **1** and **2** with methanol formed H-bonded complexes; the excited state of these H-bonded complexes (e.g., **13** in Scheme II) fluoresced to give new emission peaks close to the peaks in benzene. The plot of Φ^0/Φ for furanyl ethers **3** in the presence and absence of methanol according to the Stern–Volmer relation gave a straight line with a slope ($k_q\tau^0$ value) of 2.7, but that for **6** started to level off at

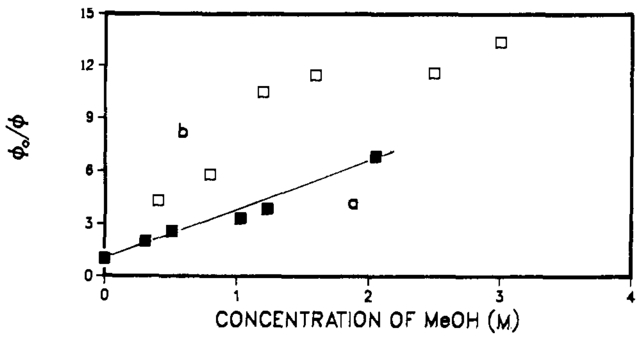
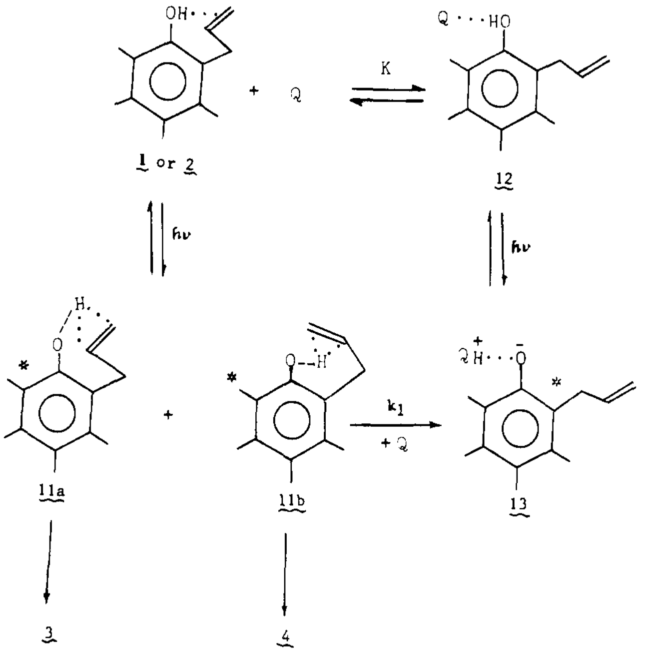


Figure 5. Stern–Volmer plots of the quenching of the quantum yields of furanyl ether **3** (a) and **6** (b) by methanol in benzene.

Scheme II



[MeOH] > 1.7 M, approaching a maximum (Figure 5). The slope for the quenching of **6** obtained from the Φ^0/Φ points at [MeOH] < 2.0 M was 6.7 (Table I). The Φ^0/Φ plot for the quenching of pyranyl ether **7** showed concave curvature through the whole range of methanol concentrations and approached a maximum at [MeOH] > 2.0 M. The quantum yield of pyranyl ether **4** was too small to be accurately measured in low conversion experiments.

The IR spectra of allylnaphthol **1** in carbon tetrachloride in the presence and absence of tetrahydrofuran were recorded as in Figure 6. The free and intramolecularly H-bonded OH stretching vibrational bands[21] were clearly shown at 3620 and 3525 cm^{-1} in the absence of tetrahydrofuran. These bands began to be replaced by the intermolecularly H-bonded band at 3360 cm^{-1} in the range of [THF] > 10^{-2} M. It was significant that the quenching of the formation of the photocyclization products started to show at [MeOH] > 10^{-2} M.

