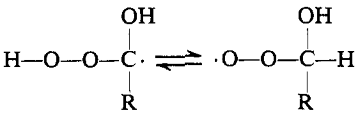
Methanol as ·OH Scavengers. When methanol is used as on ·OH scavenger in a solution which is saturated with nitrous oxide, one observes a first-order growth of the 330-nm absorption. From the known concentration of I, one calculates the rate constant $k = 2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ for the reaction of the hydroxymethyl radical with I. However, during the build-up of the absorbance, the conductivity increases only 20% as much as it does in the water–2-propanol solvent, which indicates that the reaction of the hydroxymethyl radical with *p*-nitroperoxybenzoic acid is not, exclusively, a reduction similar to reaction 4. Rather, it appears that I must undergo addition of $\cdot CH_2{-}OH$ to yield an adduct which absorbs strongly but which is not as strong an acid as *p*-nitrobenzoic acid (formed by the chain decomposition of II in the water–2-propanol mixture). The data suggest that only 20% of the reaction of $\cdot CH{-}OH$ with I proceeds by electron transfer.

Concluding Remarks

The question arises whether the OH elimination that has been observed for the peroxo acid radical V can take place also with other peroxo radicals. The peroxo radical VI formed by the reaction of an alcohol radical with oxygen[3] can be considered as a tautomeric form of V. When the equilibrium is laying on the left side, depending on the group R, and it is established fast enough (*e.g.*, by H^+ catalysis), the OH elimination could take place from the alcohol peroxo radicals. This would lead to the corresponding acid, as has been observed in the radiolysis of acidic oxygen containing solutions of alcohols.[20]


V VI

$$H{-}O{-}O{-}\overset{OH}{\underset{R}{C}}\cdot \rightleftharpoons \cdot O{-}O{-}\overset{OH}{\underset{R}{C}}{-}H$$

Acknowledgment. Two of us (R. C. L. and E. H.) wish to express appreciation to Dr. A. Henglein and to the administration of the HMI for having sponsored us through Visiting Professorships at the HMI during the summer of 1973.

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Photodecarboxylation of Esters. Photolysis of α- and β-Naphthalenemethyl Derivatives[1-3]

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Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66045. *Received February 14, 1974*

Abstract: The photochemistry of the three naphthalenemethyl esters, α- and β-naphthalenemethyl phenylacetates (**1** and **5**) and β-naphthalenemethyl β-naphthylacetate (**10**), and two benzyl esters, benzyl α- and β-naphthylacetate (**8** and **9**), was examined in detail. The photodecarboxylation was shown to proceed by way of the singlet state by sensitization and quenching experiments yielding benzyl or naphthalenemethyl (α or β) radicals which coupled or abstracted hydrogen from solvent. Measurements of quantum efficiencies for reaction and for fluorescence and determination of relative reaction rates established the order of reactivity of the five esters as **5** $\sim$ **10** $>$ **1** $\gg$ **8** $\sim$ **9**. Factors affecting the order of reactivity of the esters are also discussed.

Our studies on the photodecarboxylation of arylmethyl esters[3,6-8] and other investigations of ester photochemistry[9-12] have shown that photodecarboxylation can be a competitive and often a major photolysis pathway. We have directed our attention to the naphthyl analogs in an effort to gain more information about the scope and mechanism for the photodecarboxylation reaction. The naphthyl derivatives were selected for study because the naphthyl chromophore absorbs above 300 nm permitting quenching studies that are free of competitive absorption problems, the naphthyl residue has a triplet energy of 57–62 kcal/mol[13] which does not vary appreciably with alkyl substitution and would be suitable for sensitization studies with available triplet sensitizers, and, finally, a comparison of effects of α- and β-naphthyl systems would be possible. Furthermore, photochemical studies of esters of α- and β-naphthalene carboxylic acids[14] have been reported recently and provide a comparison with this study.

Results

A. Synthetic and Preparative Photochemical Studies. Synthesis of α- and β-naphthalenemethyl phenylace-

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(1) Mechanistic and Synthetic Studies in Organic Photochemistry. Part XII. For part XI, see R. S. Givens, L. Strekowski, and R. Devonshire, *J. Amer. Chem. Soc.*, **96**, 1631 (1974).

