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Investigation of the Photo-Fries Rearrangements of Two 2-Naphthyl Alkanoates by Experiment and Theory. Comparison with the Acid-Catalyzed Reactions

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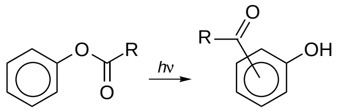
A detailed investigation of the photochemistry of 2-naphthyl acetate (**1a**) and 2-naphthyl myristate (**1b**) has been conducted under a variety of conditions. Factors related to the reactions such as temperature and solvent type have been explored. The results, most easily interpreted by photo-Fries type processes, are contrasted with those from the Lewis-acid catalyzed (dark) Fries reactions of **1a**. They are also compared to the predictions of semiempirical and *ab initio* calculations using 2-naphthyl propanoate (**1c**) and species derived from it as models. Unsuccessful triplet sensitization experiments with benzophenone and calculations point to the excited singlet states of **1** as the immediate precursor to the acyl/2-naphthoxy radical pairs that recombine to form keto intermediates **2**, reform **1**, or diffuse apart and eventually yield 2-naphthol (**4**); enolization of **2** results in the isolated rearrangement products, *n*-acyl-2-naphthols (*n*-**3**). Static and dynamic fluorescence studies provide some insights into the nature of the lysis process. Irradiation of a mixture of appropriately labeled derivatives of **1** led to none of the expected "cross-over" products, indicating that the intermediates **2** arise from recombination of radical pairs from the same parent molecule. Irradiation of **1b** in ethanol and 1-octanol provides no evidence for the intermediacy of dodecylketene and supports out-of-cage mechanisms as the exclusive source of **4**. There are indications of subtle solvent effects and a conformational dependence on the distribution of photoproducts.

Introduction

The photo-Fries rearrangements of aromatic alkanoates (eq 1) have been investigated for many years.[1] Phenyl esters are known to provide products like those from the Lewis-acid-catalyzed (dark) Fries reactions. The mechanisms of the dark- and radiation-induced Fries processes are very different, however. Whereas the dark reaction involves ionic species,[2] the photoreactions proceed via radical intermediates.[3,4] Electronic excitation is followed by homolytic cleavage from what is usually an excited singlet state to yield aryloxy and acyl radical pairs. They can combine to form the starting ester or one of several isomeric keto intermediates, or diffuse apart and form phenols (plus other products from the acyl portion).



(1)

The major photoproducts from 1-naphthyl alkanoates are 2- and 4-alkanoyl-1-naphthols and 1-naphthol.[1,5,6] Less is known about the photo-Fries rearrangements of 2-naphthyl alkanoates, but the photochemistry of the acetate (**1a**),[7,8] benzoate,[9] and thioacylates[10] has been investigated somewhat. In solvents like hexane and benzene, the products from **1a** are reported to be 1-acetyl-2-naphthol (1-**3a**), 6-acetyl-2-naphthol (6-**3a**), and 2-naphthol (**4**).[7] The Lewis-acid-catalyzed Fries rearrangement of **1a** affords 1-**3a** as the preponderant product at 70 °C.[11]

Here, we present a detailed investigation of the photochemistry of **1a** and a longer chained homologue, 2-naphthyl myristate (**1b**). Factors related to the rearrangements such as temperature and solvent type are explored. The results are contrasted with those from the Lewis-acid-catalyzed (dark) Fries reactions of **1a** and compared with the predictions of semiempirical and *ab initio* calculations using 2-naphthyl propanoate (**1c**) and species derived from it as models. The general features of the radiation-induced processes are summarized in Scheme 1.

The extreme sensitivity of these rearrangements to local environment and the nature of the acyl group should make **1** a very attractive probe of the size, shape, polarity, and wall stiffness of the cavities in which it reacts.[12] Before such environmental factors can be analyzed in detail, the reactivity of the probe must be understood.

⊗ Abstract published in *Advance ACS Abstracts*, February 15, 1996.

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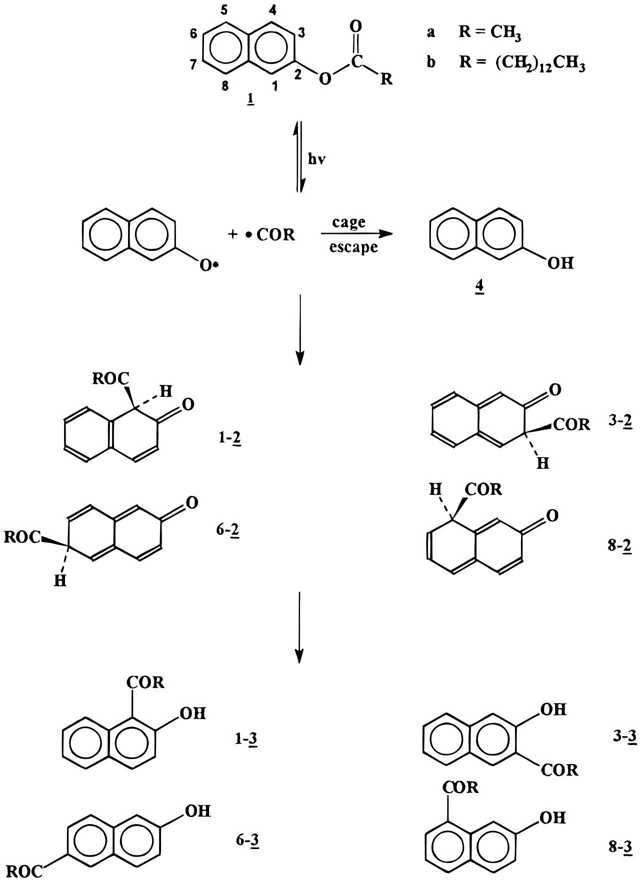
The objective of this study is to provide information necessary to gain that understanding.

Scheme 1



Results

Syntheses of Naphthyl Esters and Their Photo-Fries Products. Each of the expected photoproducts from irradiation of **1a** and **1b** (Scheme 1; by HPLC analyses, **4** and the isomers of **3** represent $>$90% of the aromatic photoproducts in almost all of the experiments) was synthesized independently in $>$95% purities (HPLC).

1-Acetyl-2-naphthol was prepared by the Lewis-acid-catalyzed Fries rearrangement of 2-naphthyl acetate.[13] 3-Acetyl-2-naphthol was made from the reaction of 2-hydroxy-3-naphthoic acid with methyllithium[14] rather than using a more involved procedure.[15] 8-Acetyl-2-naphthol was separated as one of the products from the Lewis-acid-catalyzed Fries rearrangements of 2-naphthyl acetate at 150 °C (*vide infra*) and was also synthesized by a reported method.[16] 6-Acetyl-2-methoxynaphthalene was demethylated by fusion with pyridinium hydrochloride.[17] A different workup procedure led to product, mp 171−172 °C (lit.[18] mp 170−171 °C), whose ^{1}H NMR spectrum in the aromatic region was very similar to that of 2-hydroxy-6-naphthoic acid.

Table 1. Relative Yields of Fries Products from 1a or 1-3a and AlCl$_3$ upon Heating for 5 h

		relative product yields, %						
substrate	*T* (°C)	**1a**	1-**3a**	3-**3a**	6-**3a**	8-**3a**	**4**	other[a]
1a	70	44.2	44.4	0.1	0.6	*b*	11.2	0.1
1a	150	4.2	45.2	7.9	2.8	2.5	27.9	9.5
1-**3a**	150	2.8	47.5	8.6	0.7	4.5	31.4	4.6

[a] Unidentified peaks; yields assume a molar extinction coefficient of 15000. [b] Not detected.

2-Naphthyl myristate was prepared by modifying a procedure of Kreisky.[19] 1-Myristoyl-2-naphthol and 6-myristoyl-2-naphthol were prepared by modifications of reported procedures for syntheses of 1-acetyl-2-naphthol[13] and 6-acetyl-2-naphthol,[17] respectively. 3-Myristoyl-2-naphthol was prepared by the reaction of 2-hydroxy-3-naphthoic acid with a mixture of *n*-butyllithium and 1-bromotridecane. The key step in the synthesis of 8-myristoyl-2-naphthol is the preparation and decomposition of the diazonium salt of 2-amino-8-myristoylnaphthalene *in glacial acetic acid* followed by the hydrolysis of 8-myristoyl-2-naphthyl acetate; use of aqueous sulfuric or hydrochloric acid as solvent yielded none of the desired product, probably due to solubility and secondary reaction problems.

^{1}H NMR, FT-IR, and mass spectra of **1a**, **1b**, and their photo-Fries products and tables of molar extinction coefficients of the same molecules in various solvents at 254 nm (the wavelength of detection by HPLC) are included as supporting information.

Acid-Catalyzed Fries Reactions of 2-Naphthyl Acetate.[7,11,18] At 70 °C and in the absence of solvent, the predominant Fries product from **1a** is known to be 1-**3a** when AlCl$_3$ is the acid.[7,11] At 120 °C, the major product remains 1-**3a**, but large amounts of **4** and smaller amounts of 6-**3a** and 8-**3a** were detected also.[7] Conspicuously absent from the mix of isolated products is 3-acetyl-2-naphthol. We have repeated these experiments, analyzing the products by a more sensitive technique, HPLC, and have heated **1a** or 1-**3a** and AlCl$_3$ at 150 °C (Table 1). The results are qualitatively consistent with those found previously except for the presence of 3-**3a** and some minor unidentified species.

Irradiations of 1. General Considerations. Each of the isomers of **3** absorbs beyond 300 nm more strongly and to longer wavelengths than **1**. The absorption spectra of the precursor isomers, **2**, also overlap that of **1** in the regions of excitation.[20] Since prolonged irradiation (to $>$25% conversions) of **1b** in N$_2$-saturated *tert*-butyl alcohol resulted in loss of some 1-**3b**, conversions were kept low in all of the analytical experiments. In spite of these precautions, some secondary photolyses may have occurred.

Irradiations of **1b** in N$_2$-saturated purified hexane or *tert*-butyl alcohol at 254, 313, and 318 nm were conducted since there are indications of conformationally-dependent photochemistry (*vide infra*) that might be detected as wavelength-dependent protoproduct distributions. Although only 1-**3b** and 6-**3b** were analyzed, the results in Table 2 show no discernible wavelength dependence. In hexane, the low yields of 6-**3b** are responsible for the dispersion of the ratios. On the basis of these observations, most samples of **1a** and **1b** were excited at $>$300 nm, using only Pyrex glass and water as filters.