Discussion

The quenching studies described above unequivocally show that allylnaphthols **1** and **2** undergo photocyclization from their singlet excited state to give furanyl ethers **3** and **6** and pyranyl ethers **4** and **7** as the primary products. A secondary photodehydrogenation of **3** (or **6**) can occur to give furanyl ether **5** (or **8**) but can be prevented by adjusting irradiation conditions to cause minimum excitation of **3** (or **6**). However, the available information is too scant to provide a mechanism for the dehydrogenation and much less for the participation of the allylnaphthols **1** (or **2**). The dissociation constants at the singlet excited state (pK^*) of **1** and **2** obtained from the fluorescence maxima according to the Förster's cycle,[2-4] though only approximations, indicate that their acidity could be strong enough to protonate intramolecularly the olefinic bond. In view that the pK^* value of 1-naphthol has been determined by direct measurements of proton transfer[14] to be 0.5, the true pK^* values of **1** and **2** could be more negative than those shown in Table I. This and evidence from quenching experiments lead us to conclude that the primary photocyclization is initiated by the ESPT of the singlet excited-state naphthols.

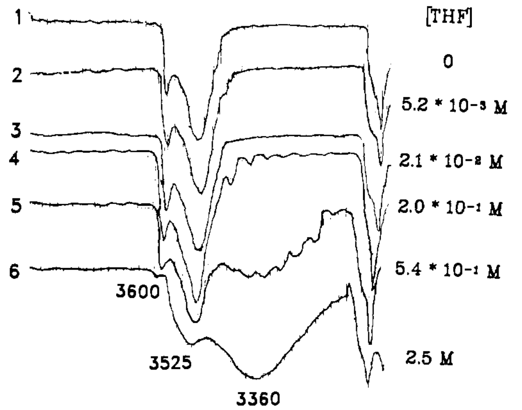


Figure 6. IR absorptions (3000–4000-cm^{-1} range) of allylnaphthol **1** in CCl_4 in the presence of increasing amounts of tetrahydrofuran: [THF] 0 (1), 5.2 × 10^{-3} (2), 2.1 × 10^{-2} (3), 2 × 10^{-1} (4), 5.4 × 10^{-1} (5), and 2.5 M (6).

The singlet excited state of allylnaphthols **1** and **2** is likely to have only fleeting existence (say $<10^{-12}$ s) and promptly leads to intramolecular π-complex **11** from proton transfer which fluoresces in benzene (Figure 3) and collapses to the products (Scheme II). The proton-transfer species **11** is estimated to have a short lifetime of <10 ns from the failure of oxygen to quench fluorescence and photocyclization in benzene. In other words, the cyclization of **11** to **3** and **4** must be fast so as to be able to compete with emission and radiationless decay processes; these processes deexcite and cause the reversion to the ground-state acidity. The cyclization is in effect initiated by proton transfer from momentary high acidity and completed within the lifetime of **11** in a nanosecond time scale; this phenomenon arises from excited-state acidity as contrasted to thermodynamic acidity in ground-state acid catalysis. The poor regioselectivity in the photocyclization of **1** and **2** is probably caused by fast and irreversible cyclizations induced by excited-state acidity since the proton-transfer π-complex **11** probably has all possible conformations (inherited from the ground-state conformations); these conformers decay rapidly to the products or starting material without a chance to relax to a more stable conformation.

The quenchers are bases capable of forming H-bonding complexes with ground-state allylnaphthols as shown in **12**. Tertiary amines such as Et_3N have been shown to form a H-bonded complex with phenols[22] and to act as competitive proton acceptors in the dynamic quenching of the ESPT-promoted self-nitrosation of 1-naphthol with NND.[15] As demonstrated by IR spectroscopy in Figure 6, tetrahydrofuran can destroy the intramolecular H-bonding of allylnaphthol **1** (between the OH and olefinic bond) with the competitive formation of intermolecular H-bonding as in **12**. Upon excitation of **12**, the excited-state OH proton preferentially transfers to a quencher, resulting in a simple acid–base equilibrium; this is the static quenching pathway arising from ground-state association. It is expected that a quencher also can compete for the proton of the excited-state π-complex **11** to give a noncyclizing species such as **13**, constituting a dynamic quenching process of the photocyclization arising from collision processes. The overall quenching processes as shown in Scheme

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[21] Nakanishi, K. *Infrared Absorption Spectroscopy, Practical*; Holden-Day: San Francisco, 1962; p 30.