(2) This work was presented at the Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., on Nov 8–10, 1972, Abstract 318a.

(3) A preliminary account of this work has appeared: B. Matuszewski, R. S. Givens, and C. Neywick, *J. Amer. Chem. Soc.*, **95**, 595 (1973).

(4) On leave from A. Mickiewicz University, Poznan, Poland.

(5) NSF Summer Trainee, 1970; NDEA Title IV Fellow, 1971–1973.

(6) R. S. Givens and W. F. Oettle, *J. Org. Chem.*, **37**, 4325 (1972).

(7) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3301 (1971).

(8) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3961 (1971).

(9) (a) T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 1989 (1972), and references cited therein; (b) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Jap.*, **45**, 2571 (1972).

(10) I. S. Krull and D. R. Arnold, *Tetrahedron Lett.*, 1247 (1969), and references cited therein.

(11) R. Simonaitis and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **91**, 108 (1969), and references cited therein.

(12) R. A. Finnegan and D. Knutson, *J. Amer. Chem. Soc.*, **89**, 1970 (1967), and references cited therein.

(13) G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

(14) R. Brainard and H. Morrison, *J. Amer. Chem. Soc.*, **93**, 2685 (1971).

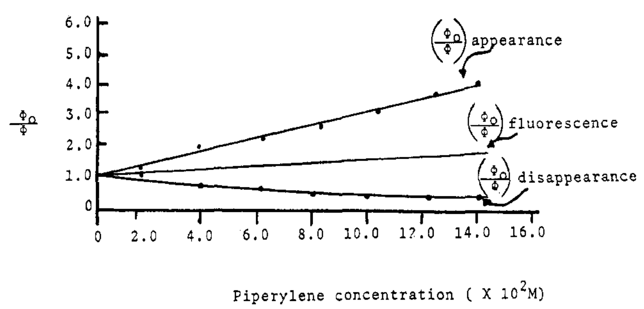
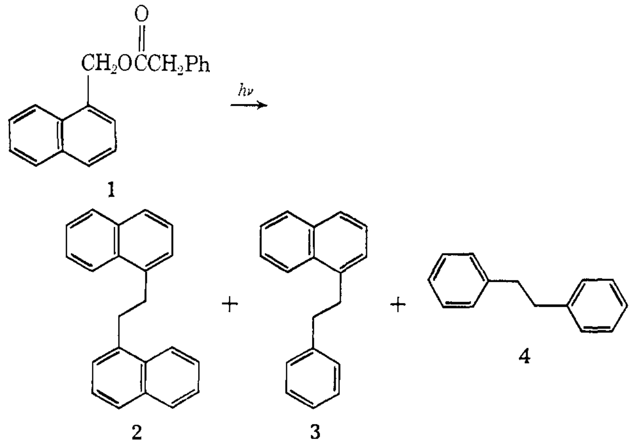


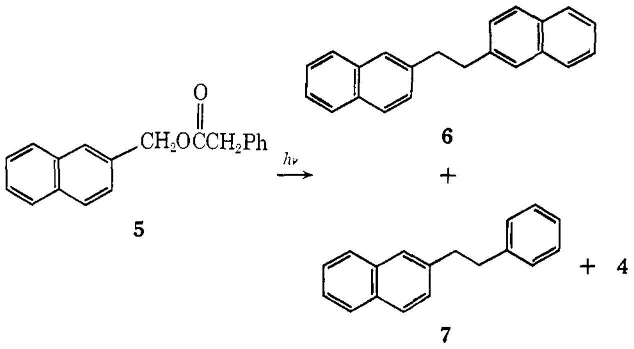
Figure 1. Piperylene quenching of product formation of **7** and disappearance of **5** at 300 nm.

tates[15a] was accomplished according to standard procedures either using phenylacetyl chloride and the α- or β-naphthalenemethanol[15b,c] or acid-catalyzed esterification of the alcohol to give the desired esters. Each ester was irradiated under the following two conditions: (1) irradiation at 254 nm in dioxane and (2) irradiation at 300 nm in benzene. Benzene proved to be a superior solvent since hydrogen abstraction was suppressed. Therefore, product studies and the initial mechanistic studies for the esters were carried out in benzene solutions. Irradiation of α-naphthalenemethyl phenylacetate (**1**) in benzene at 300 nm gave a 1:10:1 ratio of the three coupling products,[16] 1,2-di-α-naphthylethane (**2**), 1-(α-naphthyl)-2-phenylethane (**3**), and dibenzyl (**4**).