Photochemistry of 2-Naphthyl Acetate. The product distributions from irradiations of 2-naphthyl acetate

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Table 2. Wavelength Dependence of 1-3b/6-3b from Irradiations of 2.2×10^{-3} M 1b in N_2-Saturated *tert*-Butyl Alcohol and Purified Hexane at 25 °C

solvent	λ (nm)	% conv	1-**3b**/6-**3b**
tert-butyl alcohol	318	10(1)	6.1
	313	14(1)	6.7
		11(1)	6.1
		29(1)	10
	254	7(1)	6.1
		5(1)	6.1
hexane	313	14(2)	19
		7(3)	49
		18(2)	32
		7(3)	32
	254	6(2)	32
		8(2)	24
		14(2)	32

Table 3. Relative Photoproduct Yields from Irradiations (λ > 300 nm) of ca. 5×10^{-3} M 2-Naphthyl Acetate in N_2-Saturated Solvents at 25 °C

solvent	%conv	1-**3a**	3-**3a**	6-**3a**	8-**3a**	**4**
tert-butyl alcohol	16(2)	34(1)	15(1)	14(1)	*a*	37(3)
hexane[b]						
spectrograde	11(2)	57(2)	16(1)	5(3)	*a*	21(2)
purified	6(2)	19(1)	19(1)	7(1)	*a*	54(3)
purified (0 °C)	6(2)	10(1)	19(1)	9(1)	*a*	63(3)
wet/purified	7(2)	31(1)	38(1)	8(1)	*a*	24(2)
wet/purified	27(2)	8(1)	9(1)	5(4)	*a*	79(3)
acetonitrile	14(1)	41(1)	14(1)	7(1)	*a*	39(3)

[a] Below detection limit. [b] See text.

in a variety of solvents are listed in Table 3. A typical HPLC chromatogram of a reaction mixture is shown in Figure 1. The small unidentified peaks have not been included in the relative yield calculations unless indicated otherwise. It is not known whether some are from the 4-, 5-, and 7-isomers of **3a**. None has the retention volume of 2-methoxynaphthalene.

In hexane, irradiation resulted in the formation of a yellow solid (and a yellow-tinged solution) that consisted primarily of **1a** and **4**, but also included small amounts of the 1-, 3-, and 6-isomers of **3** (or their precursors, **2**). Since the liquid component contained the same molecules, but **4** was present in much smaller amounts, the yellow color may have been from a complex between molecules of **1a** and **4**. However, a mixture of solid **1a** and **4** in hexane did not form a yellow solid that differed from the appearance of **4**, itself, when heated to 50 °C and cooled. Before HPLC analyses were performed on aliquots, a drop of ethyl acetate was added to the postirradiation mixtures to dissolve completely the solids. This procedure ensures good precision, but consecutive runs under seemingly identical conditions did not always provide consistent results. Our inability to control the rate of formation of the yellow solid is one probable source of the lack of reproducibility. No precipitate was detected when **1a** was irradiated in the other solvents listed in Table 3 or in cyclohexane.

A significant amount of the previously unreported 3-**3a** is formed in all of the solvents and a small amount of 8-**3a** is detected in cyclohexane (Table 4). As expected,[7] 1-**3a** is the major rearrangement product, but the cage-escape product, **4**, is in comparable yields in the more polar solvents.

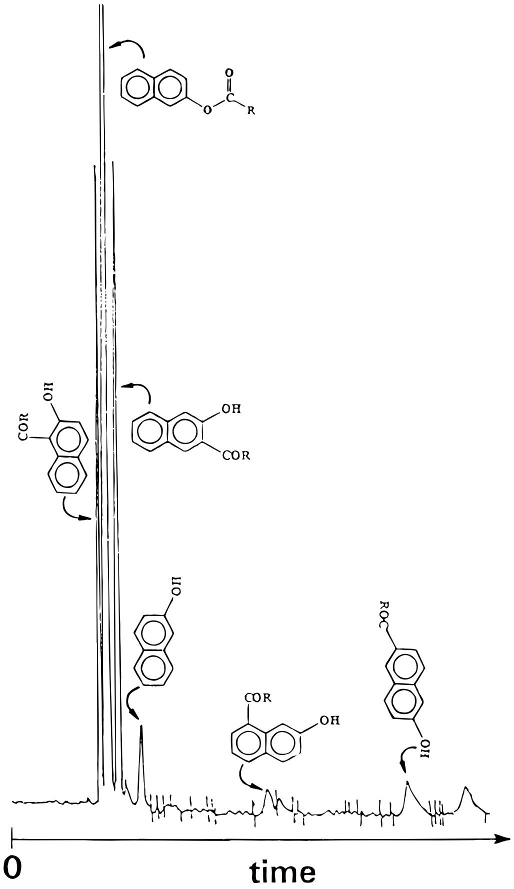

Figure 1. HPLC chromatogram from irradiation (λ > 300 nm) of ca. 5×10^{-3} M **1a** in cyclohexane (eluent: 1/15 (v/v) ethyl acetate/hexane). Note that there are several small unidentified peaks.

Table 4. Relative Photoproduct Yields from Irradiation (λ > 300 nm) of ca. 5×10^{-3} M 2-Naphthyl Acetate in N_2-Saturated Cyclohexane[a]

T/°C	% conv	1-**3a**	3-**3a**	6-**3a**	8-**3a**	**4**
8	15(2)	25(1)	18(1)	2(1)	7(1)	48(2)
10	12(1)	29(1)	22(1)	2(1)	8(1)	38(2)
15	13(1)	32(1)	20(1)	2(1)	12(1)	33(1)
16	13(1)	36(2)	27(1)	1(1)	6(1)	29(2)
20	13(1)	36(1)	23(1)	1(1)	8(1)	31(2)
23	18(4)	38(2)	18(1)	1(1)	5(1)	40(2)
26	15(2)	41(2)	18(1)	1(1)	5(1)	35(1)
32	15(2)	35(1)	12(1)	3(1)	4(1)	47(2)
50	23(3)	50(2)	18(1)	1(1)	6(1)	26(1)
25[b]	7(2)	52(3)	11(1)	3(1)	4(1)	30(2)

[a] Mallinckrodt, SpectroAR grade. [b] Water-saturated.

Carefully purified hexane as solvent led to some striking differences in photoproduct distributions. Although the relative yields of 3-**3a** and 6-**3a** are unaffected, there is a marked increase in **4**, apparently at the expense of 1-**3a**. Since the hexane purification procedure (see Experimental Section) removes molecules with unsaturated and hydroxy groups, the concentration of easily abstractable H-atoms is decreased and the lifetimes of radicals outside their initial solvent cages may be increased.

The results in hexane are further complicated by the observation that photoreaction nearly ceases after 6−8% conversion of **1a**. Qualitatively, reaction is less efficient in the purified than in spectrograde solvent. We suspect that this behavior is related to internal filtering effects by the yellow complex. In both cyclohexane, where the yellow color is not perceived, and hexane, where it is, lower temperatures results in more **4** and less 1-**3a**, but the yields of 3-**3a** and 6-**3a** (and of 8-**3a** in cyclohexane) are virtually unchanged (Tables 3 and 4).

Table 5. Product Distributions from Irradiation ($\lambda > 300$ nm) of ca. 5×10^{-3} M 2-Naphthyl Myristate in N_2-Saturated Solvents at 25 °C

solvent	% conv	1-**3b**	3-**3b**	6-**4b**	8-**3b**	**4**
tert-butyl alcohol	9(2)	64(2)	14(1)	8(1)	3(2)	12(5)
	30(2)	57(2)	12(1)	11(1)	5(2)	9(5)
	39(2)	65(2)	13(1)	11(1)	3(2)	16(5)
hexane						
a	5(3)	43(2)	32(2)	8(1)	*e*	15(6)
a	3(2)	52(2)	24(1)	9(1)	*e*	24(6)
b	4(2)	50(3)	35(2)	1(.5)	*e*	14(5)
b	3(1)	52(2)	31(1)	1(.5)	*e*	16(5)
c	9(2)	63(2)	21(1)	7(1)	*e*	<10
$C_{21}H_{44}$[d]	15(2)	22(1)	23(1)	6(1)	*e*	50(2)
	18(2)	20(1)	19(1)	6(1)	*e*	55(3)

[a] Purified. [b] Wet/purified. [c] Spectrograde/45 °C. [d] 45 °C. [e] Too small yield to be detected.

The results in Table 4 were obtained using one bottle of spectrograde cyclohexane. Due to the absence of yellow precipitate, the data could be reproduced with good precision. However, when a different batch of cyclohexane was employed, the results were internally reproducible again, but different from those reported. Especially, the ratios of 1-**3a** and **4** were altered.

When water-saturated, purified hexane was used as solvent (Table 3), photoreaction continued beyond the 6−8% limit of the dry solvent, even though the yellow solid still formed. However, the distribution of photoproducts was much more sensitive to the extent of reaction in the wet hexane than in the dry: at lower conversions, the photoproduct mixture is reminiscent of that in spectrograde hexane; at higher conversions, the product distribution is like that in dry purified hexane. The photo-Fries products **3** are formed essentially during the early periods of irradiation. Thereafter, **4** is produced in large part.

The fact that the yield of **4** is unexceptional (although that of 1-**3a** is somewhat elevated) in moist cyclohexane (Table 4) and the lack of spectroscopic evidence for the association of water and **1a** molecules in the ground or excited singlet states argue against the introduction of a photohydrolysis pathway in wet hexane. For instance, the UV/vis absorption spectra of **1a** in wet and dry hexane are indistinguishable, and the fluorescence decays of **1a** in wet and dry hexane are single exponential and correspond to a singlet state lifetime of 23.4 ns (*vide infra*). In spite of these results, water may associate with molecules of **1a** and restrict the selection of conformations that the excited states may adopt. Regardless, the absence of a clear *increase* in the yields of **4** when the solvent is changed from an aprotic nonpolar solvent to a protic, polar one (N.B., hexane and *tert*-butyl alcohol in Table 3) provides strong evidence against a heterolytic mechanism for the photo-Fries rearrangements involving naphthyloxy anions and acyl cations.

Photochemistry of 2-Naphthyl Myristate. The relative photoproduct yields from irradiation of 2-naphthyl myristate in *tert*-butyl alcohol and purified hexane are summarized in Table 5. Typical HPLC chromatograms are shown in Figure 2. The yields of **4** have large error limits because of their small integration areas in the chromatograms.

In *tert*-butyl alcohol, 1-**3b** is the principal photo-Fries product, and comparable amounts of 3-**3b** and 6-**3b** are present. Of additional interest is the formation of 8-**3b** in measurable amounts. Irradiation in hexane afforded similar amounts of 1-**3b** and 3-**3b** without evidence for the yellow solid observed during analogous irradiations of **1a**.

