to-Na^+ exchange as for the HY-100 sample; their crystallinity was in all cases higher than 90%. H-β was synthesized starting from a Et_4N^+-β by calcination and NH_4^+-exchange as described in ref 14. The Si/Al ratio was 13 as determined by NMR MAS. HZSM-5 (Si/Al = 20) was obtained following the patent literature.[15]

Reaction Procedure. Activation of the zeolites was performed "in situ" just before their use by heating the solid (1.00 g) at 150 °C under 1 Torr for 2 h. After this time, a solution of AB (150 mg) in hexane (50 mL) was poured into the Pyrex vessel containing the activated zeolite. The resulting suspension was magnetically stirred at reflux temperature while being photolyzed with an array of 400-W high-pressure mercury lamps. At the end of the irradiation, the zeolite was filtered and washed with CH_2Cl_2, and the organic solutions were concentrated in vacuum and weighed. Analysis by GC (HP 5890 provided with a 25-m capillary column of cross-linked 5% phenylmethylsilicone) and GC-MS (HP 5988A spectrometer) showed that in all cases the residue consisted almost exclusively of AB. The zeolite was submitted to continuous solid-liquid extraction using micro-Soxhlet equipment and CH_2Cl_2 as solvent. After removal of the solvent, the residue was weighed and analyzed by GC, GC-MS, and GC-FTIR (HP 5890 GC coupled with a 5965A FT-IR detector). These extracts consist of variable mixtures of AB and BC.

IR spectra of the adsorbed organic compounds were carried out in a greaseless IR cell using a Perkin-Elmer 580B spectrophotometer equipped with a data station. Wafers of 10 mg cm^{-2} were pretreated at 200 °C and 10^{-3} Pa dynamic vacuum. The spectra in the 4000–1300-cm^{-1} region were recorded at room temperature.

Acknowledgment. Financial support by the Spanish Comisiôn Interministerial de Ciencia y Tecnología (Project PB90-0747) is gratefully acknowledged. One of us (V.M.) thanks to the Generalitat Valenciana for a grant.

Supplementary Material Available: Photographs of Biosym molecular modeling program visualizations of azobenzene inside the cavities of β (E) and ZSM-5 (F) structures (1 page). Ordering information is given on any current masthead page.

(14) Climent, M. J.; Corma, A.; García, H.; Iborra, S.; Primo, J. *Stud. Surf. Sci. Catal.* **1991**, *59*, 557–564.
(15) Argauer, R. J.; Landlolt, G. R. *U.S. Patent* **1982**, *3*, 702, 886.

Photochemistry of Substituted 1-Naphthylmethyl Esters of Phenylacetic and 3-Phenylpropanoic Acid: Radical Pairs, Ion Pairs, and Marcus Electron Transfer

Dayal P. DeCosta† and James A. Pincock*

Contribution from the Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada. *Received September 4, 1992*

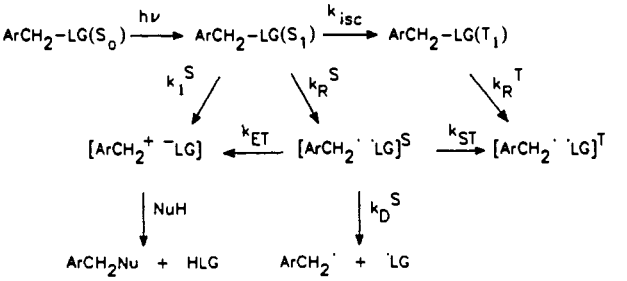
Abstract: The ring-substituted 1-naphthylmethyl esters of phenylacetic (**3a–k**) and 3-phenylpropanoic (**5a–c**) acid have been photolyzed in methanol solvent. The major products of these reactions are derived from two critical intermediates, the 1-naphthylmethyl radical/acyloxy radical pair and the 1-naphthylmethyl cation/carboxylate anion ion pair. The radical pair results in formation of the in-cage coupled products **8a–k** and **10a–c** after loss of carbon dioxide from the acyloxy radical. The ion pair leads to the methyl ethers **6a–k** and the carboxylic acids **7** and **9**. The competition between the radical and ionic pathways is very dependent upon the substituents on the naphthalene ring. Analysis of these substituent effects results in a proposed mechanism of initial homolytic cleavage of the carbon–oxygen bond of the ester from the excited singlet state. This radical pair then partitions between two pathways: decarboxylation of the acyloxy radical and electron transfer converting the radical pair to the ion pair. The rates of electron transfer are shown to fit Marcus theory in both the normal and the inverted region.

Introduction

The photochemistry of benzylic compounds with leaving groups ($ArCH_2$–LG) has been extensively studied in recent years. In most cases, products are obtained that result from an intermediate arylmethyl cation and the leaving group anion ($ArCH_2^+$ $^-$LG) as well as from an arylmethyl radical and the leaving group radical ($ArCH_2^\bullet$ $^\bullet$LG). The ion pair, at least formally, results from heterolytic cleavage of the carbon-to-leaving-group bond. In analogy to ground-state solvolysis, the cation can be trapped by nucleophilic solvents (water, alcohols, etc.) and, therefore, this process is often called photosolvolysis. The radical pair results from homolytic cleavage of the same bond. Typical radical coupling and hydrogen atom abstraction products are obtained in this case. An excellent review that summarizes this material up to the early 1980s has been written.[1]

The competition between the pathways for formation of these two possible intermediates is dependent on many factors, including the leaving group, the aryl ring (i.e., benzene versus naphthalene or benzene versus substituted benzene), the solvent, and the multiplicity (singlet versus triplet) of the excited state involved.

Scheme I. General Mechanism for the Photolysis of Benzylic Substrates with Leaving Groups



As yet, these factors are not well enough understood to allow reliable predictions about product distribution for any given case. This is because there is more than one mechanistic pathway for the formation of the critical cation and radical intermediates after the initial absorption process gives the excited singlet state. These are outlined in Scheme I. For simplicity in this scheme, the

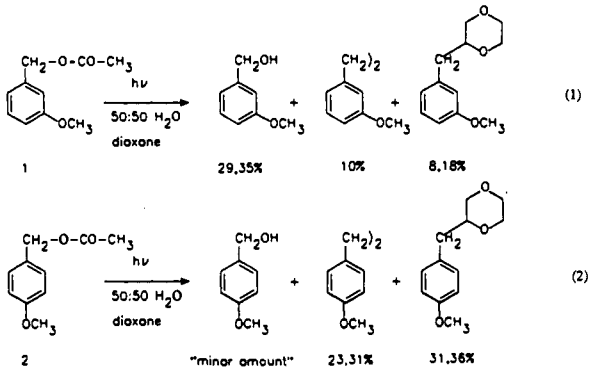
† Current address: Department of Chemistry, University of Colombo, Colombo, Sri Lanka.

(1) Cristol, S. J.; Bindel, T. H. *Organic Photochemistry*; Marcel Dekker: New York, 1983; Vol. 6, p 327.

0002-7863/93/1515-2180$04.00/0

leaving group is shown as neutral and becomes negatively charged after heterolytic cleavage. In practice, many of the good leaving groups are positively charged ($-NR_3^+$,[2] $-PR_3^+$,[3] $-OH_2^+$,[4] $-SR_2^+$,[5]) and become neutral after heterolytic cleavage. After homolytic cleavage, the positively charged leaving groups become radical cations. This scheme has been simplified in two other important ways. First, the species in square brackets represent contact or caged ion pairs (necessarily a singlet state and formed directly only from S_1, not T_1) or radical pairs (either a singlet state formed from S_1 or a triplet state formed from T_1). The diffusional separation of these species to free ions or radicals is shown as one step although solvent-separated but still interacting species may be important. Second, no internal return to $ArCH_2$–LG (S_0) is indicated although there is evidence for this process in the photocleavage reactions of sulfones (LG = $-SO_2R$)[6] and phosphates (LG = $-OP(=O)(OCH_2CH_3)_2$).[7] For esters (LG = $-O_2CR$),[8,9] oxygen scrambling in the starting material has been observed but has been ascribed to a concerted 1,3-sigmatropic migration rather than internal return of radical or ion pairs. For ammonium salts (LG = $-N(CH_3)_3^+$),[10] no evidence for internal return was found for the photolysis of an optically active benzylic substrate.

In a much-cited fundamental paper published in 1963, Zimmerman and Sandel[11] reported on the photochemical cleavage of 3- and 4-methoxybenzyl acetate (**1** and **2**) in aqueous dioxane. As shown in eqs 1 and 2, the 3-methoxy isomer gave higher yields[12]



of the product derived from the benzylic cation than did the 4-methoxy isomer. Moreover, the quantum efficiency of reaction was considerably higher for the 3-methoxy isomer. The authors used charge density calculations from simple Hückel MO theory to rationalize these observations. In the ground state, as expected, the methoxy group is a better electron donor to a benzylic carbon when it is conjugated by its resonance effect from the 4-position. In contrast, in the excited state, electron donation is more efficient from the 3-position. This observation and others related to it in nucleophilic aromatic substitution[13] became known as the photochemical "meta effect". This explanation relies on the assumption that product distribution is controlled, at least mostly, by the competition between heterolytic and homolytic cleavage of the initially formed excited state. In Scheme I, the two important rate constants would be k_1^S and k_R^S.

Many photochemical studies have been directed toward understanding substituent effects for aromatic rings.[14] The hope is that a scale of σ values might be established that would be as useful to photochemistry as the various σ scales are to the study of ground-state reactions. The benzylic cleavage reaction, which, at least superficially, is a simple one-step (presumably rate-determining) process, seemed an ideal case to establish such a scale. Moreover, the competition between a homolytic and a heterolytic pathway raised the possibility that two excited-state scales reflecting very different charge requirements could be established at the same time. In order to approach this problem in a systematic way, it seemed important that actual rate constants of reaction for bond cleavage (k_1^S and k_R^S in Scheme I) would be necessary. Most previous studies had relied only on semiquantitative information based on quantum yields of reaction and product distributions. In 1985, we began a set of studies designed to obtain these rate constants.[2,15] The first problem was the choice of a system (aromatic ring, leaving group, solvent) that would be the best for reliably obtaining these rate constants.

The choice of aromatic ring was based on the well-known fact[16] that compounds with naphthalene rings are easier substrates to study for quantitative photochemistry than are those with benzene rings. As Givens[16] et al. have outlined previously, the naphthyl chromophore absorbs beyond 300 nm, so diene quenching studies free of competitive absorption are possible. As well, the lower triplet energy for naphthalene (≈251 kJ/mol) than for benzene (≈334 kJ/mol) allows unambiguous triplet sensitization experiments necessary to explore excited-triplet-state reactivity. Moreover, the lower excited-state energies (≈376 kJ/mol for the singlet and ≈251 kJ/mol for the triplet) make it likely that a leaving group with low enough photofugacity can be found that reaction rates will be slow enough for convenient nanosecond lifetime measurement. The difficulties doing reaction rate studies with benzene derivatives are clearly shown in Cristol and Bindel's detailed study[17,18] on the photosolvolysis of substituted benzyl chlorides in *tert*-butyl alcohol. Reaction rates for bond cleavage of the triplet state were at or beyond the limit for Stern–Volmer quenching studies. No information could be obtained about the reactivity of the singlet state. Our initial study on 1-naphthylmethyl derivatives[15] demonstrated that much slower reaction rates from the singlet state resulted for leaving groups $-N(CH_3)_3^+Cl^-$, $-O_2CCH_3$, and $-O_2P(OEt)_2$. Moreover, none of these substrates reacted after triplet sensitization with xanthone. This eliminates k_R^T in Scheme I. Finally, Breslin and Saeva[3] have shown that singlet radical pairs resulting from benzylic cleavages in onium salts (LG = $MPh_3^+BF_4^-$; M = N, P, As) are converted efficiently to triplet radical pairs only if there is a large value for the nuclear hyperfine coupling constant. In the absence of this effect, k_{ST} for conversion of the caged singlet radical pair to the triplet radical pair is small. Removal of the two processes described by k_R^T and k_{ST} obviously simplifies Scheme I considerably since ion pairs and singlet radical pairs are now the only two species to consider in the mechanism.

A referee of the initial version of this paper has suggested that naphthalenes may not be very good models for developing arguments about how substituent effects are transmitted in benzene rings because of inherent photochemical differences between the two. For instance, 1-methoxynaphthalene, in the excited singlet state, is protonated mainly in the other ring (C_5 and C_8).[19,20] However, the "meta effect" can be viewed, in a general way, as an explanation based on the concept that substituents change

(2) Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehmbey, C. *Can. J. Chem.* **1987**, *65*, 1599.
(3) Breslin, D. T.; Saeva, F. D. *J. Org. Chem.* **1988**, *53*, 713.
(4) Wan, P.; Chak, B.; Krogh, E. *J. Photochem. Photobiol. A* **1989**, *46*, 49.
(5) (a) Saeva, F. D.; Breslin, D. T.; Martic, P. A. *J. Am. Chem. Soc.* **1989**, *111*, 1328. (b) Saeva, F. D.; Breslin, D. T. *J. Org. Chem.* **1989**, *54*, 712.
(6) Givens, R. S.; Hrinczenko, B.; Liu, J. H.-S.; Matuszewski, B.; Tholen-Collison, J. *J. Am. Chem. Soc.* **1984**, *106*, 1779.
(7) Givens, R. S.; Matuszewski, B. *J. Am. Chem. Soc.* **1984**, *106*, 6860.
(8) (a) Givens, R. S.; Matuszewski, B. *J. Am. Chem. Soc.* **1975**, *97*, 5617. (b) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. *J. Am. Chem. Soc.* **1977**, *99*, 1896.
(9) Jaeger, D. A.; Angelos, G. H. *Tetrahedron Lett.* **1981**, 803.
(10) Lillis, V.; McKenna, J.; McKenna, J. M.; Smith, M. J.; Taylor, P. S.; Williams, I. H. *J. Chem. Soc., Perkin Trans. II* **1980**, 83.
(11) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.
(12) The yields given in eqs 1 and 2 were determined by gravimetric analysis after chromatographic separation. This may, in part, explain the poor mass balance. Where there are two numbers, two separate determinations were made.
(13) Havinga, E.; Cornelisse, J. *Pure Appl. Chem.* **1976**, *47*, 1.
(14) McEwen, J.; Yates, K. *J. Phys. Org. Chem.* **1991**, *4*, 193 and references therein.
(15) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985**, *63*, 3140.
(16) Givens, R. S.; Matuszewski, B.; Neywick, C. V. *J. Am. Chem. Soc.* **1974**, *96*, 5547.
(17) Cristol, S. J.; Bindel, T. H. *J. Org. Chem.* **1980**, *45*, 951.
(18) Cristol, S. J.; Bindel, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 7287.
(19) Shizuka, H.; Tobita, S. *J. Am. Chem. Soc.* **1982**, *104*, 6919.
(20) Mathivanan, N.; Cozens, F.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 2198.