Likewise, β-naphthalenemethyl phenylacetate (**5**) when irradiated in benzene at 300 nm gave 1,2-di-β-naphthylethane (**6**), 1-(β-naphthyl)-2-phenylethane (**7**), and dibenzyl (**4**) in a 1:10:1 ratio.[16] The products **3** and **7** were characterized by their ir, nmr, and mass spectra and by elemental analysis. Products **2**, **4**, and **6** were identified by their known melting points[17] as well as their characteristic ir, nmr, and mass spectra. Isolated yields of hydrocarbons from preparative runs ranged from 31% for the α ester to 65% for the β ester.

For comparison, the benzyl esters of α- and β-naphthylacetic acid were synthesized and irradiated. Neither benzyl α-naphthylacetate (**8**) nor benzyl β-naphthylacetate (**9**) underwent facile photodecarboxylation. Only after prolonged irradiation could the product formation be detected. The appearance of a product having the retention time of the cross-coupling product (**3** from **8** and **7** from **9**) indicated that decarboxylation did occur, albeit very inefficiently. Other reactions were not responsible for the low conversion to product since the rate of starting material disappearance for **8** and **9** was reduced greatly also. For comparison, β-naphthalenemethyl β-naphthylacetate (**10**) was synthesized and irradiated. A single major photoproduct was obtained and identified as the 1,2-di-β-naphthylethane. Qualitatively, disappearance of **10** and the appearance of product occurred at a rate comparable to that of **5**. The isolated yield of di-β-naphthylethane was 80% based on recovered **10**.



B. Mechanistic Studies. Table I shows the results of sensitization experiments with **5** using acetophenone and benzophenone, both sufficiently high energy sensitizers to assure efficient triplet energy transfer. In both cases the sensitizer was ineffective in promoting decarboxylation. Quenching studies were carried out with piperylene and with cyclohexadiene using ester **5** as the substrate. Efficient interception of the excited ester occurred giving a good Stern–Volmer relationship for product appearance as shown in Figure 1. The calculated lifetime for the excited state intercepted by these dienes was dependent on the diene employed: for cyclohexadiene, $\tau_{ES} = 3 \times 10^{-8}$ sec; for piperylene, $\tau_{ES} = 8 \times 10^{-9}$ sec. Nmr spectra of the samples from high conversion and high piperylene concentration runs showed that the naphthalene nucleus had been altered

Table I. Quantum Yields for Naphthalenemethyl Ester Irradiations of **1**, **5**, and **8**–**10**[a]

Ester	Φ_{dis} ($\times 10^{-3}$)	Φ_{app} ($\times 10^{-3}$) of major arylethane
1	5.7[c]	0.8
5	55[c]	15
5[b]	0.0	0.0
8	<0.1[d]	<0.1[d]
9	<0.1[d]	<0.1[d]
10	*e*	10

[a] Irradiation at 300 nm in benzene solution in a merry-go-round apparatus (see Experimental Section). [b] Irradiation at 350 nm in benzene with acetophenone or benzophenone present as a sensitizer. Concentrations adjusted so that the sensitizer absorbed >99% of incident light. No detectable product observed and only a very slow disappearance of ester was noted. [c] Determined on an optical bench using uranyl oxylate actinometer (see Experimental Section). [d] Too small to measure. [e] Not determined.

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(15) (a) R. N. Chakravarti and R. C. Dhar, *J. Indian Chem. Soc.*, **30**, 751 (1953); (b) K. Ziegler, *Chem. Ber.*, **54**, 737 (1921); (c) E. Bamberger and O. Boekmann, *ibid.*, **20**, 1115 (1887).

(16) The unusually large ratio for 3 (7) could be due to cage effects or to relative rates of fragment radical couplings. Currently we have no information on the nature of this reaction and we are not aware of any studies on this coupling reaction. Experiments are in progress which will differentiate between these two mechanisms.

(17) (a) N. P. Buu-Hoi and N. Hoan, *J. Org. Chem.*, **14**, 1023 (1949); (b) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956, p 313.