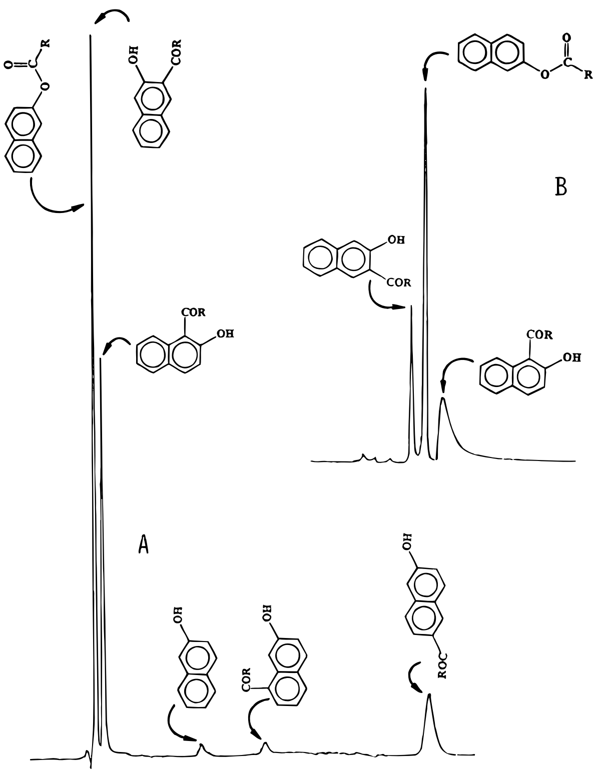

Figure 2. HPLC chromatogram from irradiation ($\lambda > 300$ nm) of ca. 5×10^{-3} M **1b** in *tert*-butyl alcohol (eluent: 1/20 (v/v) ethyl acetate/hexane). (B) 3-**3b** and **1b** can be separated using ethyl acetate/hexane (1/100, v/v) as eluent.

Saturation of hexane with water led to yields of 6-**3b** that were barely detectable, but the relative yield of **4** is similar to that found in dry hexane or in *tert*-butyl alcohol. A possible hypothesis for the loss of 6-**3b** is that isolated (groups of) water molecules hold the 2-naphthoxy and myristoyl radicals from **1b** in orientations that disfavor the migration necessary to form 6-**2b** (and, eventually, 6-**3b**). There is no indication of photohydrolysis of **1b** but, as suggested with **1a**, even traces of water may play an important mechanistic role (based upon conformational constraints) in paraffin solvents.

At 45 °C in spectrograde hexane, the yield of 1-**3b** increased slightly and the amount of **4** decreased in comparison to results from room temperature experiments. In the more viscous solvent, heneicosane ($C_{21}H_{44}$), at 45 °C, **4** (that *should* be disfavored on the basis of diffusion rates[21]) is formed in yields that exceed those in hexane or *tert*-butyl alcohol while the amount of 1-**3b** is much smaller.

Discussion

Aspects of the Thermal, Acid-Catalyzed Rearrangements of 1a. *If* Lewis acid catalysts were not complexed to the thermal Fries products from **1**, the thermodynamic preferences for formation of the various isomers of **2** (and **3**) would be gauged by their heats of formation (ΔH_f) since the entropy contents of the various isomers should be similar. However, the catalysts *do*

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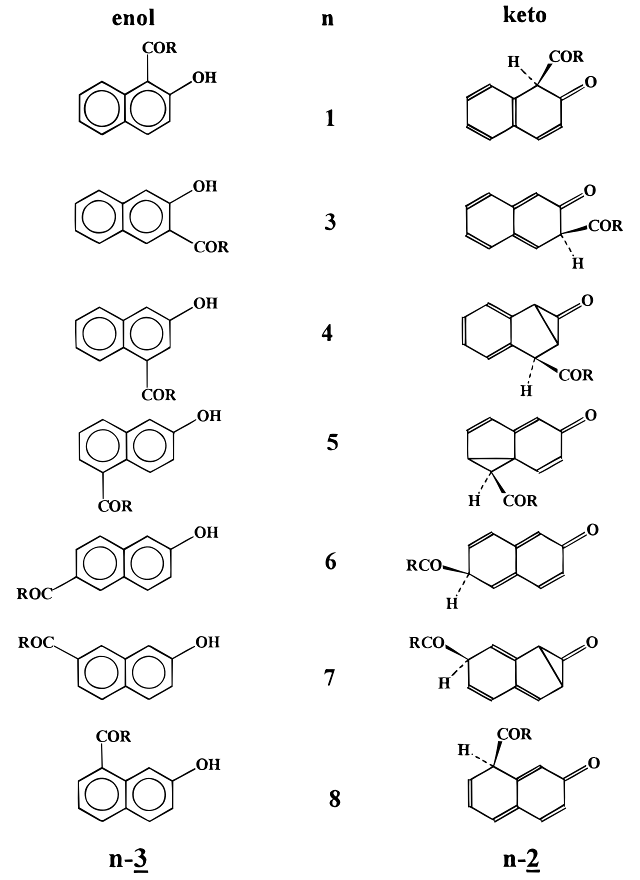

Figure 3. The possible positional isomers of *n*-**2** and *n*-**3** with the most stable electron-paired bonding structures.

Table 6. Heats of Formation (kcal/mol) of *n*-Propanoyl-2-naphthol (product *n*-3) and the Corresponding Keto Intermediates (*n*-2) by the MNDO-AM1 Method[22]

n	*n*-**2**[a]	*n*-**3**[a]
1	−34.2	−82.3
3	−21.5	−94.5
4	0.1 (20.1[b])	−86.5
5	20 (22.2[b])	−87.7
6	−19.4	−100.1
7	13.0 (22.2[b])	−99.8
8	−18.2	−87.6

[a] See Figure 5 for structures. [b] Singlet biradical forms in Figure 4.

remain complexed to the products.[2] In spite of this, the course of the thermal reaction of **1a** seems to be described qualitatively by the calculated heats.

Heats of formation for the isomeric **2c** and **3c** (from the hypothetical precursor, 2-naphthyl propanoate (**1c**)) were calculated using the MNDO-AM1 approach.[22] Initial energy minimization was on structures in which all of the ring carbon atoms are constrained to remain in a common plane (Table 6). A second calculation allowed one or more of the carbon atoms to move from the plane (Figures 3 and 4). The planarity constraint forces the 4-, 5-, and 7-isomers of **2** to exist as biradicaloid species. The ΔH_f values of the "relaxed" geometries (Figure 4) are always lower than the planar ones for these isomers, but are at least 18 kcal higher than the heats calculated for the planar 1-, 3-, 6-, and 8-isomers; the latter are the isomers of **3a** that are identified as Fries products of **1a**. They are also the products expected based upon valence bond structures for their precursors **2**.

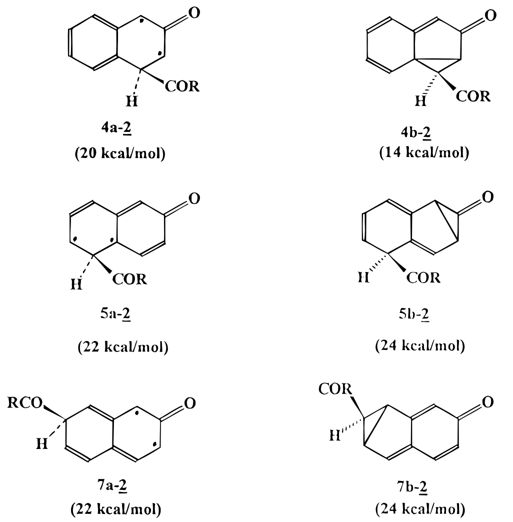

Figure 4. Structures and calculated heats of formation of 4b-**2c**, 5b-**2c**, and 7b-**2c** assuming the presence of three-membered rings and higher energy biradicals (4a-**2c**, 5a-**2c**, and 7a-**2c**) in which only one mesomeric form is shown for each is shown. **R** = C_2H_5.

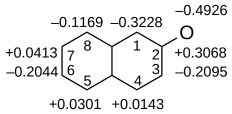

Figure 5. Electron distribution at key atoms of the 2-naphthoxy anion as calculated by the MNDO-AM1 approach.

Since all of the isomers of **3** are calculated to be significantly more stable than their keto forms **2** (Table 6) *and* than **1**, the driving force is to convert **2** to **3**, *but not back to* ***1***. It is reassuring that 1-**3**, the major rearrangement product when **1** undergoes the Fries rearrangement under acid-catalyzed *or* photoinduced conditions, emanates from 1-**2**, the keto isomer with the lowest ΔH_f.

Since the Lewis-acid-catalyzed Fries reaction involves electrophilic attack by an acyl cation on a 2-naphthoxy anion (or its Lewis acid conjugate),[2] the *kinetic* preference for formation of the various isomers of **2** should be roughly proportional to the electrostatic attraction of an acyl cation for each of the carbon atoms of the naphthyl part; as noted above, this argument assumes that entropic (i.e., steric) factors are a minor or nearly constant component of the overall energy changes. The preferences are indicated experimentally by the relative yields of the isomers of **3** when the reaction is conducted at lower temperatures and short reaction times, where the isomers of **2** (or **3**) do not interconvert.

The electron densities on the nonfused carbon atoms of a 2-naphthoxy anion were calculated by the MNDO-AM1 method (Figure 5). They lead to the same predictions as derived from the heats of formation: 1-**2** is the keto isomer preferred on the basis of electrostatic attraction, but the 3-, 6-, and 8-isomers are also expected to be formed at slower rates. The fact that the latter three are, but only at higher reaction temperatures, is consistent with greater kinetic control at 70 °C in which **1a** is converted directly to the various isomers of **2a**. However,

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[22] (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899, 4907. (b) Dewar, M. J. S.; Zoebisch, E. G.; Steward, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

the observation that **1a** and 1-**3a** yield essentially the same product mix favors a mechanism closer to thermodynamic control at 150 °C.[23]

The Photo-Fries Reactions of 1. A Mechanistic Overview (Scheme 1). Excitation of **1** is followed by homolytic cleavage of the aryloxy–acyl bond to yield a radical pair in a cage. The pair can reform the cleaved bond (yielding **1** in an energy-wasting step), recombine so that the acyl carbon adds to one of the 7 carbon atoms of the naphthyl that bears a hydrogen (yielding a keto isomer **2**), or diffuse apart (allowing the 2-naphthoxy radical to abstact a hydrogen atom from solvent to yield 2-naphthol **4**, and the acyl radical can be trapped, also[10]). As with the acid-catalyzed Fries rearrangements, the isomers of **2** tautomerize to the corresponding isomers of **3** in a dark reaction. At low conversions of **1**, where competitive excitation by **2** or **3** can be discounted, it is again reasonable to assume that the isomers of **2** neither interconvert nor revert to **1** and that the relative yields of **3** are determined in the step leading to **2**.

Of the seven possible isomers of **3**, only the four expected by valence bond considerations with **2** and favored by theoretical calculations (*vide infra*) have been detected as major rearrangement products. They are 1-**3**, 3-**3**, 6-**3**, and 8-**3**. The cage-escape product **4** is also an important contributor; no attempt to isolate the eventual products from the acyl radicals has been made. The 4-, 5-, and 7-isomers of **3**, if formed, must be present in very small amounts.

Absent, also, were 2-methoxynaphthalene and 2-(tridecyloxy)naphthalene, the ethers that could arise if the acyl radicals from **1a** and **1b**, respectively, were to decarbonylate in-cage and then readd to the oxygen atom of the 2-naphthoxy radical. The relatively slow rates of decarbonylation of alkanoyl radicals at and near room temperature (10^5–10^6 s^{-1})[24] due to substantial activation energies (ca. 10–20 kcal/mol)[24] apparently cannot compete with the other in-cage processes of the radical pair.