Table I. Yields of Products for the Photolysis of the Esters 3 and 5 in Methanol

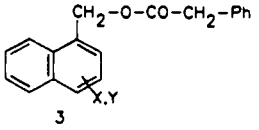
esters 3	% 6[a]	% 7[b]	% 8[a]	% 11[a,c]	log k_{ET}	E^{ox} [d]
a: X = H, Y = H	84	60	16		10.4	0.47
b: X = 3-OCH_3, Y = H	31	38	52	8	9.44	0.52
c: X = 4-OCH_3, Y = H	74	59	24		10.15	0.04
d: X = 4-CH_3, Y = H	93	72	7		10.78	0.35
e: X = 4-CN, Y = H	12	12	80		8.84	0.72
f: X = 4-OCH_2CH_3, Y = H	80	60	22		10.22	e
g: X = 4-CO_2CH_3, Y = H	10	11	52	20	8.94	0.81
h: X = 4-OCH_3, Y = 5-OCH_3	42	25	46		9.62	−0.05
i: X = 4-OCH_3, Y = 7-OCH_3	35	29	48	8	9.53	−0.06
j: X = 4-OCH_3, Y = 8-OCH_3	47	51	33	7	9.65	−0.05
k: X = F, Y = H	83	74	12		10.50	0.46

Esters 5	% 6[a]	% 9	% 10	% 11[a,c]
a: X = H, Y = H	96	83	6	
b: X = 3-OCH_3, Y = H	39	31	19	12
c: X = 4-OCH_3, Y = H	86	72	7	

[a] By calibrated HPLC, estimated error ±2%. [b] By weight of isolated product. [c] Yields are less than 5% when no value is given. [d] From ref 29. [e] Not determined but assumed the same as the 4-methoxy compound.

electron density at a reactive site of an excited state and that these changes will be different from those in the ground state. This effect is still predicted to be operative for 3- and 4-methoxynaphthalene derivatives in reactions from the excited singlet state requiring high electron density at C_1. For instance, semiempirical calculations using an SCF CI method by Shizuka and Tobita[19] indicate that methoxy groups at both the 1- and the 2-positions (corresponding to 4-methoxy and 3-methoxy, respectively) are better electron donors in the excited state than in the ground state. For the 1-methoxy isomer the position of calculated maximum change in electron density on excitation is at C_8 followed by C_5, in agreement with the reported experimental results for photoprotonation; C_4 (corresponding to C_1 for a 4-methoxy-1-naphthalene derivative) shows a large decrease in electron density. For the 2-methoxy isomer, the maximum calculated electron density increase upon excitation is at C_4 (corresponding to C_1 for a 3-methoxy-1-naphthalene derivative). Similar results are obtained by SHMO calculations using $^-$:CH_2 as the electron donor, in analogy to the initial model used by Zimmerman.

Based on these ideas, we have studied the photochemistry and photophysics in methanol of a series of eleven substituted 1-naphthylmethyl esters of phenylacetic acid, **3**. Part of this work



3

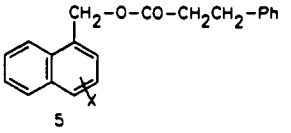
a:X=H,Y=H
b:X=3-OCH_3,Y=H
c:X=4-OCH_3,Y=H
d:X=4-CH_3,Y=H
e:X=4-CN,Y=H
f:X=4-OCH_2CH_3,Y=H
g:X=4-CO_2CH_3,Y=H
h:X=4-OCH_3,Y=5-OCH_3
i:X=4-OCH_3,Y=7-OCH_3
j:X=4-OCH_3,Y=8-OCH_3
k:X=4-F,Y=H

has appeared in a preliminary communication.[21] Our initial conclusion was that the mechanism for the photolysis involved homolytic cleavage of the carbon–oxygen bond (i.e., $k_R^s \gg k_1^s$ in Scheme I) from the excited singlet state. Product distribution is then controlled by factors that follow this step and not by changes in electron density in the excited state. In this paper, we report the full experimental details and a more extensive discussion of the results in order to justify this conclusion.

(21) DeCosta, D. P.; Pincock, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 8948.

Results and Discussion

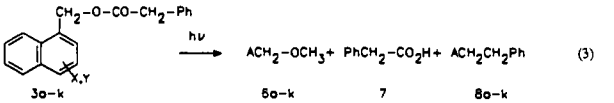
Synthesis of Esters. The esters **3** were all synthesized by reaction of the corresponding alcohol **4** with phenylacetyl chloride in benzene containing pyridine. Details, spectral data, and elemental analyses are given in the Experimental Section. Since the related propanoate esters **5** offer a useful comparison to the phenylacetates **3**, three of these were also synthesized.

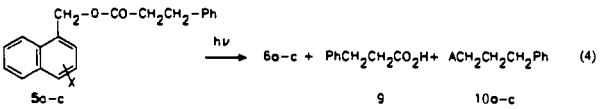


5

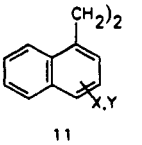
a:X=H
b:X=3-OCH_3
c:X=4-OCH_3

Photolysis of Esters 3 and 5 in Methanol. Irradiation of the esters **3** and **5** in methanol with a Pyrex-filtered medium-pressure mercury lamp led to efficient conversion to three major products, as shown in eqs 3 and 4 (A = $C_{10}H_{7-n}(X,Y)_n$). Complete reaction





of 300 mg of substrate took from 3 to 14 h, depending on the substituents. These changes in irradiation time are mainly a result of substituents increasing the absorbance beyond the approximate 290-nm cutoff of the Pyrex filter. The yields are given in Table I. The yields of the ethers **6** and the hydrocarbons **8** and **10** were determined by calibrated HPLC (estimated error ±2%). The yields of phenylacetic acid (**7**) from **3** and of phenylpropanoic acid (**9**) from **5** were determined gravimetrically by isolation of the acids after basic extraction of the photolysis mixtures and are therefore not as quantitative. By stoichiometry, the yields of **6** and **7** or of **6** and **9** for any given substrate should be identical. In general, the mass balance (sum of **6** and **8** or **6** and **10**) is very good, particularly for cases where the yield of the ether **6** is high. When the yield of **6** is lower, a peak of significant intensity at long retention time on reverse-phase HPLC was observed. This compound was identified as the dimer **11** of the substituted 1-naphthylmethyl radical. The yield of this dimer was also de-



11

termined by calibrated HPLC, and the values are shown in Table I for those cases where enough was formed to allow isolation and characterization. Traces of bibenzyl and the substituted 1-methylnaphthalene were also observed, but the yields were not quantified.

A superficial examination of the product yields indicates that these substrates are not reacting photochemically in a way that is analogous to the observations for the comparable benzylic esters in eqs 1 and 2. Thus, the unsubstituted ester **3a** gives a higher yield of the product **6a** derived from the carbocation intermediate than either the 3-methoxy (**6b**) or 4-methoxy (**6c**) isomer. Moreover, the 3-methoxy isomer gives the lowest yield of this product. Clearly, an explanation like the meta effect cannot apply in this case.

This type of product yield analysis, although common in photochemical studies, can lead to erroneous conclusions about the mechanism. The obvious reason for this is that all photochemical

Table II. Emission Properties of Esters 3 and 5 in Methanol

ester	E_S[a] (kJ/mol)	τ_S[b] (ns)	ϕ_F[c]	E_T[d] (kJ/mol)
3a: X = H, Y = H	386	49	0.14	252
3b: X = 3-OCH_3, Y = H	356	10.9	0.24	241
3c: X = 4-OCH_3, Y = H	371	7.3	0.27	250
3d: X = 4-CH_3, Y = H	381	34	0.14	251
3e: X = 4-CH, Y = H	377	5.2	0.21	239
3f: X = 4-OCH_2CH_3, Y = H	370	7.0	0.28	240
3g: X = 4-CO_2CH_3, Y = H	356	4.0	0.20	250
3h: X = 4-OCH_3, Y = 5-OCH_3	362	6.1	0.16	250
3i: X = 4-OCH_3, Y = 7-OCH_3	353	7.1	0.21	242
3j: X = 4-OCH_3, Y = 8-OCH_3	362	4.8	0.10	249
3k: X = F, Y = H	381	24	0.15	250
5a: X = H, Y = H	386	41	0.14	253
5b: X = 3-OCH_3, Y = H	356	8.8	0.23	241
5c: X = 4-OCH_3, Y = H	372	7.6	0.27	250

[a] From overlap of the 0,0 band in methanol at 25 °C. [b] By single photon counting in methanol at 25 °C. [c] Relative to naphthalene as 0.24. [d] From estimation of the 0,0 band of the phosphorescence spectrum at 77 K in 1:4 methanol:ethanol glass.

Table III. Quantum Yields for the Formation of 6 and 8 for the Photolysis of the Esters 3 in Methanol at 25 °C

esters 3	ϕ6	ϕ8	τ_S(ns)	$10^{-5}\ k_1^S$	$10^{-5}\ k_R^S$
a: X = H, Y = H	<0.005		49	<1.0	
b: X = H, Y = 3-OCH_3	0.008	0.013	11	7.3	12
c: X = H, Y = 4-OCH_3	0.017	0.006	7.3	23	8.2

yields are a function of competing processes. For instance, the quantum yield of reaction, eq 5, is the ratio of the rate constant

$$\phi_r = k_r/k_D^S = k_r\tau^S \quad (5)$$

of reaction divided by the rate constant for decay of the reactive excited state. Since it is now well established[2,16,22] that the triplet state of 1-naphthylmethyl esters is unreactive, the reactive state in these reactions is the excited singlet state. With this in mind, we have measured the excited-singlet-state energies, fluorescence quantum yields, and singlet lifetimes in methanol at 25 °C. These are given in Table II. For completeness, phosphorescence spectra were also recorded and triplet energies estimated.

Quantum yields of reaction in methanol were determined only for compounds **3a**, **3b**, and **3c**. The reactions are quite inefficient, making reliable measurement difficult. However, as shown in Table III, these values, along with the required singlet lifetimes, allow evaluation of the operational rate constants k_1^s and k_R^s in Scheme I. Calculation of these values assumes that product yields are determined solely by a rate- and product-determining cleavage of the carbon–oxygen bond in the excited singlet state. The results in Table III indicate neither a normal ground-state order for cation formation since k_1^S(3-CH_3O) ≫ k_1^S(H) nor an excited-state meta effect order for cation formation since k_1^S(4-CH_3O) > k_1^S(3-CH_3O). Once again, product yield and rate constant information in a benzylic cleavage reaction seemed to be eluding prediction.

Two facts allowed us to propose a mechanism which rationalizes all the yield information in Table I. The first fact was presented by comparing the esters **3** and **5**. In particular, the comparisons between **3a** and **5a**, **3b** and **5b**, and **3c** and **5c** were revealing. In each case, small but significant increases in the yield of the ether **6** at the expense of the coupling products **8** or **10**, were observed (Table I). From the values given in Table II, the excited-state properties of the compounds in each pair were essentially identical. Clearly, some factor following excited-state cleavage must be contributing to changes in product distribution.

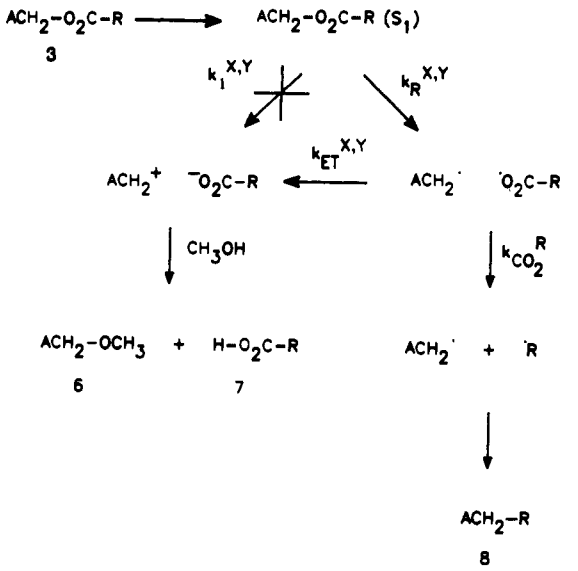
The second was the observation that the yield of the ether **6** was highest for cases where the substituents were neither strongly electron-donating or electron-withdrawing (H, 4-F, 4-CH_3) but decreased for both stronger donors (4-OCH_3 and the dimethoxy compounds) and stronger electron-withdrawing groups (4-CN, 4-CO_2CH_3). This reminded us of the well-known parabolic log rate versus free energy plot, the Marcus equation (eq 6).[23] In

$$\Delta G^{\ddagger} = \lambda/4(1 + \Delta G^{\circ\prime}/\lambda)^2 \quad (6)$$

this simple form of the equation, $\Delta G^{\ddagger}$ is the free energy of activation for electron transfer, $\Delta G^{\circ\prime}$ is the free energy change associated with the electron-transfer redox process, and λ is the reorganization energy. As will be discussed later, a more complex expression is now often used. Since the Marcus equation is used to describe electron-transfer rates, we were forced to examine the electron-transfer process that converts the singlet radical pair to the ion pair (k_{ET} in Scheme I). There is precedent for this idea. In the pyrolysis of ester peroxides, products derived from carbocation intermediates are formed, but CIDNP results demonstrate that the products originate from an original radical pair.[24] At about the same time, values for oxidation potentials of substituted benzyl radicals in solution were being measured and were shown,[25] as expected, to correlate very well with σ^+. The connection between yield of **6** and the electron-donating ability of the substituent was then made. The yield of **6** depends on the rate of formation of the ion pair, which is determined by the magnitude of k_{ET}, which is, in turn, controlled by the oxidation potential of the naphthylmethyl radical. In a previous paper,[2] we had wondered how it was ever possible to observe products derived from radical intermediates. For the standard leaving groups in photosolvolysis reactions, the ion pair is always more stable in polar solvents than the radical pair. How, then, could the radical pair avoid the potentially very rapid electron-transfer process that converts it to the ion pair? Marcus theory of electron transfer provides the necessary barrier, the reorganization energy, which slows the rate enough to allow other processes to compete.