Table II. Fluorescence Quantum Yields and Relative Rates for Singlet Processes of α- and β-Naphthyl Esters **1**, **5**, **8**, and **9**

Ester	$10^{-3}\Phi^a$	$k_r(\text{rel})^b$	$\Phi_f(\text{rel})^{b,c}$	$10^{-9}\tau_0$, sec^d	$10^{-9}\tau_s$, sec^e
1	5.7	0.11 ± 0.02	1.08 ± 0.25	7.2 ± 1.0	8.0 ± 0.6^f
5	55.0	1.00	1.00	7.1 ± 1.0	8.0 ± 0.8
8	<0.1	$<(1.6 \pm 0.2) \times 10^{-3}$	1.10 ± 0.12	8.7 ± 1.0	8.2 ± 0.7
9	<0.1	$<(1.8 \pm 0.5) \times 10^{-3}$	0.88 ± 0.18	8.1 ± 1.0	10.8 ± 0.8

[a] Direct irradiations in benzene or dioxane at 300 nm. Quantum yields were determined using a potassium ferrioxalate actinometer in the apparatus described earlier[1] by extrapolating the results of several runs to 0% conversion (Table I). [b] Relative values based on ester **5**. [c] Determined peak heights of the fluorescence emission for the four esters in cyclohexane and dioxane. [d] Values obtained by integration of the uv band in dioxane and cyclohexane.[19] [e] Values obtained by oxygen quenching of the fluorescence in cyclohexane.[20] [f] This was shown to be 17 nsec by single photon counting techniques (see text).

since the characteristic nmr peaks for the naphthyl moiety were missing. Furthermore, quantitative analysis of starting ester disappearance showed that the quantum yield (Φ_d) actually increased with increasing piperylene concentration giving a negative slope to the Stern–Volmer plot for ester disappearance (Figure 1). Piperylene apparently was intercepting the excited state of the ester by chemical reaction,[18] not by physical quenching.

In an effort to establish this, fluorescence quenching by piperylene was attempted. A Stern–Volmer plot of the fluorescence intensity *vs.* the piperylene concentration gave a slope of about one-third of that from the product study (Figure 1). The remaining two-thirds was attributed to chemical quenching.

In order to quantitatively compare the reactivity of the four esters, the relative rate constants for decarboxylation were determined by two methods: a comparison of (1) intrinsic singlet lifetimes or (2) the natural fluorescent lifetimes with quantum yields for reaction. Both methods gave the same relative reactivities (Table II) and were in the same relative sequence as the quantum yields for reaction.

Emission studies were performed on the five esters. The fluorescence spectra were very similar in peak shape, intensity, and position of the maximum (340 ± 5 nm). These similarities and the fact that the reaction proceeds exclusively from the singlet excited state allowed us to quantitatively compare the relative rate constants for decarboxylation. The efficiencies for reaction (Φ_r) and for fluorescence (Φ_f) are given in eq 1

$$\Phi_r = k_r/(k_r + k_d + k_f + k_{isc}) \qquad (1)$$

and 2, where k_r, k_f, and k_d are the first-order rate con-

$$\Phi_f = k_f/(k_f + k_d + k_r + k_{isc}) \qquad (2)$$

stants for reaction, for fluorescence, and for decay of the singlet excited state, respectively.

Thus, the relative rates for reaction between any two esters are given by the following relationship

$$\frac{k_r}{k_r'} = \left(\frac{\Phi_r}{\Phi_r'}\right)\left(\frac{\Phi_f'}{\Phi_f}\right)\left(\frac{k_f}{k_f'}\right) \qquad (3)$$

The values for k_f and k_f' can be estimated from the integration of the ultraviolet band which gives the mean radiative singlet lifetime ($\tau_0 \equiv 1/k_f$).[19] It follows then that k_r/k_r' can be estimated by eq 4.

$$\frac{k_r}{k_r'} = \left(\frac{\Phi_r}{\Phi_r'}\right)\left(\frac{\Phi_f'}{\Phi_f}\right)\left(\frac{\tau_0'}{\tau_0}\right) \qquad (4)$$

As a check on the method for obtaining relative rate constants, the oxygen quenching of the fluorescence was also examined to determine the natural fluorescent lifetime, τ_s.[20] τ_s is related to the mean radiative lifetime (eq 5) and therefore allows an independent determina-

$$\tau_s = \tau_0\Phi_f \qquad (5)$$

tion of the relative rate constants (eq 6).