A possible alternative pathway for the formation of **4** is in-cage disproportionation of an initial radical pair in which 2-naphthoxy abstracts a hydrogen atom from C2 along the acyl chain to yield a ketene.[21,25] To test this hypothesis, **1b** was irradiated in absolute ethanol and 1-octanol at 25 °C and 45 °C. Careful searches by gas chromatography for ethyl myristate and octyl myristate, the products expected from addition of an alcohol to dodecylketene, were unsuccessful. The absence of the alkyl myristates does not constitute absolute proof that dodecylketene was not present since there is a possibility, although an unlikely one,[4] that it reacted exclusively with **4** in the cage to reform **1b**. Even if this is the case, we can use **4** as a monitor of the radical pairs that escape from the cage in which they were formed.[26]

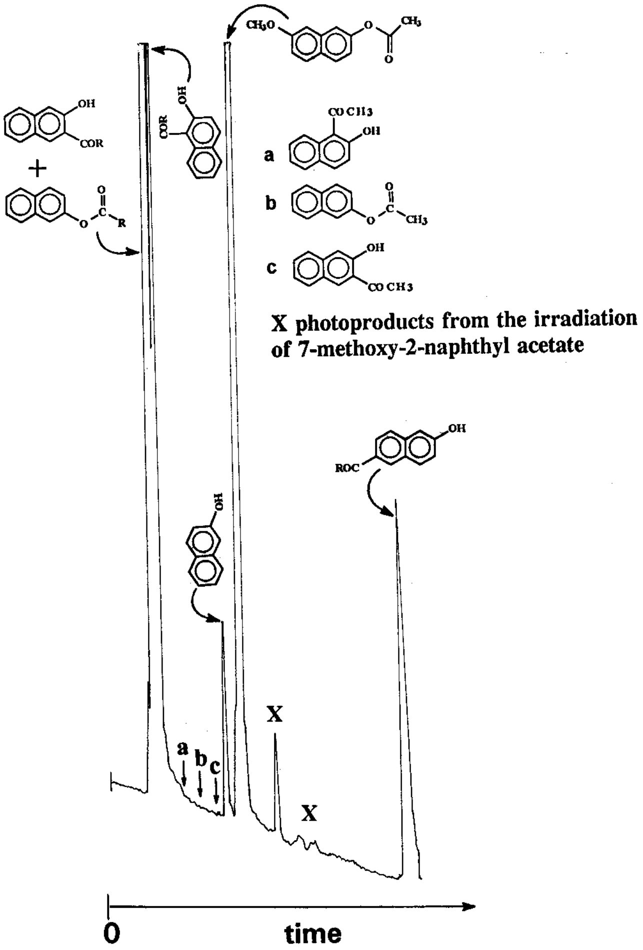

Figure 6. HPLC chromatogram from irradiation ($\lambda > 300$ nm) of ca. 5×10^{-3} M **1b** and ca. 5×10^{-3} M 7-methoxy-2-naphthyl acetate in *tert*-butyl alcohol. The a, b, and c arrows indicate the retention times of the not-observed cross-over photoproducts.

An ancillary conclusion from the lack of alkyl myristates is that the original lysis of **1** is neither *hetero*lytic nor is it homolytic followed by electron transfer to yield a naphthoxy anion and an acyl cation (as in the thermal Fries reactions). These results are consistent with the aforementioned lack of the expected influence of solvent on the yields of **4** if ions were involved.

Cage-escaped radicals are not responsible for **2** (and therefore **3**) via intermolecular recombination processes.[7c] No "cross-over" photoproducts were detected when equimolar (and approximately equally absorbing) amounts of **1b** and 7-methoxy-2-naphthyl acetate were irradiated in *tert*-butyl alcohol. Although the HPLC chromatograms contain peaks from the photoproducts of **1b** and 7-methoxy-2-naphthyl acetate (when irradiated separately), they lack peaks corresponding to the expected major cross-over products, **1a**, 1-**3a**, and 3-**3a** (Figure 6); if out-of-cage formation of the **3** isomers were important, some of these should have been present. From their absence, the lack of naphthyl ethers, and the evidence against ketenes, we conclude that the sum of the yields of the **3** isomers is the portion of photoreaction occurring "in-cage".

Photolysis Considerations. As with phenyl esters[7] and 1-naphthyl alkanoates,[5,6] the first excited singlet state of 2-naphthyl alkanoates is the primary source of reaction. Attempted triplet sensitization of **1a** by benzophenone (E_T = 3.0 eV)[27] in N_2-saturated benzene solutions at >360 nm (where only benzophenone absorbs)

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[23] Olah, G. A. in *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley: New York, 1966; Vol. I, p 1.

[24] Vollenweider, J.-K.; Paul, H. *Int. J. Chem. Kinet.* **1986**, *18*, 791 and refs cited therein.

[25] (a) Ghibaudi, E.; Colussi, A. *Chem. Phys. Lett.* **1983**, *94*, 121. (b) Plank, E. D. A.; Ph.D. Thesis, Purdue University, 1966 as cited in ref 21.

[26] However, *one* of several explanations for the (contraintuitive) increase of **4** and decrease of 1-**3b** in heneicosane, at 45 °C (compare with results in hexane at 45 °C; Table 5) is that disproportionation is promoted in the viscous hydrocarbon above room temperature. If correct, the yield of **4** represents the sum of the pathways involving cage escape of the initially formed radical pairs *and* of ketene from disproportionation. Until the presence or absence of ketene is demonstrated definitively, we will assume that the disproportionation mechanism is not an important contributor to the fate of the radical pairs.

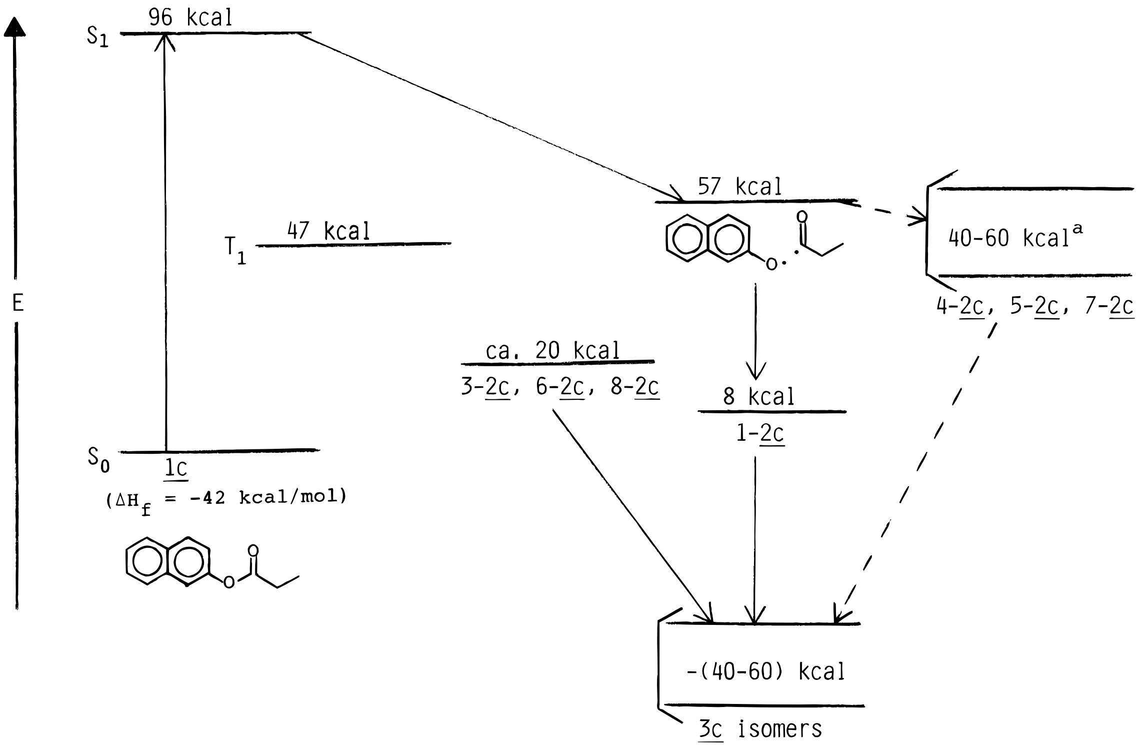


Figure 7. Calculated energies of 2-naphthyl propanoate (**1c**) and the species derived from it in a hypothetical photo-Fries reaction.

led to no detected photo-Fries products. MNDO-UHF calculations predict $E_T = 2.03$ eV for 2-naphthyl propanoate (**1c**); this seems a bit low since E_T of 2-ethoxynaphthylene is 2.6 eV.[28a] Regardless, irradiation of benzophenone should result in population of the triplet state of **1a** at a diffusion-controlled rate, and the experimental evidence indicates that it did: irradiation of solutions containing **1a**, benzophenone, and benzhydrol led to very little loss of benzophenone; irradiation of a solution containing only benzophenone and benzhydrol under equivalent conditions depleted almost completely the benzophenone.[29]

From the intersection points of normalized absorption and fluorescence spectra in hexane, the singlet excitation energy (E_S) of both **1a** and **1b** is estimated to be 90 kcal (3.9 eV); $E_S = 4.2$ eV is calculated by the MNDO-UHF method for the model compound **1c**. Since the calculated heats of formation for **1c** and the sum of the radical fragments (by MNDO-UHF also), 2-naphthoxy and propanoyl, are -1.8 and 2.47 eV, respectively, the initial bond dissociation energy from **1** is predicted to be 57 kcal from the ground state. This value is reasonable since the dissociation energies of $PhO-CH_2CH_3$ and of $PhCH_2-COCH_3$ are both 63 kcal.[28d] It follows that the bond cleavage is *exothermic* by 39 kcal from the excited singlet state of **1** and *endothermic* by 10 kcal from the excited triplet state. These calculations, summarized in Figure 7, are consistent with the experimental observations in spite of the fact that they do not consider zero-point energies, solvation, and entropic effects.