With these ideas in mind, we proposed a mechanistic pathway, Scheme II, to account for the product yields in Table I. The major change from previous mechanistic schemes is that $k_1^{X,Y}$ is assumed to be considerably smaller than $k_R^{X,Y}$ so that homolytic cleavage of the carbon–oxygen bond in the excited singlet state of the ester dominates heterolytic cleavage. If this is true, then the product distribution reflects rate constant changes in processes that follow the excited-state chemistry. For esters, those two processes are electron transfer converting the radical pair to the ion pair ($k_{ET}^{X,Y}$) and decarboxylation of the acyloxy radical ($k_{CO_2}^{R}$). For the esters **3**, the rate of decarboxylation will be a constant, i.e., the rate of

Scheme II. Mechanism for the Photolysis of the 1-Naphthylmethyl Esters of Phenylacetic Acid, 3



(22) Matuszewski, B.; Givens, R. S.; Neywick, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 1973.

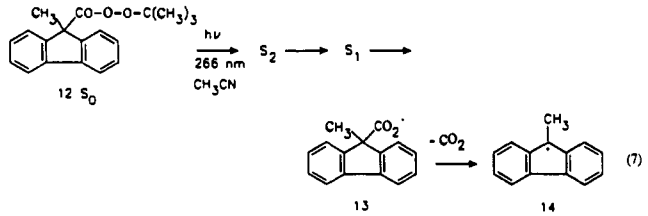
(23) Eberson, L. *Electron Transfer Reaction in Organic Chemistry*; Springer-Verlag: New York, 1987; p 32.

(24) Lawler, R. G.; Barbara, P. F.; Jacobs, D. *J. Am. Chem. Soc.* **1978**, *100*, 4912.

(25) Sim, B. A.; Griller, D.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 754.

decarboxylation of the phenylacetyloxy radical ($PhCH_2CO_2^{\bullet}$) is serving as a "clock" for the rate of electron transfer. Quantitatively, the change in product yields (increased yield of ether **6** at the expense of the coupling product **8**) for the esters **5** relative to **3** now makes sense. The rate of decarboxylation of the phenylpropanoyloxy radical ($PhCH_2CH_2CO_2^{\bullet}$) should be slower since the resulting radical is primary rather than benzylic. Therefore, $k_{ET}^{X,Y}$ (Scheme II), which is a function of the substituents (X,Y) on the naphthalene ring but not a function of the carboxylic acid side of the ester, becomes proportionally more important. In other words, $k_{ET}^{X,Y}/k_{CO_2}^{R}$ (R = $PhCH_2CH_2$) > $k_{ET}^{X,Y}/k_{CO_2}^{R}$ (R = $PhCH_2$) and the yield of ether **6** increases.

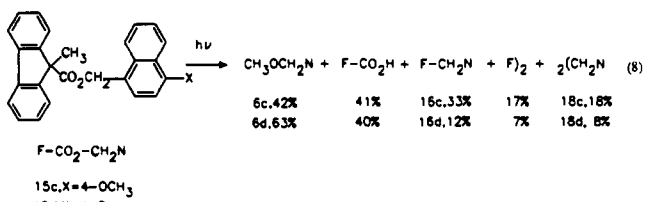
Determination of the Radical Clock Decarboxylation Rate for $PhCH_2CO_2^{\bullet}$. Putting this proposal on a more quantitative basis required an estimate of the rate constant for the clock reaction, the decarboxylation of phenylacetyloxy radical. Decarboxylations of acyloxy radicals at sp^2 [26,27] and sp-hybridized[26] carbons are slow enough to be measured by conventional laser flash photolysis, and recently a number of rate constants of this type have been determined. As an aside, a useful observation from these results[27] is that the 4-methoxybenzoyloxy radical reacts with a hydrogen atom donor like diethyl ether with a rate constant of $\approx 10^6$ M^{-1} s^{-1}. This process is therefore slow enough that the closely related hydrogen atom abstraction from the solvent cage (methanol) in our experiments is not likely to compete with other rapid unimolecular processes of the acyloxy radicals generated. For acyloxy radicals at sp^3-hybridized carbons, the lower bond dissociation energy makes decarboxylation very rapid. Values of around 10^9 s^{-1} have been estimated for the $CH_3CO_2^{\bullet}$ radical.[28,29] To our knowledge, the only decarboxylation rate that has been directly determined (picosecond flash photolysis) is for the (9-methyl-9-fluorenoyl)oxy radical (**13**).[30] The radical was generated by photolysis of the peroxide precursor **12**, eq 7. Even this value



(7)

is not directly determined since the spectral change monitored was the appearance of a signal corresponding to the 9-methylfluorenyl radical (**14**). The fluorenoyloxy radical **13** itself was not observed. However, arguments were advanced to demonstrate that the excited-state processes that precede the conversion of **13** to **14** are faster than $k_{CO_2} = 1.8 \times 10^{10}$ s^{-1}. This value can be used as a clock for ester photolysis reactions as follows.

Photolysis of esters **15c** and **15d** in methanol gave the products shown in eq 8. Again, the yield of acid, which should be identical to the yield of ether **6**, was determined gravimetrically after



(8)

isolation and cannot be expected to be reliable. The other yields were determined by calibrated HPLC. The yield of out-of-cage coupling products **17** and **18** are much higher here than in previous cases. Presumably the high stability of the fluorenyl radical **14** makes cage escape compete with in-cage coupling to **16**. If the mechanism outlined in Scheme II is correct, then product ratios are determined by the competition between $k_{ET}^{X,Y}$ and $k_{CO_2}^{R}$. Products **16**, **17**, and **18** all result from decarboxylation and product **6** from electron transfer. Therefore, $k_{ET}^{X,Y}$ (X = 4-OCH_3, Y = H)/$k_{CO_2}^{R}$ (R = **14**) = 0.83 ± 0.03 and $k_{ET}^{X,Y}$ (X = 4-CH_3, Y = H)/$k_{CO_2}^{R}$ (R = **14**) = 3.2 ± 0.1. Since $k_{CO_2}^{R}$ (R = **14**) = 1.8×10^{10} s^{-1}, $k_{ET}^{X,Y}$ (X = 4-OCH_3, Y = H) = $(1.5 \pm 0.1) \times 10^{10}$ s^{-1} and $k_{ET}^{X,Y}$ (X = 4-CH_3, Y = H) = $(5.8 \pm 0.2) \times 10^{10}$ s^{-1}.

These values can now be used for the product yields obtained for substrates **3c** and **3d** (Table I). The assumption made here is that the rate of electron transfer depends only on the substituents (X,Y) on the naphthalene ring and not on the structure of the acyloxy radical. This is reasonable since the R group on an acyloxy radical ($RCO_2^{\bullet}$) is at a node and not directly conjugated to the sites of odd electron density or to the sites of negative charge that result after electron transfer reduces the acyloxy radical to the anion. If this assumption is true, then it follows that $k_{ET}^{X,Y}$ (X = 4-OCH_3, Y = H)/$k_{CO_2}^{R}$ (R = $PhCH_2$) = %**6c**/%**8c** = 3.1 ± 0.1 and $k_{ET}^{X,Y}$ (X = 4-CH_3, Y = H)/$k_{CO_2}^{R}$ (R = $PhCH_2$) = %**6d**/%**8d** = 13.3 ± 0.5. Using the rates of electron transfer determined above gives two values for $k_{CO_2}^{R}$ (R = $PhCH_2$) = (4.8 ± 0.4) × 10^9 s^{-1} (from **3c**) and (4.4 ± 0.4) × 10^9 s^{-1} (from **3d**). The similarity between the values determined from product yields of two independent substrates gives us considerable confidence that the mechanistic proposal in Scheme I is correct. Therefore, for the critical clock reaction required to analyze the data in Table I, we have chosen the average value of these two determinations, 4.6×10^9 s^{-1}, for the rate of decarboxylation of the phenylacetyloxy radical.

The radical clock procedure described in this section clearly relies quite heavily on the value for the decarboxylation of the (9-methyl-9-fluorenoyl)oxy radical (**13**). Any error in this determination will lead to parallel errors in all the values for rates of electron transfer ($k_{ET}^{X,Y}$) discussed here and, in more detail, in other published work.[31] However, it is important to realize that changes in this calibrating rate constant will only result in all values being scaled proportionally; no changes in the relative order would result. For instance, the value initially determined[30] in acetonitrile is being used here where methanol is the solvent, which fortunately has a very similar dielectric constant to that of acetonitrile. Although solvent effects on radical reaction rates are generally expected to be small, this may not always be the case. For instance, the rate of decarboxylation of the (4-methoxybenzoyl)oxy radical has been shown to decrease by a factor of 20 on changing the solvent from carbon tetrachloride to acetonitrile.[24] Of course, in this case the polarity is also considerably different.

Application of Marcus Theory to the Electron-Transfer Rates ($k_{ET}^{X,Y}$) for Conversion of the Radical Pair to the Ion Pair. In order to apply Marcus theory to an electron-transfer process, the required data are the rate of electron transfer and the free energy of electron transfer. By applying the mechanistic ideas outlined in Scheme II and the previous section, the electron-transfer rate constant for converting the radical pair to the ion pair can easily be obtained as in eq 9. These values are given in Table I in logarithmic form.

$$k_{ET}^{X,Y} = (\text{yield of } \mathbf{6}/\text{yield of } \mathbf{8}) \times k_{CO_2}^{R} \text{ (R = PhCH}_2\text{)} = (\text{yield of } \mathbf{6}/\text{yield of } \mathbf{8}) \times 4.6 \times 10^9 \text{ s}^{-1} \quad (9)$$

Obtaining the values for the free energy of electron transfer is a greater problem. Normally, this is done by applying eq 10, where ΔG° is estimated from reversible redox potentials, eq 11,

$$\Delta G^{\circ\prime} = \Delta G^{\circ} - e^2/Dr_{12} \quad (10)$$

$$\Delta G^{\circ}\ (\text{kJ/mol}) = 96.7\ (E^{\circ}_{ox} + E^{\circ}_{rcd}) \quad (11)$$

(26) Korth, H. G.; Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 5929.
(27) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877, 2886.
(28) Kaptein, R.; Brokken-Zijp, J.; de Kanter, F. J. J. *J. Am. Chem. Soc.* **1972**, *94*, 6280.
(29) Braun, W.; Rajbenbach, L.; Eirich, F. R. *J. Phys. Chem.* **1962**, *66*, 1591.
(30) Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419.
(31) Hilborn, J. W.; Pincock, J. A. *J. Am. Chem. Soc.* **1991**, *113*, 2683.

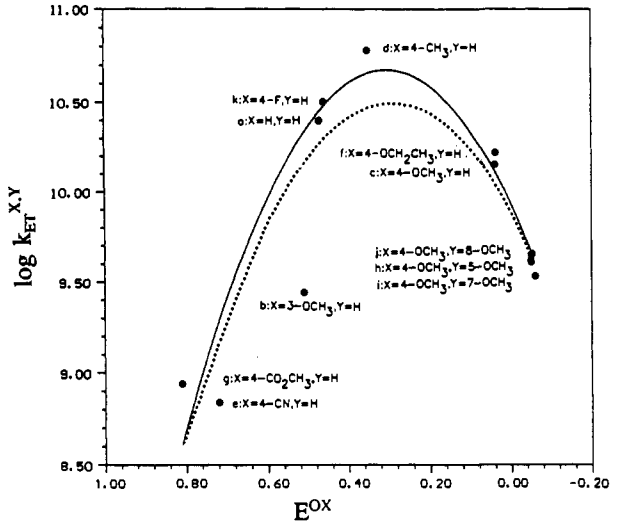


Figure 1. Plot of the rate of electron transfer for converting the radical pair to the ion pair as a function of the oxidation potential of the 1-naphthylmethyl radical. The dashed line includes the point for the 3-methoxy compound; the solid line does not. The fits are to eqs 14–18, and the derived parameters for the solid line are $\lambda = 0.52$ eV, $B = -0.82$ eV, and $A = 5.0 \times 10^{10}$ s^{-1}.

and the second term is the electrostatic term required to correct for the distance r_{12} of separation of the ions in a solvent of dielectric constant D. The value of this electrostatic term is usually small; for instance, for intermolecular excited-state electron transfer the values often used for acetonitrile $D = 35$ and $r_{12} = 7$ Å lead to a result of only 7.5 kJ/mol. However, this term could be significantly greater for an in-cage ion pair where the distance should be shorter and the dielectric constant smaller (vide infra).