[22] (a) Nagakura, S.; Gouterman, M. *J. Chem. Phys.* **1957**, *26*, 881. (b) Devaure, J.; Huong, P. V. *Bull. Soc. Chim. Fr.* **1971**, 3917.

II can be related to fluorescence intensity as well as quantum yield decreases by quadratic eq 1, where τ^0 is the lifetime of the allylnaphthols, and [Q] is the concentration of a quencher; *I* and Φ are the fluorescence intensity of **1** and quantum yields of the products.

$$I^0/I = \Phi^0/\Phi = (1 + K[\mathrm{Q}])(1 + k_1\,\tau^0[\mathrm{Q}]) \qquad (1)$$

In a low concentration range of the quencher, where the $[\mathrm{Q}]^2$ term is insignificant, eq 2 can be applied as an approximation

$$I^0/I = \Phi^0/\Phi = 1 + (k_1\tau^0 + K)[\mathrm{Q}] \qquad (2)$$

instead of eq 1. Alternatively, if one of the quenching processes, for example, the collision-controlled dynamic process, is much smaller than the other process, eq 1 is simplified to eq 3. Equation

$$I^0/I = \Phi^0/\Phi = 1 + K[\mathrm{Q}] \qquad (3)$$

3 represents the extreme situation in which the ground-state association process dominates the quenching, e.g., $K \gg k_1\tau^0 \leq 0.01$ in eq 1.

The quenching of the formation of pyranyl ether **7** by $\mathrm{NEt_3}$ in the photocyclization of **2** (Figure 4a) exhibits upward curvature as required by the quadratic eq 1; it is obvious that both the ground-state interaction (**2** → **12**) as well as the singlet excited-state interaction with $\mathrm{NEt_3}$ (**11** → **13**) contribute to the quenching of the formation of pyranyl ether **7**. A similar plot for the quenching of furanyl ether **6** by $\mathrm{Et_3N}$ exhibits a straight line (Figure 4b), indicating that the quenching pattern pertaining to either eq 2 or eq 3 prevails; in view of the fact that the Φ^0/Φ does not deviate from the straight-line plot even when $[\mathrm{Et_3N}] > 0.1$ M, it is concluded that one quenching pathway, that of static quenching process, dominates the formation of **6**; eq 3 represents the pattern. That is, $\mathrm{Et_3N}$ does not quench the formation of **6** by a dynamic quenching process as it does with the formation of **7**. As the quenching of fluorescence intensities of **2** (Figure 4c) represents the overall quenching of singlet excited-state **2** by $\mathrm{Et_3N}$, the close agreement of the slope of the Φ^0/Φ versus $[\mathrm{Et_3N}]$ plot (Figure 4b) with that of the I^0/I versus $[\mathrm{Et_3N}]$ plot (Figure 4c) as shown in Table I suggests that the contribution of the dynamic quenching in Figure 4a is a minor component in the overall picture. Therefore, the observed slopes in Figure 4b and c, are essentially equal to the equilibrium constant *K* according to eq 3; i.e., $K = 70\ \mathrm{M^{-1}}$ for **2** with $\mathrm{NEt_3}$. A similar treatment of the data derived from **1** gave $K = 25\ \mathrm{M^{-1}}$.