The nearly identical shapes of the emission spectra of 10^{-2} M (Figure 8) and 10^{-6} M (not shown) **1a** and **1b** in hexane argue against the formation of (emissive) excimers at the higher concentration. On the basis of the directly measured singlet lifetime of **1a** in hexane, 23.4 ns (*vide infra*), and a rate constant for selfdiffusion of 10^{10} M^{-1} s^{-1},[28b] we estimate that ca. 70% of the excited singlets of **1a** encounter a ground state molecule of **1a** at the higher concentration. Ground state aggregation by **1** appears to be unimportant, also, since dilute and concentrated solutions provide excitation spectra of simi-

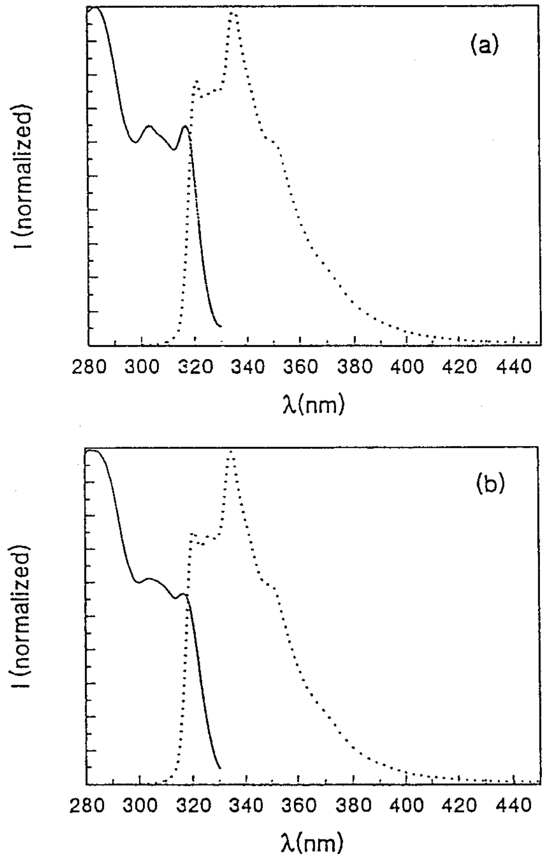


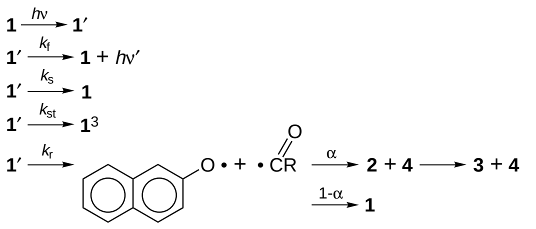
Figure 8. Fluorescence (····; $\lambda_{ex} = 280$ nm) and excitation spectra (—; $\lambda_{em} = 340$ nm) of 1.0×10^{-2} M **1a** (a) and **1b** (b) in hexane at room temperature.

Table 7. Fluorescence Quantum Yields, Calculated and Measured Singlet Lifetimes, and Calculated Fluorescence Rate Constants of 1a and 1b in Hexane

compound	ϕ_f	$k_f \times 10^{-6}$ (s^{-1})[c]	τ_f (ns)[d]
2-naphthol	0.27[28c,53]	20	13 (13.3)[53]
2-methoxynaphthalene[a]	0.37[b]	25	15
2-naphthyl myristate	0.14[b]	2.6	29
2-naphthyl acetate	0.08[b]	2.3	18 (23.4)[e] (23.4)[f] (3.4, 21.3)[g]

[a] $\phi_f = 0.42$ in toluene.[34] [b] This work; based upon ϕ_f of 2-naphthol as a standard. [c] From eq 4. [d] Calculated values from eq 3. Measured values in parentheses; see Experimental Section for details. The reduced χ^2 values are the weighted sum of squared residuals between the data and a single or double exponential function. The *A* are pre-exponential coefficients for the biexponential function. [e] $\chi^2 = 1.4$. [f] $\chi^2 = 1.4$. In water-saturated hexane. [g] $\chi^2 = 1.1$; $A(3.4) = 0.85$, $A(21.3) = 0.15$. In *tert*-butyl alcohol.

Scheme 2



lar shape that are independent of the monitoring emission wavelength.

Fluorescence quantum yields of **1** were calculated using eq 2,[29b] where ϕ_s is the fluorescence quantum yield of a standard, and A_x and A_s are the areas of the fluorescence spectra of the sample and standard plotted in cm^{-1}.

$$\phi_f = \phi_s A_x / A_s \qquad (1)$$

Fluorescence lifetimes (τ_f) were also estimated from eq 3, and the rate constants for fluorescence emission (k_f) were calculated from absorption spectra and eq 4.[29b]

$$\tau_f = \phi_f / k_f \qquad (3)$$

$$k_f = 8\pi\nu^2_{max} c2303\mathrm{AR}/N \qquad (4)$$

Since the first and second lowest energy electronic transitions of 2-naphthyl alkanoates have overlapping absorption bands,[30] the absorption spectra of **1a** and **1b** were dissected and the areas (AR) corresponding to the lowest energy transition were integrated using AXUM (Trimetrix, Inc.) and eq 5.[29b] The calculated rate data and the measured lifetimes from fluorescence decay curves are collected in Table 7. The agreement between the calculated and measured τ_f values is surprisingly good.

$$\mathrm{AR} = 10^7 \int [\epsilon(\lambda)/\lambda^2] d\lambda \qquad (5)$$

The mechanism in Scheme 2 can account for the data presented thus far. Accordingly, the quantum yield for reaction (ϕ_f) is equal to $\alpha k_r \tau_f$ and $\tau_f = (k_f + k_s + k_{st} + k_r)^{-1}$. Attempts to calculate k_r (and, therefore, α) by assuming that τ_f of 2-methoxynaphthalene is equal to $(k_f + k_s + k_{st})^{-1}$, where the values of $k_s + k_{st}$ are the same for **1a**, **1b**, and 2-methoxynaphthalene, failed to provide consistent results. Either $k_s + k_{st}$ is not constant (as implied by the differences between the values of k_f for **1** and 2-methoxynaphthalene) or the errors inherent in the calculations of the parameters in Table 7 are too large.

Table 8. Spin Densities (Atomic Units) of Carbon Atoms of the 2-Naphthoxy Radical from MNDO-UHF Calculations and ESR Spectroscopic Data

position[a]	MNDO-UHF[25,b]	ESR[34]
1	0.399	0.454
3	0.055	0.061
4	0.005	*c*
5	0.004	0.062
6	0.134	0.228
7	0.000	0.051
8	0.100	0.181

[a] See Scheme 1 for ring positions. [b] The calculated spin densities at oxygen, C_2, and the ring fusion carbons *meta* and *para* to C_2 are 0.110, 0.032, 0.004, and 0.168, respectively. [c] Position not included in calculations; value assumed to be zero.

Concerning the Formation of 2 and 3. As mentioned previously, the in-cage radical pair can recombine to yield **1** or rearrange to an isomer of **2**. The temporal decay profile of the 2-naphthoxy radical is determined by the sum of the pseudo first-order rate constants in Scheme 2. The in-cage portion of reaction (and probably that associated with **4** as well) must be complete within a few microseconds after initial excitation of **1** at room temperature since preliminary flash-photolyses (20 μs flash) of **1a** in 9/1 water/acetonitrile[31] show no rise component in transient signals ascribed to the **2a** isomers (*vide infra*). Shizuka *et al.*[32] found that the analogous keto intermediates from phenyl acetate were formed within the duration of their laser pulses (8 ns), and Nakagagi *et al.*[33] estimate the radical pair from 1-naphthyl acetate to have a lifetime of only 25 ps. A similar time-frame probably holds for **1**.

In analogy to the analysis of the thermal Fries reactions and with the same caveats concerning solvation and entropy effects, we employ the free electron densities at each of the nonfused carbon atoms of a 2-naphthoxy *radical* as an indicator of the *kinetic* preferences for formation of the various isomers of **2** (and **3**); under our reaction conditions (low conversions of **1** to avoid secondary photolyses), the only course for **2**, once formed, is enolization to the corresponding isomer of **3** (Scheme 2). Enolization of **2**[3,4,32b] is the rate-limiting step to **3** at least in nonpolar solvents.[32b]

The ESR derived spin density distributions of the 2-naphthoxy radical at room temperature (generated from 2-naphthol in dilute H_2SO_4 containing cerium sulfate)[34] and those calculated by the MNDO-UHF

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(27) Leigh, W. J.; Arnold, D. R. *J. Chem. Soc., Chem. Commun.* **1980**, 406.

(28) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993. (a) p 78. (b) p 208. (c) p 33. (d) p 280.

(29) (a) Moore, W. M.; Hammond, G. S.; Foss, R. P. *J. Am. Chem. Soc.* **1961**, *83*, 2789. (b) Cowan, O. D.; Drisko, R. L. *Fundamental of Photochemistry*; Plenum: New York, 1976.

(30) Johnson, J. R.; Jordan, K. D.; Plusquellic, D. F.; Pratt, D. W. *J. Chem. Phys.* **1990**, *93*, 2258.

(31) (a) Private communication, 1994, Mr. Gaby Persy and Professor Jakob Wirz, Institut fur Physikalische Chemie der Universitat Basel, Klingelbergstrasse 80, CH-4056, Basel, Switzerland. (b) Kim, J.; Urwyler, B.; Wirz, J. *J. Am. Chem. Soc.* **1994**, *114*, 954.

(32) (a) Arai, T.; Tobita, S.; Shizuka, H. *J. Am. Chem. Soc.* **1995**, *117*, 3968. (b) Arai, T.; Tobita, S.; Shizuka, H. *Chem. Phys. Lett.* **1994**, *223*, 521.

(33) Nakagaki, R.; Hiramatsu, M.; Watanabe, T.; Tanimoto, Y.; Nagakura, S. *J. Phys. Chem.* **1985**, *89*, 3222.

(34) (a) Dixon, W. T.; Foster, W. E. J.; Murphy, D. *J. Chem. Soc. Perkin Trans. 2* **1972**, 2124. (b) Stone, T. J.; Waters, W. A. *J. Chem. Soc.* **1962**, 253.

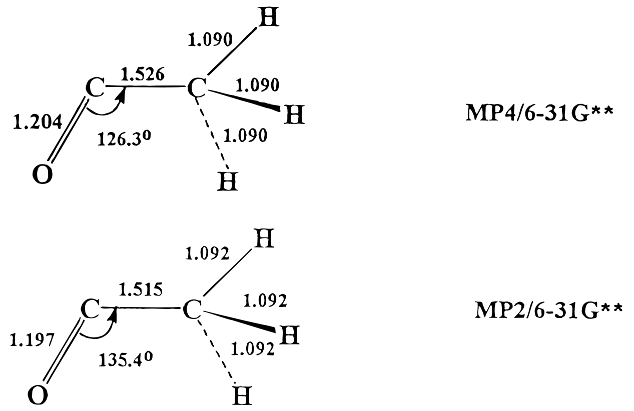

Figure 9. Optimized geometries of the acetyl radical at the MP2/6-31G** and MP4/6-31G** levels.

method[22] on the fully optimized geometry agree reasonably well (Table 7). Like the calculated heats of formation, the spin densities predict that an acyl radical will prefer to add to the 1-position. Solvent, environmental effects, and the nature of the model chosen to analyze the ESR spectrum may contribute to the minor discrepancies between te two data sets; see, especially, footnote c in Table 8.

Although the exact trajectories of approach of the acyl radical to the naphthoxy carbon atoms are not known, they must be at an angle between 90° and 55° with respect to the plane of the rings. These limits represent the idealized projections of the (π and σ) orbital on a naphthyl carbon before and after bonding to a singly occupied orbital of the acyl radical. The full developed bond is σ in character, between sp^3-like (naphthyl) and sp^2-like (acyl) orbitals.