Recently, we have measured[32] the required solution oxidation potentials ($E^{X,Y}$) for substituted 1-naphthylmethyl radicals in acetonitrile. These are also shown in Table I. These values can be used in eq 12 where F is the Faraday constant, $E^{X,Y}$ is the

$$\Delta G_{ET}^{X,Y} = FE^{X,Y}(ACH_2^{\bullet}, CH_3CN) + A^{X,Y} + FE(PhCH_2CO_2^{-}, CH_3OH) - e^2/Dr_{12} \quad (12)$$

oxidation potential of the 1-naphthylmethyl radical in acetonitrile, E is the oxidation potential of the phenylacetate anion in methanol, and $A^{X,Y}$ is an unknown factor that corrects for the fact that the measured values of $E^{X,Y}$ are in acetonitrile but the photochemistry was done in methanol. This problem cannot be easily avoided since the solution oxidation potential measurement method normally requires acetonitrile as solvent but the photochemistry requires a nucleophilic solvent to trap the ionic intermediates. The reasonable assumption that the solvent correction factor $A^{X,Y}$ is independent of X and Y converts eq 12 to eq 13 since the last three unknown terms are all constant.

$$\Delta G_{ET}^{X,Y} = FE^{X,Y}(ACH_2^{\bullet}, CH_3CN) + B \quad (13)$$

With this assumption, a correlation can be made beginning with eq 14 which relates $k_{ET}^{X,Y}$ to $\Delta G_{ET}^{X,Y}$. Substituting eq 13 into eq 14, reorganizing and taking logarithms gives eq 15, the quadratic Marcus relationship, where a_1, a_2, and a_3 (as defined in eqs 16, 17, and 18) are the fitting parameters.

$$k_{ET}^{X,Y} = A \exp[(-\lambda/4)(1 + \Delta G_{ET}^{X,Y}/\lambda)^2/RT] \quad (14)$$

$$\log k_{ET}^{X,Y} = a_1 + a_2(E^{X,Y}) + a_3(E^{X,Y})^2 \quad (15)$$

$$a_1 = \log A - [(\lambda + B)^2/(2.3 \times 4\lambda RT)] \quad (16)$$

$$a_2 = -2F(\lambda + B)/(2.3 \times 4\lambda RT) \quad (17)$$

$$a_3 = -F^2/(2.3 \times 4\lambda RT) \quad (18)$$

(32) Milne, P. H.; Wayner, D. D. M.; DeCosta, D. P.; Pincock, J. A. *Can. J. Chem.* **1992**, *70*, 121.

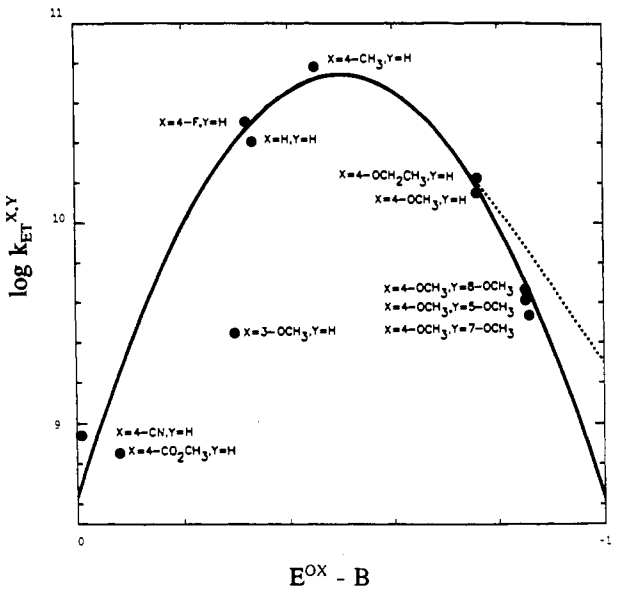


Figure 2. Plot of the rate of electron transfer for converting the radical pair to the ion pair as a function of the oxidation potential of the 1-naphthylmethyl radical. The fits are to eqs 19–21. The solid line has $\lambda_S = 0.5$ eV and $\lambda_V = 0.0$ eV; the dashed line has $\lambda_S = 0.45$ eV and $\lambda_V = 0.05$ eV.

A plot of log $k_{ET}^{X,Y}$ versus $E^{X,Y}$ (solid line) fitted by a weighted least-squares analysis of eq 15 ($a_1 = 9.95 \pm 0.07$, $a_2 = 4.9 \pm 0.6$, $a_3 = -8.2 \pm 0.9$) is shown in Figure 1. This leads to values of $\lambda = 0.52$ eV, $B = -0.82$ eV, and $A = 5.0 \times 10^{10}$ s^{-1}. This plot is made omitting the point for the 3-methoxy compound. The dashed line in Figure 2 is the same plot including the 3-methoxy values. The correlation is clearly worse ($a_1 = 9.90 \pm 0.13$, $a_2 = 3.8 \pm 1.0$, $a_3 = -6.8 \pm 1.7$), but the values of $\lambda = 0.66$ eV, $B = -0.90$ eV, and $A = 2.7 \times 10^{10}$ are probably not significantly different. We have no reason, in principle, for omitting the point for the 3-methoxy compound although it is possible that there is a second Marcus-type curve for meta isomers. Since these meta-substituted naphthalenes are difficult to synthesize, the 3-methoxy compound is the only one of that type studied and therefore, this possibility of two separate correlations cannot be excluded.

A discussion of the physical significance of the values obtained from eq 6, the original form of the Marcus equation, requires comparison with those obtained by more recent theories of electron transfer that employ a golden rule-type formula, eqs 19–21.[33]

$$k_{ET}^{X,Y} = \sum_{j=0}^{\infty} F_j V^2 \left(\frac{4\pi^3}{h^2 \lambda_S k_B T}\right)^{1/2} \exp\left[-\frac{(jh\nu_V + \Delta G_{ET} + \lambda_S)^2}{4\lambda_S k_B T}\right] \quad (19)$$

$$F_j = \frac{e^{-S} S^j}{j!} \quad (20)$$

$$S = \lambda_V/h\nu_V \quad (21)$$

Fitting data to these equations allows separation of the reorganization energy λ into λ_V and λ_S. The former term is associated with changes that occur in the nuclear positions of the species undergoing electron transfer. These high-frequency skeletal vibrations are often represented by a single "average mode" with frequency ν. Low-frequency modes, associated with reorientation of the solvent, have reorganization energy λ_S. Our data give a good fit[34,35] ($V^2 = 12.4$, $\lambda_S = 0.5$ eV, $\lambda_V = 0$ eV) to this equation

(33) (a) Van Duyne, R. P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (b) Ulstrop, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (c) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741, 748. (d) Brunschweig, B. S.; Logan, J.; Newton, M. D.; Sutin, N. *J. Am. Chem. Soc.* **1980**, *102*, 5798.

(34) Fitting software provided by Dr. Samir Farid, Eastman Kodak Co., CRL, Rochester, NY, 14640-2109.

(35) This fit requires subtracting 0.82 V (the value of B determined using eq 15) from the measured oxidation potentials in Table I.

(Figure 2) but only when λ_V is set equal to 0. Any contribution that λ_V makes to the total reorganization energy will result in an asymmetry in the shape so that the parabola widens on the exergonic side. This effect is shown by the dashed line in Figure 2 with $\lambda_V = 0.05$. The symmetric shape of the parabola in Figure 2 strongly suggests that nuclear reorganization makes an insignificantly small contribution to the total reorganization energy.

The suggestion of a very small vibrational reorganization energy (λ_V) certainly makes qualitative sense. During the electron-transfer process, an electron is being transferred from a nonbonding MO of the 1-naphthylmethyl radical to, at least on a very naive Lewis structure basis (vide infra), the nonbonding MO of the acyloxy radical. As has been pointed out previously,[36] a more quantitative estimate of λ_V can be made by calculating the difference between the energy of the acceptor and the donor (the radical pair) at their equilibrium nuclear geometry and the energy of the same species at the equilibrium nuclear geometry of the species that result after electron transfer (the ion pair). We have done this at the AM1 level using Gaussian 90.

As expected, for the 1-naphthylmethyl radical the energy required to reorganize its structure to that of the cation at its minimized geometry is very small (2.4 kJ/mol), and changes in bond lengths are insignificant. For instance, at the methyl carbon the change in the C–C bond length is only 0.02 Å and in the two C–H bond lengths, 0.01 Å.

To model the phenylacetyloxy radical we have chosen acetyloxy ($CH_3CO_2^{\bullet}$) in order to simplify the calculations. The energy required to reorganize the structure of this radical to that of the anion at its minimized geometry is considerably larger (20.4 kJ/mol). The minimized geometry of the acetate ion has, as expected, equal C–O bond lengths of 1.27 Å. The radical, on the other hand, has two C–O bonds of quite different length (1.23 and 1.33 Å) and is of $^2A'$ symmetry. It is well established by previous calculations that there are three states for radicals like the formyloxy ($HCO_2^{\bullet}$)[37,38] and the acetyloxy ($CH_3CO_2^{\bullet}$)[38] radicals which are very close in energy, a π-state and both symmetric and antisymmetric σ-states. For formyloxy, if the C–O bonds are restricted to be of equal length (C_{2v}) these states are labelled $^2A_2$, $^2A_1$, and $^2B_2$ respectively. If the C–O bonds are allowed to vary independently in length, the low-energy states are now $\pi(^2A'')$ and $\sigma(^2A')$. Only with large basis sets, extensive CI, and geometry optimization is it possible to calculate the ordering in energy of these states. The current consensus is that the ground state is $^2a'$; this state has calculated C–O bond lengths of 1.25 and 1.35 Å. The $^2B_2$ state with equal (1.26 Å) C–O bond lengths is 30.9 kJ/mol higher in energy. Considering the simplicity of the AM1 method, the calculations for the reorganization energy of the acetyloxy radical reported above are in remarkably good agreement with these high-level calculations.

The conclusion from this section is that the calculated λ_V for electron transfer converting the radical pair to the ion pair is ~23 kJ/mol = 0.24 eV. This value represents almost entirely the reorganization energy required for the acyloxy radical changing to the symmetric structure necessary for the carboxylate anion. This result is in disagreement with the experimental observation of the symmetrical parabola in Figure 2, which implies that λ_V is very small (<0.05 eV). Of course, the assumption made in the calculated reorganization energy is that the acyloxy radical is in its ground state ($^2A'$) with unequal C–O bond lengths. If the photochemical reaction proceeds by bond cleavage from the excited singlet state of the substrate to the excited state of the acyloxy radical ($^2A_2$), then the C–O bond lengths would be equal. If electron transfer to form the ion pair then occurs more rapidly than conversion of the π-state ($^2A_2$) to the antisymmetric σ-state ($^2A'$), then the reorganization energy λ_V would be very small. The suggestion that these two states could be important in acyloxy radical chemistry has been made previously,[39] although the results have been questioned.[31] However, the possibility does allow a highly speculative agreement between the experimental observations and theory.

Electron-Transfer Parameters. As discussed above, if $\lambda_V = 0$, then the only parameters required to fit the data are λ and A (the preexponential factor) from eq 14 or λ_S and V (the matrix coupling element) from eq 19. In fact, if $\lambda_V = 0$, the two equations become identical.

The value of $\lambda_S = 0.5$ eV is certainly typical of solvent reorganization values determined previously for electron transfer over short distances. This has been shown clearly by Gould, Farid, et al.[40] in their detailed studies on return electron transfer in radical ion pairs. A value of 0.55 eV was obtained for charge-transfer complexes (contact ion pairs) and a much higher value of 1.6 eV for solvent separated radical ion pairs. Similarly, Closs, Miller, et al.,[41] in their now classic study of intramolecular electron transfer in the inverted region, estimated a value of 0.47 eV for a charge shift reaction over a distance of about 6 Å.

The value of V, the electronic coupling matrix element, that determines the rate maximum of the Marcus curve, can vary tremendously. There has been considerable interest in distance[41] and orientation effects[42] on the value of V. Strong coupling and high values of $V = 200$ cm^{-1} have been estimated[40] for radical ion pairs in charge-transfer complexes where the distance is short and the orbital overlap probably is very large. The value drops (11 cm^{-1}) for the solvent-separated ion pair, in agreement with the predicted exponential dependence on distance. For intramolecular electron transfer where through-bond mechanisms are possible, both distance and orientation effects are important in determining V.[41] For the electron transfer that converts the contact radical pair to the ion pair reported in this work, a value of $V = 12$ cm^{-1} has been determined. This is small for a case where the distance is very short but perhaps reasonable since the orbital overlap could be very poor. There are not, to our knowledge, good precedents in the literature for comparison.

Finally, as discussed above, we have determined a value of $B = -0.82$ V, which is the constant in eq 13 that replaces the three constants in eq 12. Reasonable estimates of 2.4 V for the oxidation potential in water of $CH_3CO_2^-$ are available,[43] and the value for $PhCH_2CO_2^-$ is probably not much different. The oxidation potential of the 1-naphthyl radical is probably similar in methanol and acetonitrile since the dielectric constants are so similar and the product 1-naphthylmethyl cation is delocalized. Therefore, the electrostatic term (eqs 10 and 12) is probably about 1.6 eV (150 kJ/mol). This is in remarkably good agreement with Suppan's model[44] for the generation of contact ion pairs in electron-transfer reactions. Using his equation for the Coulombic term, a calculated value of 153 kJ/mol is obtained assuming a distance of 3 Å, which does not seem unreasonable for the contact ion pair generated in the photolysis of esters.

Our conclusion from this section is that all electron-transfer parameters derived from the experimental facts are reasonable.