$$\frac{k_r}{k_r'} = \left(\frac{\Phi_r}{\Phi_r'}\right)\left(\frac{\tau_s'}{\tau_s}\right) \qquad (6)$$

Both analyses yield the same relative rates. Furthermore, the relative rates parallel the relative efficiencies for photodecarboxylation. Esters **5** and **10** react an order of magnitude faster than **1**, which in turn reacts an order of magnitude faster than the two benzyl esters, **8** and **9**. The inefficiencies of **8** and **9** in this reaction are in agreement with our expectations based on the earlier results with phenyl lactones and esters. The chromophore of lowest energy must be α to the C–O ether bond. Thus, initial cleavage of that bond must be occurring.

Finally, the lifetimes of esters **5** and **10** were determined by time-correlated single photon counting techniques. The values for these were 17.0 and 17.6 nsec,[21] approximately twice the value obtained by indirect methods.[22]

The relative fluorescence efficiencies, radiative lifetimes, and natural lifetimes for the five esters are given in Table II. For each of the esters, the quantum yield accurately reflects the relative rate constant for the decarboxylation. The order of reactivity of the singlet excited state is **10** ≈ **5** > **1** ≫ **8** ≈ **9**.

Phosphorescence spectra in ether–isopentane–ethanol (5:2:2) (EPA) and methylcyclohexane–isopentane glasses (1:3) revealed an emission band with maxima at 475, 505, and 540 (sh) nm for both of the β-naphthylmethyl esters (**5** and **10**). The other esters showed similar patterns, although the spectrum was shifted slightly (±10 nm). The 0,0 band at 475 nm corresponds to a triplet energy of 60.2 kcal/mol, typical of the naphthyl chromophore. No evidence from emission and absorption studies could be found for unusual complex formations of these bichromophoric esters. The spec-

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[18] Yang has identified photoadducts of naphthalene and piperylene [N. C. Yang, *et al.*, *J. Amer. Chem. Soc.*, **94**, 9226, 9228 (1972)].

[19] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 48.

[20] I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971.

[21] We gratefully acknowledge the efforts of Dr. Colin Lewis, The Royal Institution, London, in obtaining these values for us.

[22] A similar comparison of direct and indirect methods for obtaining rate constants was observed by H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **95**, 5094 (1973).

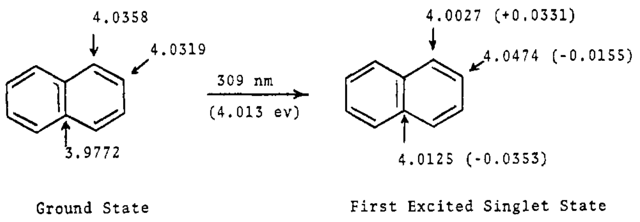

Figure 2. Electron populations and change in electron populations for the first excited singlet state of naphthalene.

Table III. Singlet Transition Energies and Oscillator Strengths for Naphthalene

Transitions	Absorption, nm Calcd	Found[a]	*f* Calcd	Found[a]	ϵ
α (B_{3u})	309	312	0.01	0.002	280
P (B_{2u})	285	289	0.23	0.18	9,300
β (B_{3u})	220	220	1.92	1.70	133,000

[a] H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

tra were consistent with those expected from the nonesterified components.

The relative efficiencies of the α- and β-naphthalenemethyl phenylacetates, **1** and **5**, respectively, are understood less easily. By the usual ground-state arguments, the cleavage of the α-naphthalenemethyl–oxygen bond ought to be more facile, whereas, in fact, the opposite is true. Attempts to explain this reversal of ground-state behavior in terms of the electronic distributions in the first excited singlet state are more successful. By employing a SCF–all-valence-electron open shell CNDO/M-CI method of Del Bene and Jaffe[23] the calculation of the charge redistribution was performed on naphthalene, the basic chromophore for the three reactive esters. The results given in Figure 2 show that the β position as well as the tetrasubstituted bridging carbons becomes extensively electron rich while the α carbon becomes electron deficient. This enhanced charge build-up would explain the increased reactivity of the leaving group attached to the β-methylene. In Table III the calculated singlet transition energies and the oscillator strengths are compared with the experimental values. The good agreement supports the use of this method for describing the excited states.