The shape of the acyl radical is bent. Figure 9 shows the calculated optimized geometries at the MP2/6-31G** and MP4/6-31G** levels using the Gaussian 92 *ab initio* computation program.[35] A bent structure was predicted by previous calculations in which no electron correlation was considered.[36] If the acetyl radical is forced to be linear about its C−C−O axis, extended Huckel theory[37] (using bond lengths from the MP4/6-31G** level of the bent geometry) predicts that the odd electron will reside in one of two energy and symmetry degenerate orbitals. According to the Jahn−Teller theorem,[38] the radical will attempt to remove this degeneracy through geometric distortion. In this case, bending about the C−C−O bond axis is the only reasonable distortion available. Thus, the orbitals of the acyl radical should suffer little change in hybridization (and little change in structure) during the formation of the isomers of **2**. More importantly, a bent acyl may approach with its oxygen atom and alkyl chain directed away from a naphthyl ring, allowing the p-like orbital of naphthyl and the sp^2-like orbital of acyl to overlap significantly before steric hindrance is felt. This may be the reason why steric factors appear to be unimportant in determining the relative yields of the **2** isomers from even **1b**.

Conversions of keto intermediates to enols like **3** (and *vice versa*) are known to be catalyzed by acid or base.[32,39] Preliminary flash photolyses of **1a** in 9/1 (v/v) water/acetonitrile[31] produced weakly absorbing transient signals around 300−320 nm that decay with a rate constant k_{obs} of 21 ± 2 s^{-1} at room temperature. The decay was accelerated by hydrochloric acid: $k_H = 29 \pm 3\ M^{-1}\ s^{-1}$. In hexane, a similar transient signal that decayed very slowly ($k_{obs} = 3 \times 10^{-3}\ s^{-1}$) was observed. These characteristics are consistent with **2** being the source of the transient signals.[20]

The protracted lifetimes of the isomers of **2** in saturated hydrocarbons *may* be related to why the isolated photoproduct distributions are so dependent upon the purity of this class of solvents. Conceivably, some 1-**2a** can undergo an efficient secondary photolysis leading to **4**. Alternatively, solvent may be involved at an earlier stage of the mechanism, directing the radical species toward out-of-cage products through control of excited state conformations.

Other Important Considerations. Regardless of the presence or absence of moisture and over a range of temperatures from ca. 0 °C to 45 °C, the sum of the relative yields of 1-**3a** and **4** from irradiation of **1a** in the various solvents remains about 70−80% of the total. Even in hexane, where the distributions were difficult to reproduce from run-to-run, the sum of the relative yields for 1-**3a** and **4** remains fairly constant. Similarly, the formations of 1-**3b** and **4** from **1b** seem to be mechanistically linked. For instance, at 45 °C in hexane, the yield of 1-**3b** is large (63%) and that of **4** is small (<10%); at the same temperature but in the more viscous heneicosane, the yield of 1-**3b** is reduced to 20−22%, but that of **4** is increased to 50−55%. In *tert*-butyl alcohol, the sum of the yields of 1-**3b** and **4** are again near 75%.

In spite of the aforementioned absence of a wavelength effect,[40] there may be some conformational dependence on the course of the photoreactions. Twisting about the 2-naphthyl−acyloxy[30] and 2-naphthyloxy−acyl bonds (α and β, respectively; Figure 10) are probably the most important degrees of freedom available to **1** in the ground and excited states. As conjectured before, specific conformations involving the torsional angles α and β (in the excited singlet state) may be responsible for the complementary yields between 1-**3** and **4**.

The relative energies of some of the potentially important conformations of **1c** in its ground state were calculated by the MM+ (force field) method using the parameters in the HyperChem package.[41] Three mirror-image pairs of energy-minimized conformers (one of each pair shown in Figure 10) were found by starting with 16 structures in which α and β are 0° and incremented sequentially and serially by 90°. Two conformations of nearly equal energy (C_1 and C_3) have the carbonyl oxygen atom pointed toward C-1 or C-3 of the naphthyl ring. In the third, more energetic conformation (**C_p**), the carbonyl bond axis is nearly perpendicular to the naphthyl plane.

The initial distribution of conformers in the excited singlet manifold immediately after excitation will be the

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(35) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Ragharachari, K.; Melius, C. F.; Martin, C. L.; Steward, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, D. J.; Defrees, R. A.; Whitesides, D. J.; Fox, E. M.; Pople, J. A. *Gaussian 92*; Carnegie Mellon University: Pittsburgh, 1992.

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(39) (a) Kresge, A. J. *Acc. Chem. Res.* **1990**, *23*, 43. (b) Urwyler, B.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 790.

(40) (a) Other investigations employing **1b** in anisotropic media[40b] have provided strong evidence for the existence of a wavelength dependence on photoproduct yields that can be linked to conformational effects. (b) Cui, C. Ph.D. Thesis, Georgetown University, Washington, D.C., 1995.

(41) "Allinger, MM2(91)*" from Dr. Norman Allinger.

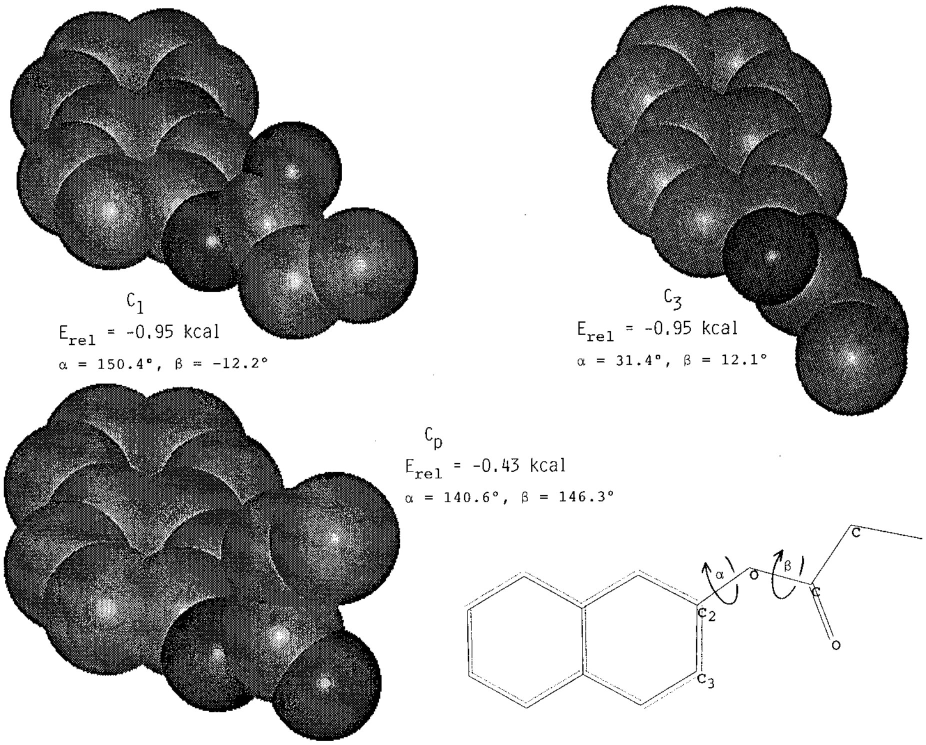

Figure 10. Representations of the most stable ground state conformations of **1c** from MM+ calculations.

same as that in the ground state. Their equilibration to the preferred excited state structures should be much more rapid than the time required for lysis of the acyl—oxy bond (ca. 20 ns) if the torsional barriers in the ground and excited singlet states are similar in magnitude.

Simple orbital considerations indicate that the preferred excited state conformations for cleavage will have α = 90° or 270° regardless of whether they are at energy minima (and they are not in the ground state); this conformation affords 2-naphthoxy in which the putative singly-occupied orbital on oxygen is in maximal conjugation with the aromatic π-system. The relatively long fluorescence lifetimes of **1a** and **1b** may be related to difficulties in attaining these torsional angles as well as the necessity of the π,π^* singlet state to cross to a dissociative σ,σ^* state.

The orbitals of the acyl portion interact *electronically* similarly with each other and with those of naphthoxy at all values of β. However, the ground and excited state values of β are probably similar, placing the acyl oxygen atom near C-1 and C-3 of naphthyl with about equal preference. The trajectories mandated by these β values for the initial relative motions of the naphthoxy and acyl radical pair may influence strongly the distribution among the photoproducts (N.B., 1-**3**/**4** ratio) and they, in turn, will be influenced strongly by solvation factors like hydrogen-bonding and dispersion forces. Available data do not allow these considerations to be discussed in more than qualitative terms. They are being probed by conducting the photorearrangements in organized media.[42]

Experimental Section

Instrumentation. ^{1}H NMR spectra were obtained on a Brucker AM-300 WB spectrometer; singlet, triplet, quintet, and multiplet peaks of NMR spectra are abbreviated as s, t, q, and m, respectively. Fluorescence spectra were recorded at room temperature on a Spex Fluorolog 111 spectrofluorometer. Mass spectral data were obtained on a Finnigan 4500 spectrometer (electron impact and 105 °C) by Dr. Quinlong Pu at the National Institutes of Health.

Analyses of photoproduct mixtures were conducted by high performance liquid chromatography (HPLC) with an Alltech 250 mm × 4.4 mm 5 μm silica gel column. Various combinations of hexane and ethyl acetate separated all of the expected photoproducts in mixtures made from authentic compounds. Peak areas were corrected for differing molar extinction coefficients at the wavelength of detection (254 nm). Unless stated otherwise, relative yields are the average of at least three chromatograms, and relative errors reflect primarily the precision limits of the molar extinction coefficients. All synthesized samples of **1** and **3** were at least 95% pure by HPLC peak areas.

Gas chromatographic analyses (flame ionization detectors) used an Alltech RSL-300 10 m × 0.53 mm open bore column.

The source of radiation was the water- and Pyrex-filtered output of a 450 W Hanovia medium pressure mercury lamp. Wavelength dependent studies employed a 254 or 313 nm interference filter or a 318 nm narrow band-pass filter, closed quartz cuvettes for the samples, and the medium pressure lamp in a water-filled quartz jacket.

Syntheses. All solvents and reagents were ACS grade or better and were used without further purification unless otherwise specified. Solvents for irradiations were *tert*-butyl alcohol (Fischer Certified), cyclohexane (Mallinckrodt SpectroAR), hexane (EM Science OmniSolv), ethanol (Warner Graham Absolute), and acetonitrile (Mallinckrodt Analytical Reagent). Heneicosane (Humphrey Chemical) was purified to >99% purity (GLPC) by Dr. Alberto Nunez: mp 36.5−37.0 °C (lit.[43] mp 36.6 °C). Hexane was also purified by a known procedure.[44] It was distilled from sodium under an argon atmosphere before use. A drop of distilled water was placed in 1 mL of hexane and then the mixture was sonicated to produce water-saturated solvent.

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2-Naphthol (Aldrich, 98%) was purified by precipitation with concd HCl from aqueous base and recrystallization (benzene/heptane) to yield mp 122.5−123.0 °C (lit.[45] mp 122−123 °C). 2-Naphthyl acetate (Aldrich, 98%) was distilled (by 111 °C/0.9 mm) and recrystallized twice from hexane to yield white crystals, mp 71.0−71.5 °C (lit. mp 71−72 °C,[46] 70 °C[47]).