Generation of Ion Pairs in Benzylic Photosolvolysis Reactions. As discussed in the Introduction to this paper, there has been a considerable literature that discusses heterolytic cleavage of benzylic compounds in the singlet excited state to form the ion pair directly. Our results can be rationalized by a pathway of exclusive homolytic cleavage of the excited singlet state to the radical pair followed by electron transfer that converts the radical pair to the ion pair. *No heterolytic cleavage is required!*

An important observation about this mechanistic conclusion is that the λ value is small (0.5 eV), so the Marcus electron-transfer parabola is narrow on the ΔG scale. This means that

(36) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.
(37) Feller, D.; Huyser, E. S.; Borden, W. J.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459.
(38) Peyerimhoff, S. D.; Skell, P. S.; May, D. D.; Buenker, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 4516.
(39) Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1983**, *105*, 3999.
(40) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.
(41) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.
(42) Siders, P.; Cave, R. J.; Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 5613.
(43) Reference 21, 40–47.
(44) Suppan, P. *Chimia* **1988**, *42*, 320.

the Marcus inverted region behavior can only be observed if the set of compounds studied happens to fall in the region close to the maximum on the log k versus ΔG plot. One has to be as lucky as we were! Moreover, the variation in substituents has to cover a wide enough range on the oxidation potential scale to be on both sides of the maximum. In many cases, all compounds could have redox potentials for the radical pair that put them in the normal region. In this case a σ^+ correlation with positive slope would be observed. Conversely, all compounds could form radical pairs with redox potentials that put them in the inverted region. A σ^+ correlation with negative slope would be observed, and this would look like the meta effect (3-CH_3O > H > 4-CH_3O). Our recent results[45] for benzyl acetates, the compounds that originally led to the postulation of the meta effect,[11] indicate that this second possibility is, in fact, probably the case. The implication that these results have on other benzylic photosolvolysis reactions requires further consideration.

Experimental Section

General. All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B IR spectrometer and are given in wavenumbers (cm^{-1}). Most ^1H NMR spectra were obtained on a Nicolet 360 instrument at 360 MHz with chemical shift relative to TMS. The mass spectra were run on a CEC 21-104 mass spectrometer at 70 eV; all signals over 10% of the intensity of the base peak are reported as m/z (relative intensity). High-pressure liquid chromatographic analyses were performed on a Waters System employing a Model 6000A pump, a Model 450 variable wavelength UV detector, and a Model U6K injector. A Brownlee RP-8 analytical column was used with an 80% methanol: water mixture as the eluent and detection at 280 nm. Absorption spectra were obtained using a Varian Cary 219 spectrophotometer. GC/MS were done on a Hewlett-Packard capillary 5% phenylsilicone column temperature programmed from 50 to 250 °C using a HP 5970 Series Mass Selective Detector. C, H, and N analyses were done by Canadian Microanalytical Service Ltd, Delta, BC, V5G 1G7. 1-Naphthylmethanol, 1-methoxynaphthalene, 1-aminonaphthalene, 1-methylnaphthalene, 1,8-naphthalene sultone, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 4-fluoro-1-naphthoic acid, and phenylacetyl chloride were purchased from the Aldrich Chemical Co. The preparation of 4-methoxy-1-naphthylmethanol[46] was by a literature procedure.

Preparation of Naphthylmethanols. 3-Methoxy-1-naphthylmethanol (4b). 1-Cyano-3-methoxynaphthalene. Starting from 1-aminonaphthalene, 1-bromo-3-methoxynaphthalene was prepared as described previously.[47] The cyanation procedure was that of Friedman and Shechter.[48] A solution of the bromide (2.37 g, 10 mmol) and CuCN (1.03 g, 11.5 mmol) in 6 mL of DMF was refluxed for 6 h. The resulting mixture was poured into a solution of 6 mL of H_2O, 1 mL of concentrated HCl, and 4 g of $FeCl_3$ and heated at 65 °C for 20 min. The mixture was extracted with 3 × 15 mL of toluene, and the extracts were washed with 30 mL of 15% HCl and 25 mL of 10% NaOH, dried over $MgSO_4$, and concentrated to give 1.7 g of crude product. Recrystallization from hexane gave 1.3 g (70%) of pure 1-cyano-3-methoxynaphthalene as colorless needles: mp 104–105 °C (lit.[49] mp 103 °C); ^1H NMR ($CDCl_3$) δ 8.3–8.1 (m, 1 H), 8.0–7.8 (m, 1 H), 7.7–7.5 (m, 3 H), 7.3 (d, 1 H, J = 2 Hz), 3.95 (s, 3 H); IR (Nujol) 2200 cm^{-1}; mass spectrum m/z 184 (17), 183 (100), 168 (39), 153 (37), 141 (39), 140 (100), 113 (68), 63 (46).

3-Methoxy-1-naphthoic Acid. The method of Amin et al.[50] was used with little change. A solution of the nitrile (1.4 g, 7.7 mmol) in 15 mL of hot ethanol was added to 20 mL of 2.5 M NaOH solution. The mixture was refluxed for 24 h followed by evaporation of most of the ethanol and filtration. The filtrate was washed with 2 × 20 mL of $CHCl_3$ and then acidified with concentrated HCl to give 1.47 g (7.3 mmol, 95%) of the acid. Crystallization from ethanol–water gave the pure acid as fine colorless needles: mp 156–157 °C; IR (Nujol) 1685, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.05 (dd, 1 H, J = 2.5, 8.5 Hz), 8.15 (d, 1 H, J = 2.5 Hz), 8.0–7.8 (m, 1 H), 7.65 (t, 1 H, J = 7.8 Hz), 7.50 (t, 1 H, J = 7.6 Hz), 7.40 (d, 1 H, J = 2.2 Hz), 8.5 (br s, 1 H, exchangeable), 3.95 (s, 3 H); mass spectrum m/z 203 (13), 202 (100), 185 (12), 159 (16), 131 (92), 127 (21), 115 (21), 114 (10).

3-Methoxy-1-naphthylmethanol (4b). The method of Brown et al.[51] was used. To a solution of 3-methoxy-1-naphthoic acid (11.5 g, 57 mmol) in 25 mL of dry THF were added dropwise 76 mL of 1 M borane/THF solution at 0 °C. The mixture was stirred for 1 h at room temperature, and excess hydride was destroyed by 80 mL of 1:1 water:THF. The mixture was then saturated with K_2CO_3 and extracted with 2 × 100 mL of ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated to give 9.8 g (52 mmol, 92%) of crude product. Recrystallization from hexane yielded the pure alcohol: mp 87–88 °C (lit.[2] mp 88–89 °C).

4-Methyl-1-naphthylmethanol (4d). 4-Methyl-1-naphthoic Acid. Starting from 1-methylnaphthalene, 1-bromo-4-methylnaphthalene was prepared as described by Fieser and Bowen.[52] The cyanation method of Friedman and Shechter[48] was used. Recrystallization from dilute ethanol yielded pure 1-cyano-4-methylnaphthalene as colorless plates: mp 53–54 °C (lit.[53] mp 53–54 °C).

The nitrile was hydrolyzed to the acid by the method described for 3-methoxy-1-naphthoic acid. Recrystallization from ethanol–water gave colorless needles: mp 178–179 °C (lit.[54] mp 180 °C).

4-Methyl-1-naphthylmethanol (4d). 4-Methyl-1-naphthoic acid was reduced to 4-methyl-1-naphthylmethanol by the method described for 3-methoxy-1-naphthylmethanol from 3-methoxy-1-naphthoic acid. The yield of the alcohol was 90%, which is much better than yields obtained for the same reduction using $LiAlH_4$.[55] This alcohol was crystallized from hexane to give fine colorless needles: mp 76–77 °C (lit.[56] mp 77 °C).

4-Cyano-1-naphthylmethanol (4e). 4-Cyano-1-naphthaldehyde was prepared from 4-cyano-1-methylnaphthalene by the method of Dewar et al.[57] This aldehyde was reduced to 4-cyano-1-naphthylmethanol with $NaBH_4$ in ethanol as described previously.[2] Recrystallization from ethanol yielded colorless crystals: mp 118–119 °C (lit.[58] mp 118–119 °C).

4-Ethoxy-1-naphthylmethanol (4f). 1-Ethoxynaphthalene was formylated by the method of Buu-Hoi and Lavit.[46] Recrystallization from acetic acid gave colorless crystals: mp 74–75 °C. This aldehyde was reduced to 4-ethoxy-1-naphthylmethanol with $NaBH_4$ in ethanol as described previously:[2] mp 75–76 °C; ^1H NMR ($CDCl_3$) δ 8.4–8.0 (m, 2 H), 7.6–7.4 (m, 2 H), 7.3 (d, 1 H, J = 8.0 Hz), 6.7 (d, 1 H, J = 8.0 Hz), 5.0 (s, 2 H), 4.2 (q, 2 H, J = 7.6 Hz), 1.8 (s, 1 H, exchangeable), 1.5 (t, 3 H, J = 7.6 Hz).

4-Carbomethoxy-1-naphthylmethanol (4g). 1-Methyl-4-cyanonaphthalene was converted to 1-bromomethyl-4-cyanonaphthalene by the method of Dewar et al.[57] This compound (5 g) was then refluxed in 30 mL of 20% aqueous NaOH for 5 days. The hot solution was filtered, diluted with 20 mL of water, and washed with 25 mL of chloroform. Acidification of the aqueous layer and filtration yielded crude 4-hydroxymethyl-1-naphthoic acid (3 g, 72%). Recrystallization from ethanol/water yielded colorless needles: mp 171–172 °C; ^1H NMR ($CDCl_3$ + DMSO-d_6) δ 9.1–8.9 (m, 1 H), 8.3–8.0 (m, 2 H), 7.8–7.5 (m, 3 H), 7.0 (br s, exchangeable, 2 H), 5.2 (s, 2 H).

The ester was obtained from the acid using diazomethane in ether. Crystallization from ethanol gave colorless crystals: mp 59–60 °C; ^1H NMR ($CDCl_3$) δ 9.0–8.8 (m, 1 H), 8.1–7.8 (m, 2 H), 7.6–7.3 (m, 3 H), 5.0 (s, 2 H), 3.9 (s, 3 H), 3.0 (s, exchangeable, 1 H).

4,5-Dimethoxy-1-naphthylmethanol (4h). 1,8-Dimethoxynaphthalene was obtained from the sultone by the method of Parker and Iqbal.[59] This compound was formylated by the method of Buu-Hoi and Lavit.[60] Recrystallization from ethanol yielded colorless crystals: mp 94–95 °C (lit.[60] mp 95 °C); ^1H NMR ($CDCl_3$) δ 10.13 (s, 1 H), 8.95 (d, 1 H, J = 8.1 Hz), 7.9 (d, 1 H, J = 8.0 Hz), 7.60 (d, 1 H, J = 8.1 Hz), 6.98 (d, 1 H, J = 8.0 Hz), 6.90 (d, 1 H, J = 8.0 Hz), 3.98 (s, 3 H), 3.90 (s, 3 H).

The aldehyde was reduced to 4,5-dimethoxy-1-naphthylmethanol (**4h**) with $NaBH_4$ in ethanol as described previously:[2] mp 97–98 °C; ^1H NMR ($CDCl_3$) δ 7.65 (d, 1 H, J = 7.9 Hz), 7.60 (t, 1 H, J = 8.0 Hz),

(45) Hilborn, J. W.; MacKnight, E.; Pincock, J. A.; Wedge, P. J. *J. Am. Chem. Soc.*, submitted for publication.
(46) Buu-Hoi, N. P.; Lavit, D. *J. Chem. Soc.* **1955**, 2776.
(47) Newman, M. S.; Sankaran, V.; Olsen, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 3237.
(48) Friedman, L.; Shechter, H. *J. Org. Chem.* **1961**, *26*, 2522.
(49) Hodgson, H. H.; Birtwell, S. *J. Chem. Soc.* **1944**, 539.
(50) Amin, S.; Hecht, S. S.; Hoffmann, D. *J. Org. Chem.* **1981**, *46*, 2394.
(51) Yoon, M. N.; Pak, C. S.; Brown, H. C.; Krishnamurthy, S.; Stocky, T. P. *J. Org. Chem.* **1973**, *38*, 2786.
(52) Fieser, L. F.; Bowen, D. M. *J. Am. Chem. Soc.* **1940**, *62*, 2103.
(53) Rule, H. G.; Campbell, N.; McGregor, A. G.; Woodham, A. A. *J. Chem. Soc.* **1950**, 1816.
(54) Bonnier, J. M.; Rinudo, J. *Bull. Soc. Chim. Fr.* **1966**, 3901.
(55) Dixon, E. A.; Fischer, A.; Robinson, F. P. *Can. J. Chem.* **1981**, *59*, 2629.
(56) Jefford, C. W.; Rossier, J. C.; Kohomoto, S.; Boukouvalas, J. *Helv. Chim. Acta* **1985**, *68*, 1804.
(57) Dewar, M. J. S.; Grisdale, P. J. *J. Am. Chem. Soc.* **1962**, *84*, 3541.
(58) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4645.
(59) Parker, K. A.; Iqbal, J. *J. Org. Chem.* **1980**, *45*, 1149.
(60) Buu-Hoi, N. P.; Lavit, D. *J. Chem. Soc.* **1956**, 2412.

7.55 (d, 1 H, J = 7.0 Hz), 6.92 (d, 1 H, J = 7.8 Hz), 6.78 (d, 1 H, J = 7.9 Hz), 4.98 (s, 2 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 2.4 (s, 1 H, exchangeable).

4,7-Dimethoxy-1-naphthylmethanol (4i). 1,6-Dimethoxynaphthalene was obtained from the dihydroxy compound by the method of Buu-Hoi and Lavit.[61] This compound was formylated by the method of Buu-Hoi and Lavit.[62] Recrystallization from ethanol yielded colorless crystals: mp 78–79 °C (lit.[63] mp 78–79 °C); ^{1}H NMR ($CDCl_3$) δ 10.13 (s, 1 H), 8.82 (d, 1 H, J = 2.0 Hz), 8.20 (d, 1 H, J = 8.4 Hz), 7.80 (d, 1 H, J = 8.0 Hz), 7.17 (dd, 1 H, J = 2.1, 8.2 Hz), 6.74 (d, 1 H, J = 8.0 Hz), 4.03 (s, 3 H), 3.95 (s, 3 H).