The slope of $1.2\ \mathrm{M^{-1}}$ for methanol quenching (Table I) of fluorescence intensities of **1** is less accurate because of the emergence of the closely placed new peaks (see Figure 3A) from the emission of H-bonded species **13**; for allylnaphthol **2**, the overlapped emission of the two species corresponding to **11** and **13** (see Figure 3B) does not allow the quenching experiment. Taking the slopes derived from the Φ^0/Φ plots of furanyl ethers **3** and **6** (Figure 5) as the more reliable values, the reasonably good straight-line plots up to relatively high concentration of methanol indicate that the equilibrium constants of H-bonding association between the allylnaphthols and methanol can be represented by their slopes; i.e., $K = 2.7$ and $6.7\ \mathrm{M^{-1}}$ for **1** and **2**, respectively. In Figure 5, the Φ^0/Φ plot for **6** is obviously an asymptote approaching a maximum of 12~13 in the $[\mathrm{MeOH}] > 2$ M region; that is, the quantum yield of **6** is approaching a finite minimum value which is not quenchable by methanol. This minimum value must correspond to the quantum yield of **6** in methanol which has been shown to be small in a prolonged irradiation of **2** in methanol. The Φ^0/Φ plot for furanyl ether **3** showed a straight line up to fairly high concentration of $[\mathrm{MeOH}] = 3$ M; it is also observed that the photocyclization of **1** does not occur in methanol to a detectable extent by GC analysis. It appears that, for the case of **2**, there is a small leakage from the excited-state methanol–**2** complex (corresponding to **13**) to the excited-state intramolecular complex (corresponding to **11**).

The consequence of different quenching patterns by $\mathrm{NEt_3}$ arrived at in the above discussion may be explained by a proposal of two different proton-transfer complexes of **11**, most likely different in conformation; one is to give pyranyl ethers **4** and **7** and is quenchable by $\mathrm{NEt_3}$, and the other to give furanyl ethers **3** and **6** and is not quenched by $\mathrm{NEt_3}$. The different quenching patterns of the formations of **6** and **7** by methanol also support different pathways for the furanyl and pyranyl ether formations. Among many possible conformations of the proton-transfer species **11**, two extreme cases of conformations are depicted intuitively as **11a** and **11b**; each conformation (and its proximate analogues) undergoes its own pathway to afford either **3** or **4** and shows dissimilar reactivities toward a base. This assumption also implies that conformations outside the domain of these two excited-state molecular assemblies would undergo emissive or radiationless decays as suggested by low quantum yields of the photocyclization. The presence of dual excited-state complexes as well as the requirement of a high degree of geometric controls over a chemical transformation initiated by ESPT is also exhibited in a nitrosation caused by the intermolecular ESPT from singlet excited-state 1-naphthol to NND.[15] In this nitrosation reaction, $\mathrm{NEt_3}$ has been used as a competitive proton acceptor to demonstrate similar ESPT to NND. Obviously, NND also quenches the photocyclization of **1** by a similar ESPT mechanism to form the self-nitrosation product **10**; this provides supporting evidence for the mechanism proposed in Scheme II.

An excited-state electron-transfer mechanism[5] was suggested to explain similar photocycloadditions of allylphenols. $\mathrm{NEt_3}$ is a good electron donor[23] and its participation as such has to be seriously considered. However, an electron-transfer mechanism is less likely, since even if mechanistically $\mathrm{NEt_3}$ participates in electron-transfer quenching, avenues are available for the formation of expected furanyl and pyranyl ethers. Furthermore, the successful Stern–Volmer correlations of the quenchings of the product formations by methanol have clearly demonstrated that an electron-transfer mechanism is not likely to be involved since methanol and tetrahydrofuran possess high ionization potentials (10.85 and 9.42 eV) and do not donate an electron readily.[24] It is speculated that appropriate phenolic compounds in nature may biogenetically follow ESPT pathways to photolytically cyclize to give furan or pyran derivatives in a hydrophobic environment; the transformation of cannabidiol to tetrahydrocannabinol may be mentioned as a possibility in this type of biogenetic photocyclization.

In conclusion, the primary photoprocess of allylnaphthols **1** and **2** involves the singlet excited-state proton transfer leading to two types of identifiable excited-state proton-transfer complexes that collapse to pyranyl and furanyl ethers, respectively. However, the light-promoted dehydrogenation of dihydrofuranyl ethers **3** and **6** and the formation of naphthalene from **2** are two concurring side reactions and their mechanisms remain obscure.