2-Naphthyl Myristate (1b). 2-Naphthol (7.0 g, 49 mmol) and myristoyl chloride (Aldrich 98%, 15 mL, 55 mmol) were dissolved in 20 mL of benzene and were refluxed for 3 h under a dry atmosphere. Standard workup and recrystallization (2×) from 1-butanol afforded 2-naphthyl myristate as white crystals (15.0 g, 87%): mp 64.5−65.0 °C. IR (CCl_4): 3061, 2926, 2855, 1761, 1632 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 7.67−7.20 (m), 2.61 (t, $J = 7.5$ Hz), 1.84 (q, $J = 7.2$ Hz), 1.54−1.27 (m), 0.88 (t, $J = 6.6$ Hz). UV/vis (ethyl acetate, 9.2×10^{-5} M) $\lambda_{max}(\epsilon)$ 276 (3790), 304 (309), 318 nm (276). Mass *m/z* calcd for $C_{24}H_{34}O_2$ 354, found 354.

1-Myristoyl-2-naphthol (1-**3b**) was synthesized by a modification of the method of Fries for the preparation of 1-acetyl-2-naphthol.[13] After recrystallization of the crude product from hexane, a yellow solid, mp 43.5−44.5 °C, was obtained in 60% yield. IR (CCl_4): 3060, 2990, 2950, 2890, 1650 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 12.22 9s), 8.05−7.13 (m), 3.17 (t, $J = 7.2$ Hz), 1.81 (q, $J = 6.9$ Hz), 1.55−1.25 (m), 0.88 ppm (t, $J = 6.3$ Hz). UV/vis (ethyl acetate, 7.6×10^{-5} M): $\lambda_{max}(\epsilon)$ 254 (6690), 312 (3740), 338 (2720), 360 (2760). Mass *m/z* calcd for $C_{24}H_{34}O_2$ 354, found 354.

2-Methoxy-6-myristoylnaphthalene, mp 73.0−73.5 °C, was prepared from 2-methoxynaphthalene and myristoyl chloride in 33% yield by a modification of the method for the preparation of 6-acetyl-2-methoxynaphthalene.[48] IR (CCl_4): 3090, 2920, 2850, 1700, 1630, 1600 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.40−7.15 (m), 3.95 (s), 3.07 (t, $J = 7.5$ Hz), 1.78 (q, $J = 7.2$ Hz), 1.55−1.26 (m), 0.88 ppm (t, $J = 6.3$ Hz). UV/vis (ethyl acetate, 5.4×10^{-5} M) $\lambda_{max}(\epsilon)$ 242 (8800), 246 (8000), 260 (26000), 306 (nm) 10500). Mass *m/z* calcd for $C_{25}H_{36}O_2$ 368, found 368.

6-Myristoyl-2-naphthol (6-3b). The procedure for demethylation of 2-methoxy-6-myristoylnaphthalene was adapted from the one used with 6-acetyl-2-methoxynaphthalene.[17] Yellow-brown needles, mp 99.0−99.5 °C, were obtained in 68% yield after two recrystallizations of the crude product from ethyl acetate. IR (CCl_4): 3590, 3040, 2910, 2850, 1700 cm^{-1}; IR (KBr): 1660 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.41−7.15 (m), 5.18 (br s), 3.08 (t, $J = 7.2$ Hz), 1.78 (q, $Q = 7.2$ Hz), 1.39−1.26 (m), 0.88 (t, $J = 6.3$ Hz). UV/vis (ethyl acetate, 1.9×10^{-5} M) $\lambda_{max}(\epsilon)$ 260 (24300), 312 nm (8950). Mass *m/z* calcd for $C_{24}H_{34}O_2$ 354, found 354.

3-Myristoyl-2-naphthol (3-3b). Under an argon atmosphere, 0.6 mL of a 10.0 M solution of *n*-butyllithium in hexane was added rapidly by syringe to a cold (dry ice/acetone bath) solution of 1.0 mL (4 mmol) of 1-bromotridecane in 20 mL of dry THF. It was stirred for 15 min at 0 °C, and then a solution of 0.15 g (0.8 mmol) of 3-hydroxy-2-naphthoic acid (Aldrich, 98%) in 5.0 mL of dry THF (5.0 mL) was injected via syringe. After being stirred for 30 min at 0 °C, the reaction mixture was poured into 150 mL of dilute HCl and extracted with 100 mL of ethyl ether. The ether was washed thrice with water and dried (anhyd Na_2SO_4). The residue, after evaporation of the ether, was eluted on a 60−200 mesh silica gel column with 150 mL of hexane and then 1/40 (v/v) ethyl acetate/hexane. Further purification by semipreparative TLC (Kieselgel 60; eluent: 1/40 (v/v) hexane/ethyl acetate) afforded a yellow solid which became yellow-green needles (0.1 g, 36%), mp 78.5−79.0 °C, after recrystallization from hexane. IR (CCl_4): 3080, 2930, 2855, 1657 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 11.72 (s), 8.40−7.29 (m), 3.18 (t, $J = 7.0$ Hz). UV/vis (methanol, 1.1×10^{-5} M): $\lambda_{max}(\epsilon)$ 245 (56000), 291 (11500), 310 (12000), 384 nm (2400). Mass *m/z* calcd for $C_{24}H_{34}O_2$ 354, found 354.

2-Acetamido-8-myristoylnaphthalene. Myristoyl chloride (Aldrich, 98%; 0.9 g, 3.6 mmol), 0.5 g (2.7 mmol) of 2-acetamidonaphthalene (mp 133−134 °C; lit.[16] mp 132 °C), 1.9 g (14 mmol) of anhyd $AlCl_3$, and 25 mL of methylene chloride were stirred in a round bottom flask at ambient temperature for 1 h under a dry atmosphere. Sequentially, 50 mL of ice-cold water and 15 mL of concd HCl were added slowly. The organic layer was separated and evaporated to residue. The residue was dissolved in ether, dried (anhyd Na_2SO_4), and eluted on a silica gel column with 1/1 (v/v) hexane/ethyl acetate to afford 0.7 g (65%) of colorless crystals, mp 89−90 °C. IR (KBr): 3292, 3040, 2933, 2847, 1675, 1665, 1584 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.46−7.40 (m), 7.50 (s), 3.05 (t, $J = 7.1$ Hz), 2.20 (s), 1.81 (q), 1.77−1.10 (m), 0.87 ppm (t, $J = 7.0$ Hz). Mass *m/z* calcd for $C_{26}H_{37}NO_2$ 395, found 395.

2-Amino-8-myristoylnaphthalene. 2-Acetamido-8-myristoylnaphthalene (0.5 g, 1.3 mmol), 5.0 mL of glacial acetic acid, and 1.0 mL of 18 N sulfuric acid were refluxed in a round bottom flask for 4 h and cooled to room temperature. Water (10 mL) and then sufficient 30% aqueous NaOH were added to cause precipitation of 0.45 (95%) of yellow solid, mp 97−100 °C. IR (KBr): 3372, 2927, 2848, 1679, 1621 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.37−7.13 (m), 6.60 (s), 2.82 (t, $J = 7.2$ Hz), 1.80 (q), 1.80−1.10 (m), 0.85 ppm (t, $J = 7.0$ Hz). Mass *m/z* calcd for $C_{24}H_{35}NO$ 353, found 353.

8-Myristoyl-2-naphthol (8-3b). Sodium nitrite (0.11 g, 1.6 mmol), 0.5 g (1.4 mmol) of 2-amino-8-myristoylnaphthalene, and 20 mL of glacial acetic acid were stirred at 16 °C for 20 min, heated to boiling, and cooled to room temperature. Water (50 mL) and the mixture was extracted with ethyl ether (3 × 20 mL). The organic layers were combined, dried (anhyd Na_2SO_4), and treated with Darco decolorizing carbon. The residue obtained after removing ether was eluted on a silica gel column 10/1 (v/v) hexane/ethyl acetate. Recrystallization from methanol/water afforded 0.15 g (30%) of 8-myristoyl-2-naphthyl acetate, mp 50−51 °C, as light yellow, cottonlike needles. It was hydrolyzed[16] and separated by semipreparative TLC (Kieselgel 60; eluent 10/1 (v/v) hexane/ethyl acetate). The yellow oil solidified (mp 56−57 °C) after refrigeration at −15 °C for 24 h. IR (KBr): 3225, 2925, 2850, 1650, 1608, 1600 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.27−7.17 (m), 6.09 (br s), 3.06 (t, $J = 7.3$ Hz), 1.77 (q, $J = 7.7$ Hz), 1.70−1.10 (m), 0.87 ppm (t, $J = 7.0$ Hz). UV/vis (methanol, 2.16×10^{-4} M): $\lambda_{max}(\epsilon)$ 348 (4100), 230 (32000). Mass *m/z* calcd for $C_{24}H_{34}O_2$ 354, found 354.

1-Acetyl-2-naphthol (1-3a).[13] 2-Naphthyl acetate (1.0 g, 5.4 mmol) and 1.5 g (12 mmol) of anhydr $AlCl_3$ were heated in a round bottom flask for 5 h at 70 °C under a dry atmosphere and then cooled to room temperature. Dilute HCl was added, and the mixture was extracted with ether. The ether layer was dried (anhyd Na_2SO_4) and evaporated to a residue. Two recrystallizations from hexane afforded 0.3 g (30%) of a light yellow solid, mp 62.0−63.0 °C (lit.[13] mp 64 °C). HPLC analyses indicated ca. 95% purity. IR (CCl_4): 3040, 2980, 1630 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 13.50 (br s), 8.11−7.13 (m), 2.88 ppm (s). UV/vis (ethyl acetate, 6.9×10^{-5} M): $\lambda_{max}(\epsilon)$ 254 (9200), 302 (6800), 356 nm (4030). Mass *m/z* calcd for $C_{12}H_{10}O_2$ 186, found 186.

3-Acetyl-2-naphthol (3-**3a**) was prepared by the method of Rubottom and Kim[14] in 38% yield: mp 109.0−111.5 °C (lit. mp 110.0−111.8 °C,[15] 112 °C[49]). UV/vis (ethyl acetate, 1.8×10^{-5} M): $\lambda_{max}(\epsilon)$ 256 (44000), 290 (20000), 384 nm (1800). Mass *m/z* calcd for $C_{12}H_{10}O2$ 186, found 186.

6-Acetyl-2-methoxynaphthalene.[50] Under a dry atmosphere, 8.5 g (64 mmol) of powdered anhyd $AlCl_3$ was added gradually with stirring to an ice-cold solution of 5.0 g (32 mmol) of 2-methoxynaphthalene (Aldrich, 98%) and 2.4 mL (43 mmol) of acetyl chloride in 20 mL of nitrobenzene. After the mixture was stirred for 24 h, ice and dilute HCl were added, and the nitrobenzene was removed by steam distillation. The remaining liquid was extracted with chloroform. The fraction of the organic layer distilling at 195−200 °C/10 mm was recrystallized twice from hexane to afford 2.8 g (49%) of 6-acetyl-2-methoxynaphthalene as white flakes, mp 103.0−104.5° (lit.[50] mp 104−105 °C). IR (CCl_4): 3050, 3010, 2890, 2850, 1690,

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1630 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.40−7.16 (m), 2.71 (s), 3.96 ppm (s). Mass *m*/*z* calcd for $C_{13}H_{12}O_2$ 200, found 200.