The aldehyde was reduced to 4,7-dimethoxy-1-naphthylmethanol (**4i**) with $NaBH_4$ in ethanol as described previously:[2] mp 78–79 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (d, 1 H, J = 7.9 Hz), 7.60 (t, 1 H, J = 8.0 Hz), 7.55 (d, 1 H, J = 7.9 Hz), 6.92 (d, 1 H, J = 7.8 Hz), 6.78 (d, 1 H, J = 7.9 Hz), 4.98 (s, 2 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 2.4 (s, 1 H, exchangeable).

4,8-Dimethoxy-1-naphthylmethanol (4j). 4,8-Dimethoxy-1-naphthaldehyde was prepared by the method of Buu-Hoi and Lavit:[62] mp 125–126 °C (lit.[62] mp 126 °C); ^{1}H NMR ($CDCl_3$) δ 11.17 (s, 1 H), 8.13 (d, 1 H, J = 8.1 Hz), 7.95 (d, 1 H, J = 7.5 Hz), 7.47 (t, 1 H, J = 8.0 Hz), 7.05 (d, 1 H, J = 7.9 Hz), 6.90 (d, 1 H, J = 7.6 Hz), 4.07 (s, 3 H), 4.00 (s, 3 H).

This aldehyde was reduced to 4,8-dimethoxy-1-naphthylmethanol (**4j**) with $NaBH_4$ in ethanol as described previously.[2] Recrystallization from ethanol yielded colorless crystals: mp 154–55 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 1 H, J = 8.1 Hz), 7.40 (t, 1 H, J = 8.0 Hz), 7.32 (d, 1 H, J = 8.1 Hz), 6.95 (d, 1 H, J = 8.1 Hz), 6.73 (d, 1 H, J = 8.0 Hz), 4.95 (s, 2 H), 4.05 (s, 3 H), 3.98 (s, 3 H), 3.2 (s, 1 H, exchangeable).

4-Fluoro-1-naphthylmethanol (4k). 4-Fluoro-1-naphthoic acid was reduced to 4-fluoro-1-naphthylmethanol (**4k**) by the method described for 3-methoxy-1-naphthoic acid. This alcohol was recrystallized from hexane to give colorless plates: mp 84–85 °C; ^{1}H NMR ($CDCl_3$) δ 8.3–8.0 (m, 2 H), 7.7–7.4 (m, 2 H), 7.3 (dd, 1 H, J = 7.5, 5.0 Hz), 7.0 (dd, 1 H, J = 10.0, 7.5 Hz), 5.1 (s, 2 H), 1.9 (s, 1 H, exchangeable).

9-Methylfluorene-9-carbonyl Chloride. Fluorene was converted to 9-methylfluorene-9-carboxylic acid as described by Bavin.[64] Recrystallization from water gave colorless needles: mp 170–171 °C (lit.[64] mp 170–171 °C). This acid was treated with PCl_5 to give the acid chloride as described by Boyd and Harms.[65] Recrystallization from petroleum ether gave colorless needles: mp 95–96 °C (lit.[66] mp 95–96 °C).

General Method for Preparation of Esters 3. To a solution of the alcohol (20 mmol) in 75 mL of benzene and 1 mL of pyridine was added a solution of the acid chloride (22 mmol) in 20 mL of benzene. After 6 h the mixture was poured into 50 mL of water, and the organic layer was separated. This layer was washed with 40 mL each of 10% HCl, 5% NaOH, and water, dried with $MgSO_4$, and evaporated to give an oil or solid. This crude material was chromatographed on silica gel with 30% CH_2Cl_2:hexane as the eluent. The yields were 50–80%. The esters were purified either by crystallization from hexane or vacuum distillation. The boiling point or melting point, ^{1}H NMR ($CDCl_3$), IR, mass spectrum, and analytical data are given.

1-Naphthylmethyl phenylacetate (3a): bp 130–132 °C at 0.05 Torr (lit.[67] bp 212 °C at 4–5 Torr); ^{1}H NMR ($CDCl_3$) δ 7.75–7.73 (m, 1 H, H8), 7.68–7.62 (m, 2 H, H4,5), 7.33–7.29 (m, 3 H, H6,7,2), 7.22 (t, 1 H, J = 7.8 Hz, H3), 7.12–7.05 (m, 5 H, Ph), 5.39 (s, 2 H, $NpCH_2$), 3.65 (s, 2 H, $PhCH_2$); IR (neat) 3020, 2940, 1740, 1250, 1120 cm^{-1}; mass spectrum m/z 277 (7), 276 (33), 142 (13), 141 (100), 115 (10), 91 (16); UV (CH_3OH) λ_{max} = 275 nm (ϵ = 7400).

3-Methoxy-1-naphthylmethyl phenylacetate (3b): mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 7.81 (d, 1 H, J = 8.4 Hz, H8), 7.76 (d, 1 H, J = 8.1 Hz, H5), 7.44 (t, 1 H, J = 7.6 Hz, H7), 7.36 (t, 1 H, J = 7.5 Hz, H6), 7.33–7.26 (m, 5 H, Ph), 7.19 (d, 1 H, J = 2.6 Hz, H4), 7.11 (d, 1 H, J = 2.6 Hz, H2), 5.53 (s, 2 H, $NpCH_2$), 3.90 (s, 3 H, OCH_3), 3.68 (s, 2 H, $PhCH_2$); IR (Nujol) 1725, 1240, 1050 cm^{-1}; mass spectrum m/z 307 (20), 306 (72), 188 (40), 171 (100), 141 (13), 115 (10), 92 (18); UV (CH_3OH) λ_{max} 325 nm (2700), 265 nm (6100). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.37; H, 6.01.

4-Methoxy-1-naphthylmethyl phenylacetate (3c): mp 51–52 °C; ^{1}H NMR ($CDCl_3$) δ 8.32–8.30 (m, 1 H, H8), 7.88–7.85 (m, 1 H, H5), 7.55–7.49 (m, 2 H, H6,7), 7.42 (d, 1 H, J = 7.8 Hz, H2), 7.29–7.24 (m, 5 H, Ph), 6.74 (d, 1 H, J = 7.8 Hz, H3), 5.49 (s, 2 H, $NpCH_2$), 3.99 (s, 3 H, OCH_3), 3.63 (s, 2 H, $PhCH_2$); IR (Nujol) 1728, 1220, 1085 cm^{-1}; mass spectrum m/z 307 (8), 306 (40), 171 (100), 141 (10), 127 (13), 115 (10); UV (CH_3OH) λ_{max} 292 nm (8200). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92. Found: C, 78.60; H, 5.91.

4-Methyl-1-naphthylmethyl phenylacetate (3d): mp 50–51 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 1 H, J = 8.1 Hz, H8), 7.92 (d, 1 H, J = 8.1 Hz, H5), 7.53 (t, 2 H, J = 8.1 Hz, H6,7), 7.39 (d, 1 H, J = 6.9 Hz, H2), 7.28–7.24 (m, 6 H, Ph,H3), 5.55 (s, 2 H, $NpCH_2$), 3.65 (s, 2 H, $PhCH_2$), 2.70 (s, 3 H, CH_3); IR (Nujol) 1745, 1240, 1060 cm^{-1}; mass spectrum m/z 291 (1), 290 (9), 156 (14), 155 (100), 115 (5), 92 (9); UV (CH_3OH) λ_{max} 282 nm (8000). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.95; H, 6.33.

4-Cyano-1-naphthylmethyl phenylacetate (3e): mp 71–72 °C; ^{1}H NMR ($CDCl_3$) δ 8.29 (d, 1 H, J = 8.0 Hz, H5), 7.98 (d, 1 H, J = 8.2 Hz, H8), 7.86 (d, 1 H, J = 7.3 Hz, H3), 7.73 (t, 1 H, J = 7.8 Hz, H6), 7.64 (t, 1 H, J = 7.7 Hz, H7), 7.50 (d, 1 H, J = 7.3 Hz, H2), 7.33–7.25 (m, 5 H, Ph), 5.61 (s, 2 H, $NpCH_2$), 3.70 (s, 2 H, $PhCH_2$); IR (Nujol) 2025, 1745, 1250, 1120 cm^{-1}; mass spectrum m/z 301 (12), 183 (53), 167 (14), 166 (95), 140 (11), 93 (13), 92 (100); UV (CH_3OH) λ_{max} 321 nm (2900), 294 nm (9200). Anal. Calcd for $C_{20}H_{15}O_2N$: C, 79.71; H, 5.02; N, 4.65. Found: C, 79.64; H, 5.01; N, 4.77.

4-Ethoxy-1-naphthylmethyl phenylacetate (3f): mp <15 °C; ^{1}H NMR ($CDCl_3$) δ 8.36–8.32 (m, 1 H, H8), 7.87–7.84 (m, 1 H, H5), 7.50–7.45 (m, 2 H, H6, 7), 7.37 (d, 1 H, J = 7,8 Hz, H2), 7.28–7.22 (m, 5 H, Ph), 6.69 (d, 1 H, J = 7.9 Hz, H3), 5.47 (s, 2 H, $NpCH_2$), 4.15 (t, 2 H, J = 7.0 Hz, OCH_2), 3.60 (s, 2 H, $PhCH_2$), 1.50 (t, 3 H, J = 7.0 Hz, OCH_2CH_3); IR (neat) 3060, 2960, 1730, 1270, 1060 cm^{-1}; UV (CH_3OH) λ_{max} 294 nm (7900). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29. Found: C, 79.52; H, 6.07.

4-Carbomethoxy-1-naphthylmethyl phenylacetate (3g): mp 64–65 °C; ^{1}H NMR ($CDCl_3$) δ 8.90 (d, 1 H, J = 8.5 Hz, H5), 8.08 (d, 1 H, J = 7.5 Hz, H3), 7.96 (d, 1 H, J = 8.3 Hz, H8), 7.63 (dt, 1 H, J = 1.6 Hz, 8.4 Hz, H6), 7.54 (dt, 1 H, J = 1.6 Hz, 8.4 Hz, H7), 7.48 (d, J = 7.5 Hz, H2), 7.30–7.25 (m, 5 H, Ph), 5.60 (s, 2 H, $NpCH_2$), 3.99 (s, 3 H, $COOCH_3$), 3.69 (s, 2 H, $PhCH_2$); IR (Nujol) 1730, 1710, 1270, 1250, 1071 cm^{-1}; mass spectrum m/z 335 (11), 334 (45), 200 (16), 199 (100), 171 (14), 141 (12), 140 (11), 91 (25); UV (CH_3OH) λ_{max} 293 nm (7200). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.46; H, 5.49.

4,5-Dimethoxy-1-naphthylmethyl phenylacetate (3h): mp 76–77 °C; ^{1}H NMR ($CDCl_3$) δ 7.46 (d, 1 H, J = 7.8 Hz, H8), 7.42 (d, 1 H, J = 7.9 Hz, H2), 7.40 (t, 1 H, J = 7.7 Hz, H7), 7.28–7.25 (m, 5 H, Ph), 6.91 (d, 1 H, J = 7.7 Hz, H6), 6.78 (d, 1 H, J = 8.0 Hz, H3), 5.45 (s, 2 H, $NpCH_2$), 3.97 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 3.64 (s, 2 H, $PhCH_2$); IR (Nujol) 1725, 1270, 1070 cm^{-1}; mass spectrum m/z 341 (14), 340 (60), 202 (16), 201 (100), 157 (6), 91 (26); UV (CH_3OH) λ_{max} 313 nm (8400). Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.89; H, 5.72.

4,7-Dimethoxy-1-naphthylmethyl phenylacetate (3i): mp 78–79 °C; ^{1}H NMR ($CDCl_3$) δ 8.20 (d, 1 H, J = 8.5 Hz, H5), 7.39 (d, 1 H, J = 7.9 Hz, H2), 7.28–7.22 (m, 5 H, Ph), 7.13 (d, 1 H, J = 8.5 Hz, H6), 7.11 (s, 1 H, H8), 6.61 (d, 1 H, J = 8.7 Hz, H3), 5.46 (s, 2 H, $NpCH_2$), 3.96 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.62 (s, 2 H, $PhCH_2$); IR (Nujol) 1725, 1260, 1060 cm^{-1}; mass spectrum m/z 341 (8), 340 (33), 202 (15), 201 (100), 158 (8), 115 (5), 91 (11); UV (CH_3OH) λ_{max} 326 nm (2600), 281 nm (5500). Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.88; H, 5.99. Found: C, 74.96; H, 6.10.

4,8-Dimethoxy-1-naphthylmethyl phenylacetate (3j): mp 60–61 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 1 H, J = 8.5 Hz, H5), 7.37 (t, 1 H, J = 8.1 Hz, H6), 7.30 (d, 1 H, J = 8.2 Hz, H2), 7.28–7.23 (m, 5 H, Ph), 6.81 (d, 1 H, J = 7.8 Hz, H7), 6.73 (d, 1 H, J = 8.0 Hz, H3), 5.65 (s, 2 H, $NpCH_2$), 3.96 (s, 3 H, OCH_3), 3.64 (s, 3 H, OCH_3), 3.64 (s, 2 H, $PhCH_2$); IR (Nujol) 1725, 1270, 1060 cm^{-1}; mass spectrum m/z 341 (13), 340 (54), 202 (18), 201 (100), 186 (14), 185 (9), 171 (16), 128 (17), 115 (12), 91 (27); UV (CH_3OH) λ_{max} 326 nm (5200), 295 nm (10200). Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 74.97; H, 5.81.