Experimental Section

Equipment, solvents, and general conditions for this publication were the same as those stated in ref 15.

Photolysis of Allylnaphthols 1 and 2. A benzene solution (180 mL) of **1** (400 mg, 2.2 mmol) placed in a Hanovia-type reactor was irradiated at ca. 15 °C under nitrogen with a 450-W Hanovia lamp for 1.5 h. The residue from the photolysate was chromatographed on silica gel (200–60 mesh) to separate into major fractions. These fractions were analyzed by GC using 1-nitronaphthalene as the internal standard, and yields were calculated to be (30% **3**), (4% **4**), and (3% **5**). Each fraction was chromatographed again on silica gel using petroleum ether as eluant to afford an analytical sample of products **3** and **4**. The spectroscopic data of these compounds are shown in Tables II and III and are comparable to those reported.[17-19]

A benzene solution (210 mL) of **2** (390 mg, 2.1×10^{-3} mol) was photolyzed and worked up as above to give a crude product. GC analysis of the crude product against the internal standard showed the yields as (11% **6**), (13% **7**), (1% **8**), and 4% (naphthalene, **9**). These compounds were isolated by chromatography and characterized (Tables II and III).[17-19] Naphthalene was also isolated and showed an IR spectrum identical with that of an authentic sample.

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Table II. ^{1}H NMR Parameters of the Products in $CDCl_3$

compd	chemical shifts, ppm
3	1.56 (d, 3 H, J = 6.5 Hz), 3.01 (dd, J = 5.9 Hz, J = 14.3 Hz, 1 H), 3.47 (dd, J = 7.1 Hz, J = 14.3 Hz, 1 H), 4.7~5.30 (m, 1 H), 7.30~7.81 (m, 6 H)
4	~2.01–2.23 (m, 2 H), 2.90 (t, 2 H, J = 6.5 Hz), 4.38 (t, 2 H, J = 5.17 Hz), 7.09~8.10 (m, 6 H)
5	2.50 (d, 3 H, J = 1 Hz), 6.45 (q, 1 H, J = 1 Hz), 7.40~8.30 (m, 6 H)
6	1.56 (d, 3 H, J = 6.2 Hz), 2.97~3.76 (ABX, AB part, J_{AX} = 9.53 Hz, J_{BX} = 7.64 Hz, J_{AB} = 15.4 Hz, 2 H), 5.03~5.26 (ABX, X part, m 1 H), 7.05~7.86 (m, 6 H)
7	2.07~2.30 (m, 2 H), 3.08 (t, J = 6.5 Hz, 2 H), 4.28 (t, J = 5.1 Hz, 2 H), 7.02~7.86 (m, 6 H)
8	2.57 (d, J = 1 Hz, 3 H), 6.88 (q, J = 1 Hz, 1 H), 7.50~7.63 (m, 6 H)
10	3.35–3.37 (m, 2 H), 5.19 (m, 1 H), 5.22 (m, 1 H), 5.97 (m, 1 H), 7.88 (m, 2 H), 7.83 (s, 1 H), 8.18 (m, 2 H), 8.33 (s, 1 H, D_2O exch)