6-Acetyl-2-naphthol (6-3a).[18] 6-Acetyl-2-methoxynaphthalene (0.25 g, 1.3 mmol) was fused with 0.5 g of pyridine hydrochloride at 200 °C for 2 h under a dry atmosphere. At room temperature, 20 mL of dilute HCl was added and 0.5 g of yellow crystals were collected; after standing overnight, the filtrate yielded an additional 0.1 g (60% total). The combined solids were titurated from boiling alcohol by adding water: mp 171−172 °C (lit.[18] mp 170−171 °C). IR (KBr): 3353, 2981, 1662, 1614 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.6−7.1 (m), 3.5 (br s), 2.73 ppm (s). UV/vis (ethyl acetate, 1.2×10^{-5} M): $\lambda_{max}(\epsilon)$ 258 (29000), 309 nm (10400). Mass calcd for $C_{12}H_{10}O_2$ 186, found 186.

8-Acetyl-2-aminonaphthalene.[16] 2-Acetamidonaphthalene (8.0 g, 43 mmol), 28 g (0.21 mol) of anhyd $AlCl_3$, 50 mL of methylene chloride, and 3.5 g (45 mmol) of acetyl chloride were stirred in a round bottom flask for 10 min at room temperature under a dry atmosphere. Slowly, 100 mL of ice−water and 50 mL of concd HCl were added, and the reaction mixture was extracted with ether (2 × 200 mL). Removal of the ether left ca. 8.5 g of a dark brown residue. After recrystallization from ethanol/water, a small portion yielded 2-acetamido-8-acetylnaphthalene as white crystals, mp 107−108 °C. Mass *m*/*z* calcd for $C_{13}H_{14}NO_2$ 227, found 227.

The remaining 8 g of residue, 50 mL of glacial acetic acid, and 5 mL of 18 N sulfuric acid were refluxed for 4 h in a round bottom flask. At room temperature, 30% aqueous NaOH was added until a solid formed. The precipitate was filtered, dissolved in ethyl ether, and dried (Na_2SO_4). HCl gas was bubbled through the ether, and the ensuing precipitate was filtered and dissolved in hot water. Addition of 30% aqueous NaOH precipitated ca. 3 g of 8-acetyl-2-aminonaphthalene, a yellow pasty solid which became black rapidly in air. ^1H NMR ($CDCl_3$/TMS): δ 7.92−7.00 (m), 4.02 (br s), 2.72 ppm (s).

8-Acetyl-2-naphthol (8-3a). A solution of 0.6 g (8.6 mmol) of $NaNO_2$ in 5 mL of water was added slowly to a solution of 1.5 g (8.2 mmol) of 8-acetyl-2-aminonaphthalene in 20 mL of concd HCl that had been cooled in an ice-salt bath.[51] After remaining at ambient temperature for 2 days, a black precipitate was filtered and dissolved in hot ethanol/water. At room temperature, the solution was extracted with ether (2 × 50 mL). The combined organic layers were dried (anhyd Na_2SO_4) and treated with Darco decolorizing carbon. The residue from the ethers was recrystallized from 1/1 (v/v) benzene/hexane to yield 0.6 g (40%) of long yellow needles, mp 148−149 °C (lit.[16] mp 149−150 °C). IR (KBr): 3207, 1649, 1590 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 8.85−7.24 (m), 8.37 (s), 2.84 (s); ^1H NMR ($CDCl_3$/TMS/D_2O) δ 8.79−7.24 (m), 2.82 ppm (s). UV/vis (methanol, 1.9×10^{-5} M) $\lambda_{max}(\epsilon)$ 348 (4100), 230 nm (32000). Mass calcd for $C_{12}H_{10}O_2$ 186, found 186.

Ethyl Myristate. Myristic acid (Aldrich, 95%; 20 g, 8.8 mmol), 25 mL of absolute ethyl alcohol, 3.0 mL of concd HCl, and 7.0 g of anhyd $CaCl_2$ were stirred for 20 min in a water bath under a dry atmosphere. The organic layer was separated, washed thrice with warm water, and dried (anhyd $CaCl_2$), to yield 21 g (95%) of ethyl myristate as a colorless liquid, mp 12 °C (lit.[52] mp 12 °C).

7-Methoxy-2-naphthyl Acetate. Acetyl chloride (Aldrich, 98%; 3 mL, 42 mmol), 4.0 g (25 mmol) of 7-methoxy-2-naphthol (Aldrich, 98%), and 10 mL of benzene were refluxed for 4 h under a dry atmosphere. At room temperature, 20 mL of methylene chloride was added, and the organic layer was separated and the organic layer was washed thrice with water. The residue after evaporation was recrystallized thrice from ethanol to afford 2.0 g (37%) of colorless crystals, mp 119.0−119.5 °C. IR (KBr): 3019 (=C−H), 2923 and 2947 ($-CH_3$), 1725 (ester carbonyl), 1630 cm^{-1} (aromatic). NMR ($CDCl_3$/TMS): δ 7.0−7.8 (6H, m, aromatic), 3.9 (3H, s, CH_3O), 2.34 (3H, s, CH_3CO). Mass *m*/*z* calcd for 196, found 196.

Lewis-Acid Catalyzed Fries Rearrangements of 2-Naphthyl Acetate. Syntheses of 6- and 8-Acetyl-2-naphthol. 2-Naphthyl acetate (5.0 g, 27 mmol) and 12.0 g (90 mmol) of anhyd $AlCl_3$ were mixed and heated at 150 °C for 5 h under a dry atmosphere and cooled to ambient temperature. Ice and 10 mL of concd HCl were added slowly. The mixture was boiled for 20 min and extracted with ether (2 × 25 mL). The organic layers were combined and washed with satd aqueous $NaHCO_3$ three times and twice with water. After being dried, the ether was evaporated. A 0.25 g portion of the residue from the reaction at 150 °C was eluted on a 100 g column of silica gel with 1/10 (v/v) ethyl acetate/hexane. The five separated fractions consisted of 20 mg of a 1/1 mixture of 1-acetyl-2-naphthol and 3-acetyl-2-naphthol, 50 mg of 2-naphthol, 10 mg of 8-acetyl-2-naphthol, 50 mg of 6-acetyl-2-naphthol, and 50 mg of unidentified compounds. Identifications were based upon comparison of melting points or NMR spectra with those of authentic samples.

In separate experiments, smaller amounts of **1a** or 1-**3a** and $AlCl_3$ in 5/12 weight ratios were heated at various temperatures for 5 h, and the Lewis acid was removed as described above. The product residue from each experiment was analyzed by the standard HPLC protocols.

Irradiations. Unless indicated otherwise, irradiations were conducted with ca. 5×10^{-3} M 2-naphthyl alkanoates. Solutions were deoxygenated by bubbling N_2 gas for 15 min and irradiated in Pyrex vials for 5−10 min at ca. 10 cm from the lamp. Aliquots were analyzed directly by HPLC except when *tert*-butyl alcohol was the solvent. In these cases, the stream of nitrogen was passed over the solution to remove the volatile liquid and the residue was dissolved in the same liquid as the HPLC eluent.

Cross-Over Experiment. Solutions of 64 mg (0.18 mmol) of 2-naphthyl myristate and 32 mg (0.16 mmol) of 7-methoxy-2-naphthyl acetate in 50 mL of *tert*-butyl alcohol and 30 mg (0.15 mmol) of 7-methoxy-2-naphthyl acetate in 50 mL of *tert*-butyl alcohol were purged with N_2 gas for 15 min. Aliquots were transferred to 4 mL Pyrex vials with polypropylene caps and irradiated simultaneously for 10 min.

Attempted Sensitization of 1a Rearrangements. Aliquots of N_2-saturated benzene solutions containing 0.025 M benzophenone, 0.050 M 2-naphthyl acetate, and 0.050 M benzhydrol (from the reduction of benzophenone with $NaBH_4$ in ethanol: mp 65−66 °C; lit.[29a] mp 65−66 °C) (solution A) and 0.050 M benzophenone and 0.025 M benzhydrol (solution B) were sealed in Pyrex vials and irradiated (360 nm cutoff filter) simultaneously for 3.5 h. UV/vis absorption spectra of nonirradiated and irradiated aliquots, diluted to one-tenth their original concentrations, were recorded, and the decrease in optical density of the irradiated samples at 350 nm was used to determine the amount of benzophenone that had reacted. HPLC analyses of irradiated solution A contained the peak of **1a**, but none of the peaks of the expected photoproducts, **3a** and **4**.

Attempted Detection of Ethyl and Octyl Myristate. Aliquots (1.0 mL) of a solution of 12.0 mg of 2-naphthyl myristate in 50 mL of N_2-saturated absolute ethanol were irradiated for 10 min in Pyrex vials at 25 °C and 45 °C. The ethanol was evaporated under a stream of N_2 gas, and the residue was dissolved in ethyl acetate. GC and HPLC analyses gave no evidence for the presence of peaks from ethyl myristate. Analogous procedures, with 1-octanol as solvent, were employed in unsuccessful attempts to detect octyl myristate upon irradiation of 2-naphthyl myristate.

Fluorescence Measurements. Spectra of concentrated solutions (10^{-2} M) of **1a** or **1b** in N_2-saturated purified hexane were recorded from the front-face of a 1 cm quartz cuvette. Solutions containing 10^{-6} M **1** were obtained at both front-face and right-angle geometries. Wavelengths for emission and excitation were 280 and 340 nm, respectively.

Fluorescence quantum yields (Φ_f) were calculated[29b] using the spectrofluorimeter conditions above, but with very dilute samples in N_2-saturated hexane (EM Sciences, Omnisolvent) whose optical densities (OD) at 280 nm were made equal (and always <0.05). Spectra were recorded at a right-angle geometry. Areas under emission curves (intensity versus wavenumbers) were integrated and compared with those of 2-naph-

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thol ($\Phi_f = 0.27$ in cyclohexane[53,55]) and 2-methoxynaphthalene ($\Phi_f = 0.42$ in toluene[54]).

Fluorescence decay profiles for lifetime measurements were monitored at 360 nm (λ_{ex} 316 nm) by Dr. Aleksander Siemiarczuk of Photon Technologies, Inc. on a Strobemaster lifetime apparatus (N_2/He flash lamp). Solutions of 10^{-4} M **1a** were degassed by three freeze-pump-thaw cycles at $<10^{-5}$ torr and flame-sealed in 1 cm square Kimax cuvettes.

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Supporting Information Available: UV, IR, ^{1}H NMR, and mass spectra for compounds **1a**, **1b**, 1-**3a**, 3-**3a**, 6-**3a**, 8-**3a**, 1-**3b**, 3-**3b**, 6-**3b**, and 8-**3b** (37 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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