4-Fluoro-1-naphthylmethyl phenylacetate (3k): mp 49–50 °C; ^{1}H NMR ($CDCl_3$) δ 8.15–8.12 (m, 1 H, H8), 7.91–7.88 (m, 1 H, H5), 7.56 (t, 1 H, J = 6.2 Hz, H6), 7.54 (t, 1 H, J = 6.2 Hz, H7), 7.41 (dd, 1 H, J_{H-H} = 7.7 Hz, J_{H-F} = 5.5 Hz, H2), 7.31–7.22 (m, 5 H, Ph), 7.07 (dd, 1 H, J_{H-F} = 10.2 Hz, J_{H-H} = 7.9 Hz, H3), 5.51 (s, 2 H, $NpCH_2$), 3.64 (s, 2 H, $PhCH_2$); IR (Nujol) 1710, 1210, 1040 cm^{-1}; mass spectrum m/z 295 (7), 294 (33), 160 (13), 159 (100), 133 (8), 92 (10), 43 (15), 30 (58); UV (CH_3OH) λ_{max} 279 nm (7000). Anal. Calcd for $C_{19}H_{15}FO_2$: C, 77.54; H, 5.14. Found: C, 77.53; H, 5.19.

1-Naphthylmethyl 3-phenylpropanoate (5a): bp 137–139 °C at 0.05 Torr; ^{1}H NMR ($CDCl_3$) δ 7.91–7.89 (m, 1 H, H8), 7.84–7.81 (m, 1 H, H5), 7.79 (d, 1 H, J = 8.2 Hz, H4), 7.45–7.36 (m, 4 H, H2,3,6,7), 7.23–7.10 (m, 5 H, Ph), 5.52 (s, 2 H, $NpCH_2$), 2.29 (t, 2 H, J = 7.8 Hz),

(61) Buu-Hoi, N. P.; Lavit, D. *J. Org. Chem.* **1956**, *21*, 1257.
(62) Buu-Hoi, N. P.; Lavit, D. *Bull. Soc. Chim. Fr.* **1955**, 1419.
(63) Basu, B.; Mukherjee, D. *J. Chem. Soc., Chem. Commun.* **1984**, 105.
(64) Bavin, P. M. G. *Anal. Chem.* **1960**, 556.
(65) Boyd, G. V.; Harms, M. D. *J. Chem. Soc. C.* **1970**, 807.
(66) Alborz, M.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. II* **1982**, 331.
(67) Chakravarti, R. N.; Dhar, R. C. *J. Ind. Chem. Soc.* **1953**, *30*, 751.

2.64 (t, 2 H, J = 7.8 Hz); IR (neat) 3010, 2920, 1735, 1235, 1060 cm^{-1}; mass spectrum m/e 291 (8), 290 (40), 142 (14), 141 (100), 115 (11), 91 (20). Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.93; H, 6.32.

3-Methoxy-1-naphthylmethyl 3-phenylpropanoate (5b): mp 53–54 °C; ^1H NMR ($CDCl_3$) δ 7.80 (d, 1 H, J = 8.3 Hz, H8), 7.73 (d, 1 H, J = 8.1 Hz, H5), 7.44 (t, 1 H, J = 8.1 Hz, H7), 7.36 (t, 1 H, J = 8.3 Hz, H6), 7.23 (d, 1 H, J = 2.2 Hz, H4), 7.21–7.13 (m, 5 H, Ph), 7.09 (d, 1 H, J = 2.2 Hz, H2), 5.49 (s, 2 H, $NpCH_2$), 3.87 (s, 3 H), 2.95 (t, 2 H, J = 7.8 Hz), 2.67 (t, 2 H, J = 7.8 Hz); IR (Nujol) 1740, 1280, 1050 cm^{-1}; mass spectrum m/e 321 (13), 320 (50), 188 (60), 186 (61), 172 (24), 171 (72), 158 (17), 129 (28), 128 (50), 127 (25), 115 (100), 106 (17). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.53; H, 6.32.

4-Methoxy-1-naphthylmethyl 3-phenylpropanoate (5c): mp 45–46 °C; ^1H NMR ($CDCl_3$) δ 8.29 (d, 1 H, J = 8.0 Hz, H8), 7.88 (d, 1 H, J = 8.0 Hz, H5), 7.52 (t, 1 H, J = 7.8 Hz, H7), 7.51 (t, 1 H, J = 7.7 Hz, H6), 7.42 (d, 1 H, J = 7.8 Hz, H2), 7.24–7.13 (m, 5 H, Ph), 6.75 (d, 1 H, J = 7.8 Hz, H3), 5.48 (s, 2 H, $NpCH_2$), 4.00 (s, 3 H), 2.94 (t, 2 H, J = 7.8 Hz), 2.65 (t, 2 H, J = 7.8 Hz); IR (Nujol) 1735, 1270, 1100 cm^{-1}; mass spectrum m/e 321 (15), 320 (63), 172 (17), 171 (100), 129 (13), 128 (10), 93 (10). Anal. Calcd for $C_{21}H_{20}O_3$: C, 78.73; H, 6.29. Found: C, 78.89; H, 6.25.

4-Methoxy-1-naphthylmethyl 9′-methyl-9′-fluorenecarboxylate (15c): mp 80–81 °C; ^1H NMR δ 8.25 (d, 1 H, J = 8.2 Hz, H8), 7.67 (d, 2 H, J = 7.6 Hz, H1′), 7.63 (d, 1 H, J = 7.9 Hz, H4), 7.46 (t, 1 H, J = 7.8 Hz, H6), 7.42 (d, 2 H, J = 7.7 Hz, H4′), 7.39 (t, 1 H, J = 7.8 Hz, H7), 7.34 (t, 2 H, J = 7.5 Hz, H3′), 7.24 (d, 1 H, J = 7.8 Hz, H3), 7.21 (t, 2 H, J = 7.5 Hz, H2′), 6.65 (d, 1 H, J = 7.9 Hz, H3), 5.39 (s, 2 H, $NpCH_2$), 3.96 (s, 3 H, OCH_3); IR (Nujol) 1725, 1275, 1050 cm^{-1}; mass spectrum m/z 395 (2), 394 (8), 222 (25), 180 (22), 179 (54), 178 (27), 172 (14), 171 (100), 165 (19), 128 (13). Anal. Calcd for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62. Found: C, 82.19; H, 5.53.

4-Methyl-1-naphthylmethyl 9′-methyl-9′-fluorenecarboxylate (15d): mp 98–99 °C; ^1H NMR ($CDCl_3$) δ 7.98 (d, 1 H, J = 8.6 Hz, H8), 7.70 (d, 1 H, J = 8.2 Hz, H5), 7.68 (d, 2 H, J = 6.8 Hz, H1′), 7.49 (t, 1 H, J = 8.3 Hz, H7), 7.45 (d, 2 H, J = 7.6 Hz, H4′), 7.39 (t, 1 H, J = 8.3 Hz, H6), 7.35 (t, 2 H, J = 6.8 Hz, H3′), 7.23 (t, 2 H, J = 7.5 Hz, H2′), 7.17 (s, 2 H, H2, 3), 5.44 (s, 2 H, $NpCH_2$), 2.65 (s, 3 H, CH_3), 1.74 (s, 3 H, 9′-CH_3); IR (Nujol) 1720, 1230, 1050 cm^{-1}; mass spectrum m/z 379 (7), 378 (23), 180 (4), 179 (23), 178 (11), 156 (15), 155 (100), 153 (4), 128 (4), 115 (4). Anal. Calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.85. Found: C, 85.63; H, 5.60.

Fluorescence Measurements. Fluorescence studies were done using a Perkin-Elmer MPF 66 fluorescence spectrometer at 25 °C. Corrected spectra were obtained. All samples were degassed by three freeze–pump–thaw cycles. Fluorescence quantum yields were determined by comparison with a fluorescence quantum yield of 0.24 for naphthalene in methanol.[15] Singlet-state energies were determined by the position of the 0,0 band using the overlap between the emission and excitation spectrum. Fluorescence lifetimes were measured using a PRA single photon counting apparatus with a hydrogen flash lamp of pulse width of about 1 ns.

Phosphorescence Measurements. Phosphorescence spectra were recorded using an Aminco-Bowmann spectrophotometer at 77 K. Solutions were prepared in 1:4 methanol:ethanol and degassed by freeze–pump–thaw cycles. Triplet-state energies were found from the estimated position of the 0,0 band of the phosphorescence spectrum.

Preparative Photolysis. The photolysis of each of the esters was carried out in the following manner. A solution was prepared consisting of 300–400 mg of the ester dissolved in 300 mL of methanol. The solution was placed in a 300-mL Hanovia immersion well and purged with nitrogen for 15 min before and during the irradiation. The light source was a Pyrex-filtered 200-W medium-pressure Hanovia mercury lamp. Irradiation was continued until the starting ester was more than 90% consumed.

Photolysis times varied from 3 h for the more reactive esters to 16 h for the less reactive ones. The photolyzed solution was then concentrated under vacuum and dissolved in 30 mL of CH_2Cl_2. This CH_2Cl_2 layer was extracted with 2 × 15 mL of 5% NaOH. Evaporation of the CH_2Cl_2 layer gave an oil which was subjected to silica gel chromatography using 20% CH_2Cl_2:hexane as eluent. The aqueous alkaline layer was acidified with concentrated HCl and extracted with 2 × 25 mL of CH_2Cl_2. Evaporation of this CH_2Cl_2 layer gave a solid which was identified as the corresponding acid. The photoproducts were characterized by ^1H NMR and GC/MS.

Characterization of Ethers, 6. The methoxy ethers **6a–d,f,k** were prepared by reaction of the corresponding alcohols **4** with NaH in dry DMF followed by CH_3I. Boiling points, ^1H NMR, and mass spectral data are as follows.

6a, X = H: bp 108–110 °C at 5 Torr (lit.[68] bp 133 °C at 10 Torr); ^1H NMR ($CDCl_3$) δ 8.07 (d, 1 H, J = 8.4 Hz), 7.82 (d, 1 H, J = 7.5 Hz), 7.77 (d, 1 H, J = 8.1 Hz), 7.52–7.36 (m, 4 H), 4.86 (s, 2 H), 3.39 (s, 3 H); mass spectrum m/z 173 (20), 172 (100), 171 (80), 157 (10), 142 (96), 129 (79), 128 (92), 127 (50), 115 (98).

6b, X = 3-OCH_3: bp 96–100 °C at 1 Torr; ^1H NMR ($CDCl_3$) δ 7.94 (d, 1 H, J = 8.2 Hz), 7.69 (d, 1 H, J = 8.0 Hz), 7.40 (t, 1 H, J = 7.4 Hz), 7.33 (t, 1 H, J = 7.1 Hz), 7.16 (d, 1 H, J = 1.9 Hz), 7.02 (d, 1 H, J = 1.9 Hz), 4.79 (s, 2 H), 3.82 (s, 3 H), 3.39 (s, 3 H); mass spectrum m/z 203 (12), 202 (86), 187 (12), 172 (25), 171 (100), 141 (30), 128 (50), 115 (47).

6c, X = 4-OCH_3: bp 90–93 °C at 2 Torr (lit.[2] bp 70–72 °C at 0.2 Torr); ^1H NMR ($CDCl_3$) δ 8.28 (d, 1 H, J = 8.5 Hz), 8.06 (d, 1 H, J = 8.3 Hz), 7.54 (t, 1 H, J = 7.6 Hz), 7.47 (t, 1 H, J = 7.5 Hz), 7.34 (d, 1 H, J = 7.8 Hz), 6.71 (d, 1 H, J = 7.8 Hz), 4.80 (s, 2 H), 3.76 (s, 3 H), 3.39 (s, 3 H); mass spectrum m/z 203 (5), 202 (32), 172 (70), 171 (100), 157 (43), 129 (48), 128 (67), 127 (28), 115 (29).

6d, X = 4-CH_3: bp 89–93 °C at 0.2 Torr (lit.[69] bp 160–170 °C at 13 Torr); ^1H NMR ($CDCl_3$) δ 8.13–8.10 (m, 1 H), 8.02–7.99 (m, 1 H), 7.55–7.51 (m, 2 H), 7.35 (d, 1 H, J = 7.1 Hz), 7.25 (d, 1 H, J = 7.0 Hz), 4.86 (s, 2 H), 3.41 (s, 3 H), 2.67 (s, 3 H); mass spectrum m/z 187 (23), 186 (100), 172 (24), 171 (100), 156 (74), 155 (100), 153 (86), 141 (85), 128 (99), 115 (99).

6e, X = CN. This ether was prepared from bromo-(4-cyano-1-naphthyl)methane in the following manner. The bromocyano compound (10 mmol) was dissolved in 50 mL of methanol, and NaOMe (100 mmol) was added. The mixture was stirred overnight, poured into water, extracted with CH_2Cl_2, dried, filtered, and evaporated to give crude ether. Chromatography on silica gel and crystallization with CH_2Cl_2 gave colorless needles: mp 74–75 °C (lit.[51] mp 73–74 °C); mass spectrum m/z 198 (9), 197 (66), 196 (48), 167 (80), 166 (100), 154 (25), 140 (25).

6f, X = 4-OCH_2CH_3: mp 42–43 °C; ^1H NMR ($CDCl_3$) δ 8.4–8.0 (m, 2 H), 7.5–7.3 (m, 2 H), 7.2 (d, 1 H, J = 8.0 Hz), 6.7 (d, 1 H, J = 8.0 Hz), 4.8 (s, 2 H), 4.1 (q, 2 H, J = 7.4 Hz), 3.4 (s, 3 H), 1.5 (t, 2 H, J = 7.5 Hz).