Table III. FT–IR and Mass Spectral Data of the Products

compd	m/e (%, fragment)	ν_{max}, cm^{-1}
3	184 (100, M$^+$) 169 (39, M – CH_3) 141 (45, M – C_3H_7) 115 (31)	3067 (s), 2982 (s), 2937 (s), 1580 (m), 1381 (s), 1279 (s), 1070 (s)
4	184 (100, M$^+$) 169 (10, M – CH_3) 141 (10, M – C_3H_7) 128 (35, M – C_3H_4O)	3061 (s), 2982 (s), 2950 (s) 1579 (m), 1402 (s), 1371 (s), 1207 (s)
5	182 (100, M$^+$) 181 (88, M – H) 152 (27)	3069 (s), 2935 (m), 1598 (m), 1385 (m), 1177 (s), 1084 (s)
6	184 (100, M$^+$) 169 (85, M – CH_3)	3065 (s), 2982 (s), 2934 (s), 1632 (m), 1246 (s)
7	184 (100, M$^+$) 169 (16.7, M – CH_3) 156 (34) 128 (53)	3071 (s), 2984 (s), 2876 (s), 1626 (m), 1599 (m), 1240 (s) 1096 (s)
8	182 (100, M$^+$) 181 (87, M – H) 152 (23)	3065 (s), 2934 (s), 1587 (m), 1383 (s), 1265 (s)
10	213 (23, M$^+$) 196 (100, M – OH) 182 (23, M – NO) 130 (60)	3260 (br), 1635 (s), 1600 (s), 985 (s), 975 (s), 768 (s)

Heating of a benzene solution containing **1** (or **2**, 100 mg) and p-toluenesulfonic acid (10 mg) for 10 h gave **3** (or **6**) in almost quantitative yields.

Photodehydrogenation of 6. The following three solutions degassed under N_2 and sealed were photolyzed in a merry-go-round with Rayonet 3000-Å lamps for 4 h. The solution no. 1 contained **6** and **7** (1.1×10^{-2} M each) in benzene; the no. 2 solution contained **6** and **7** (1.1×10^{-2} M each) in addition to **2** (2.2×10^{-2} M); the solution no. 3 contained **2** (2.2×10^{-2} M). The GC peak areas of each compound before and after irradiation (separated by arrows) normalized against the internal standard are given here.

	6	**7**	**8**
soln 1	3.34 → 3.33	3.96 → 4.11	0.0 → 0.0
soln 2	3.53 → 3.46	4.13 → 4.17	0.0 → 0.18
soln 3	0.0 → 0.52	0.0 → 0.50	0.0 → 0.0

A similar experiment was carried out with **3** and **1**, giving comparable results.

Dissociation Constant Measurement. The acidic solution contained **1** (or **2**) 1.0×10^{-4} M and [HCl] = 1 to 0.25 N in methanol–H_2O (9:1 v/v). The basic solution contained **1** (or **2**) 1.0×10^{-4} M and [NaOH] 0.2 N in the same solvent mixture. The pH 9 solution contained **1** (or **2**) 1.0×10^{-4} M and NaH_2BO_3–H_3BO_3 buffer solution. The UV spectra of these solutions were taken, and the intensities at the maxima were used to calculate pK values according to the standard procedure.[25] These solutions were also used to take fluorescence spectra from which the 0–0 bands were located for naphthols and naphtholates emission. The pK* values were calculated according to the method of Vander Donckt.[26]

$$pK \text{ (ground state)} = pK^* \text{ (singlet excited state)} + 2.1 \times 10^{-3}(\Delta\nu)$$

where $\Delta\nu$ is the difference in wavenumbers between the 0–0 band of the naphthols and naphtholates. The 0–0 band was calculated as the average of the absorption and fluorescence maxima in cm^{-1} for the solution in strongly acidic and basic conditions. The same procedures were applied to 1-naphthol to give pK = 9.27 and pK* = 2.1.

Quantum Yield Measurements and Quenching Experiments. Solutions containing an allylnaphthol (1.2×10^{-2} M) in the presence or absence of a quencher were placed in quartz tubes and degassed by passing in nitrogen for about 10 min. These tubes were placed in a merry-go-round in a Rayonet reactor equipped with 3000-Å lamps. For solutions of **1**, the irradiation time was 7 min to cause <15% conversions and for solutions of **2**, 75 min to cause <20% conversions. A solution of benzophenone (0.05 M) and benzhydrol (0.1 M) was irradiated for 5 min to serve as an actinometer.[15] The products were analyzed with a GC using 1-nitronaphthalene as an internal standard, and the absolute yields were calculated from the preconstructed calibration curves of each product against the internal standard.

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