6g, X = 4-CO_2CH_3. This ether was prepared from bromo-(4-cyano-1-naphthyl)methane[57] in the following manner. The bromocyano compound (3 g) was refluxed in 75 mL of methanol and 15 mL of 2 M NaOH for 5 days. The hot solution was filtered, diluted with 25 mL of water, and washed with 25 mL of chloroform. Acidification of the aqueous layer and filtration yielded 2 g (60%) of crude 4-methoxymethyl-1-naphthoic acid. Recrystallization from ethanol–water gave needles: mp 136–137 °C (lit.[55] mp 136–137 °C). The ether acid was reacted with sulphuric acid/methanol in the usual manner to give the methyl ester as a colorless liquid: bp 171–174 °C at 6 Torr; mass spectrum m/z 231 (9), 230 (68), 183 (30), 171 (100), 139 (50), 128 (37), 127 (28).

The methyl ethers **6h–j** were isolated from the photolysis reaction mixtures.

6h, X = 4-OCH_3, Y = 5-OCH_3: ^1H NMR ($CDCl_3$) δ 7.8–7.2 (m, 3 H), 6.9 (d, J = 8.0 Hz, 1 H), 6.8 (d, J = 8.0 Hz, 1 H), 4.8 (s, 2 H), 4.0 (s, 3 H), 3.95 (s, 3 H), 3.4 (s, 3 H); GC/MS R_t = 13.6 min, m/z 233 (7), 232 (50), 202 (20), 201 (100), 185 (6), 171 (5), 157 (10), 128 (13), 115 (12).

6i, X = 4-OCH_3, Y = 7-OCH_3: ^1H NMR ($CDCl_3$) δ 8.2 (d, J = 8.0 Hz, 1 H), 7.4–7.0 (m, 3 H), 6.6 (d, J = 8.0 Hz, 1 H), 4.8 (s, 2 H), 3.9 (s, 3 H), 3.8 (s, 3 H), 3.3 (s, 3 H); GC/MS R_t = 13.8 min, m/z 233 (19), 232 (100), 202 (64), 201 (100), 158 (43), 143 (20), 115 (37).

6j, X = 4-OCH_3, Y = 8-OCH_3: ^1H NMR ($CDCl_3$) δ 8.1 (d, J = 8.0 Hz, 1 H), 7.6 (d, J = 8.0 Hz, 1 H), 7.4 (t, J = 8.0 Hz, 1 H), 6.9 (d, J = 7.9 Hz, 1 H), 6.7 (d, J = 7.9 Hz, 1 H), 5.1 (s, 2 H), 4.0 (s, 3 H), 3.9 (s, 3 H), 3.5 (s, 3 H); GC/MS R_t = 13.8 min, m/z 233 (11), 232 (90), 202 (40), 201 (100), 187 (25), 186 (26), 128 (26), 115 (26).

6k, X = 4F: bp 65–67 °C at 0.1 Torr; ^1H NMR ($CDCl_3$) δ 8.11 (dd, 1 H, J_{H-H} = 7.7 Hz, J_{H-F} = 6.0 Hz, H5), 8.08 (dd, 1 H, J = 8.48 Hz, H8), 7.57 (t, 1 H, J = 7.51 Hz, H7), 7.53 (t, 1 H, J = 7.5 Hz, H6), 7.37 (dd, 1 H, J_{H-F} = 5.5 Hz, J_{H-H} = 7.7 Hz, H2), 7.07 (dd, 1 H, J_{H-H} = 7.8 Hz, J_{H-F} = 10.4 Hz, H3), 4.82 (s, 2 H, $NpCH_2$), 3.42 (s, 3 H, OCH_3); mass spectrum m/z 191 (8), 190 (35), 160 (30), 159 (100), 156 (25), 133 (35), 128 (10), 115 (28).

The hydrocarbons **9a–k**, **16c,d**, and **17** were isolated from photolysis mixtures and characterized spectrally as shown below.

9a, X = H: ^1H NMR ($CDCl_3$) δ 8.1–7.9 (m, 2 H), 7.8–7.6 (m, 1 H), 7.5–7.0 (m, 4 H), 7.25 (s, 5 H), 3.4–3.2 (m, 2 H), 3.1–2.9 (m, 2 H); GC/MS R_t = 14.6 min, m/z 233 (10), 232 (56), 142 (25), 141 (100), 128 (12), 115 (65), 91 (20).

(68) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 4175.
(69) Lock, G.; Schneider, R. S. *Chem. Ber.* **1958**, *91*, 1770.

9b, X = 3-CH_3O: ^1H NMR ($CDCl_3$) δ 8.1-7.9 (m, 1 H), 7.8-7.6 (m, 1 H), 7.5-7.1 (m, 3 H), 7.2 (s, 5 H), 7.0 (d, 1 H, J = 2.0 Hz), 3.9 (s, 3 H), 3.4-3.2 (m, 2 H), 3.0-2.8 (m, 2 H); GC/MS R_t = 16.6 min, m/z 263 (16), 262 (79), 172 (100), 141 (24), 128 (39), 127 (10), 115 (24), 91 (20).

9c, X = 4-CH_3O: ^1H NMR ($CDCl_3$) δ 8.5-8.3 (m, 1 H), 8.1-7.9 (m, 1 H), 7.7-7.7 (m, 3 H), 7.2 (s, 5 H), 6.7 (d, 1 H, J = 8.0 Hz), 3.8 (s, 3 H), 3.4-3.2 (m, 2 H), 3.0-2.8 (m, 2 H); GC/MS R_t = 17.1 min, m/z 263 (3), 262 (17), 172 (11), 171 (100), 128 (28), 127 (13), 115 (6).

9d, X = 4-CH_3. Since this product was formed only in trace amounts, it was not isolated. It was identified by GC/MS: R_t = 16.4 min, m/z 247 (15), 246 (68), 156 (10), 155 (100), 141 (28), 127 (12), 115 (11).

9e, X = 4-CN: ^1H NMR ($CDCl_3$) δ 8.3-8.0 (m, 2 H), 7.8-7.5 (m, 3 H), 7.3 (d, 1 H, J = 7.8 Hz), 7.2 (s, 5 H), 3.5-3.3 (m, 2 H), 3.2-3.0 (m, 2 H); GC/MS R_t = 18.4 min, m/z 258 (6), 257 (30), 166 (23), 140 (8), 91 (100), 65 (10).

9f, X = 4-OCH_2CH_3: ^1H NMR ($CDCl_3$) δ 8.4-8.0 (m, 2 H), 7.7-7.5 (m, 2 H), 7.3-7.1 (m, 6 H), 6.8 (d, J = 7.9 Hz, 1 H), 4.3 (q, J = 7.8 Hz, 2 H), 3.5-3.0 (m, 4 H), 1.6 (t, J = 7.8 Hz, 3 H); GC/MS R_t = 17.8 min, m/z 277 (5), 276 (20), 186 (20), 185 (100), 171 (21), 157 (42), 128 (19).

9j, X = 4-OCH_3, Y = 8-OCH_3: ^1H NMR ($CDCl_3$) δ 8.0 (d, 1 H, J = 8.0 Hz), 7.5 (d, J = 8.0 Hz, 1 H), 7.3 (s, 5 H), 7.2 (t, J = 7.8 Hz, 1 H), 7.0 (d, 1 H, J = 8.0 Hz), 6.8 (d, J = 8.0 Hz, 1 H), 4.0 (s, 3 H), 3.9 (s, 3 H), 3.5-3.2 (m, 2 H), 3.1-2.8 (m, 2 H); GC/MS R_t = 20.1 min, m/z 293 (6), 292 (26), 202 (13), 201 (100), 171 (11), 128 (16), 115 (10).

9i, X = 4-OCH_3, Y = 7-OCH_3: ^1H NMR ($CDCl_3$) δ 8.3 (d, 1 H, J = 8.0 Hz), 7.5-7.1 (m, 8 H), 6.7 (d, J = 8.0 Hz, 1 H), 4.0 (s, 3 H), 3.9 (s, 3 H), 3.3-2.9 (m, 4 H); GC/MS R_t = 20.5 min, m/z 293 (5), 292 (20), 202 (19), 201 (100), 158 (11), 128 (6).

9h, X = 4-OCH_3, Y = 5-OCH_3: ^1H NMR ($CDCl_3$) δ 7.5 (d, J = 8.0 Hz, 1 H), 7.3-7.0 (m, 7 H), 6.9 (d, J = 8.0 Hz, 1 H), 6.7 (d, J = 8.0 Hz, 1 H), 4.0 (s, 3 H), 3.9 (s, 3 H), 3.3-2.9 (m, 4 H); GC/MS R_t = 19.9 min, m/z 293 (3), 292 (19), 202 (13), 201 (100), 157 (5), 128 (10).

9g, X = 4-CO_2CH_3: ^1H NMR ($CDCl_3$) δ 9.1-8.9 (m, 1 H), 8.2-7.9 (m, 2 H), 7.6-7.4 (m, 1 H), 7.3-7.1 (m, 6 H), 4.0 (s, 3 H), 3.6-3.3 (m, 2 H), 3.2-7.9 (9m, 2 H); GC/MS R_t = 20.0 min, m/z 291 (11), 290 (49), 199 (100), 171 (21), 139 (12), 128 (10).

9k, X = 4-F. Since this compound was formed only in trace amounts, isolation was not attempted. It was identified by GC/MS: R_t = 14.3 min, m/z 251 (5), 250 (24), 160 (14), 159 (100), 133 (18), 91 (6).

16c, 9-Methyl-9-(4'-methoxy-1'-naphthylmethyl)fluorene: ^1H NMR ($CDCl_3$) δ 8.4-8.2 (m, 1 H), 7.9-7.0 (m, 12 H), 6.7 (d, 1 H, J = 8.0 Hz), 4.0 (s, 3 H), 3.4 (s, 2 H), 1.5 (s, 3 H); mass spectrum m/z 350 (2), 179 (5), 178 (5), 172 (14), 171 (100), 129 (8).

17, Di-9-methyl-9-fluorene: ^1H NMR ($CDCl_3$) δ 1.6-6.8 (m, 16 H), 1.9 (s, 6 H); mass spectrum m/z 358 (16), 180 (53), 179 (70), 178 (70), 97 (100).

16d, 9-Methyl-9-(4'-methyl-1'-naphthylmethyl)fluorene: ^1H NMR ($CDCl_3$) δ 8.3-6.9 (m, 14 H), 3.5 (s, 2 H), 2.6 (s, 3 H), 1.6 (s, 3 H).

Acknowledgment. We thank NSERC of Canada for financial support. Dr. D. P. DeCosta thanks Dalhousie University for a graduate fellowship. We thank Dr. Samir Farid for helpful discussions and use of software for Marcus theory.

Remote Activation of an Aroyl Azide by Long-Distance Intramolecular Electron Transfer: Irradiation of an Amine-Steroid-Azide System

Yong Zhu and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received September 25, 1992*

Abstract: Bichromophoric compounds *cis*- and *trans*-3ξ-(*N*-(*p*-methoxyphenyl)-*N*-methylamino)-5α-androstan-17β-yl 4-(azidocarbonyl)benzoate (**1** and **2**, respectively) were synthesized and studied. Steady-state photophysical measurements indicate that the singlet excited state of the aryl amine (donor) is quenched by the remote aroyl azide (acceptor) group. These findings reveal that it is possible to activate this functional group separated in space from an absorbing "antenna" group. The mechanism of this long-distance interaction is shown by time-resolved spectroscopic measurements and by analysis of the reaction products to be through-bond and, perhaps in one case, through-space electron transfer. The triplet excited state of the donor chromophore also plays a role in the remote activation. It may participate either by long-distance electron or long-distance energy transfer. Intramolecular electron transfer in **1** or **2** generates an aryl amine radical cation and the azide radical anion. The azide radical anion exhibits unique chemical reactions dominated by protonation or by loss of nitrogen to form the nitrene radical anion.

Introduction

Examination of the photochemistry of bichromophoric molecules provides significant insight into factors that control the rate of energy-transfer and electron-transfer reactions. Closs and co-workers employed rigid saturated spacer groups to probe the effect of thermodynamic driving force, distance, solvent, and temperature on rate constants for energy and electron transfer.[1] Their work revealed the Marcus inverted region and provides a theoretical foundation to guide experimentation. Verhoeven, Paddon-Row, and their co-workers controlled the distance from donor to acceptor in rigid compounds and varied systematically donors and acceptors at a single distance.[2] They studied the dependence of the electron-transfer rate on the driving force for reaction and on the distance from donor to acceptor. Their work examined the in-

(1) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Flemming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652. Closs, G. L.; Johnson, M. D.; Miller, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3751. Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 8740. Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5012.

(2) (a) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (b) Paddon-Row, M. N.; Verhoeven, J. W. *New J. Chem.* **1991**, *15*, 107. (c) Paddon-Row, M. N.; Jordan, K. D. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publications: New York, 1988; Chapter 3. (d) Mes, G. F.; de Jong, B.; van Ramesdonk, H. J.; Verhoeven, J. W.; Warman, J. M.; de Haas, M. P.; Horsman-van der Dod, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 6524. (e) Krijnen, B.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 135. (f) Oliver, A. M.; Craig, D. C.; Paddon-Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1981**, *150*, 366. (g) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751. (h) Clayton, A. H. A.; Ghiggino, K. P.; Wilson, G. J.; Keyte, P. J.; Paddon-Row, M. N. *Chem. Phys. Lett.* **1992**, *195*, 249. (i) Pasman, P.; Rob, F.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1982**, *104*, 5127. (j) Krijnen, B.; Beverloo, H. B.; Verhoeven, J. W.; Reiss, C. A.; Goubitz, K.; Heijdenrijk, D. *J. Am. Chem. Soc.* **1989**, *111*, 4433. (k) Paddon-Row, M. N.; Oliver, A. M.; Warman, J. M.; Smit, K. J.; de Haas, M. P.; Oevering, H.; Verhoeven, J. W. *J. Phys. Chem.* **1988**, *92*, 6958. (l) Jordan, K. D.; Paddon-Row, M. N. *Chem. Rev.* **1992**, *92*, 395.

0002-7863/93/1515-2190$04.00/0