Direct analogy to these results can be found in the work of Zimmerman and Somasekhara[24] and Letsinger[25] where reversal of ground-state reactivity is explained in terms of the change in charge distribution of the excited state from the ground state. In fact, Jaffe[23] has carried out such a calculation for monosubstituted benzenes using this technique. However, this comparison has not been applied to naphthalene or other polycyclic aromatics. There are at least two additional examples of apparent reversal of the α/β naphthyl reactivity ratio upon excitation. Morrison, *et al.*,[14] found that the β-naphthylacetic acid disappearance quantum yield was at least a factor of 3 larger than that for α-naphthylacetic acid. Unfortunately, the products were not determined, precluding any further consideration of the mechanism of this reaction.

A very striking example of the reversal of ground excited-state reactivities is found in the work of Stevens and Strickler[26] on the hydrogen–deuterium exchange of naphthalene. While a tenfold faster exchange at the α position occurs in ground-state reactions, the β position exchanged at a 15% faster rate than the α position upon excitation. The reactivity of the β position has been enhanced by over ten powers of 10. The enhanced charge build-up at the β-carbon upon excitation to the first excited singlet, as predicted by the configuration interaction calculation, renders that position more reactive.

The reactivity reversals for these naphthalene derivatives parallel the earlier findings of Zimmerman,[24] Letsinger,[25] and Havinga[27] for simple monosubstituted benzenes. The important difference between these results and earlier calculations is the inclusion of configuration interaction; the results of less complete calculations show no difference between the two positions. Calculations for benzene or naphthalene derivatives by the CNDO/M method allow at least a qualitative reactivity description for excited-state reactions.[28]

Although the mechanistic details of photodecarboxylation reactions of arylmethyl esters are not complete, several common features have emerged. (1) Cleavage occurs at the C–O bond and within a series of esters, the lowest energy π system must be the one adjacent to that linkage for highest efficiency. (2) A build-up of charge density in the reactive excited state correlates with increased reactivity. (3) Cleavage occurs homolytically to give a pair of radicals and carbon dioxide (either simultaneously or stepwise). (4) The arylmethyl radicals either combine in the solvent cage or escape the cage and react. These processes are illustrated in Scheme I for the β-naphthalenemethyl ester **5**.

Experimental Section[29]

Synthesis of Esters 1, 5, and 8–10. Esters **1**, **5**, **8**, and **9** were prepared by reacting the acid chloride with the alcohol in benzene–pyridine solutions at 0°. Ester **10** was prepared by an acid-catalyzed condensation of the acid and alcohol. Normal work-up gave the crude esters which were purified by a combination of silica gel chromatography, distillation, and recrystallization. The spectral data and physical properties are recorded in Table IV. Elemental analyses obtained for the new esters **5**, **9**, and **10** were in accord with the calculated values.

Preparative Photolysis of α-Naphthalenemethyl Phenylacetate (1). A solution of 1.181 g (4.28 mmol) of **1** in 650 ml of dioxane, freshly distilled from sodium, was degassed for 30 min with purified nitrogen and irradiated with a Hanovia 450-W medium pressure lamp (Corex filter) for 54.3 hr. Vpc analysis (program: 110°/4 min, 20°/min to 270°/8 min; column: 0.125 in. × 6 ft, 10% UCW 98

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(23) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968) (QCPE Program No. 174). A similar result was obtained by Hofer and Hedges (*Chem. Phys. Lett.*, 6, 67 (1970)).

(24) H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, **85**, 922 (1963).

(25) R. L. Letsinger, O. B. Ramsay, and J. H. McCain, *J. Amer. Chem. Soc.*, **87**, 2945 (1965).

(26) C. G. Stevens and S. J. Strickler, *J. Amer. Chem. Soc.*, **95**, 3918, 3922 (1973).

(27) E. Havinga, R. O. de Jongh, and W. Dorst, *Recl. Trav. Chim. Pays-Bas*, **75**, 378 (1956).

(28) The experimental relative reactivities of the α and β positions on naphthalene have been based on the assumption that recombination of the initially formed radicals does not occur. Although this has not been experimentally established for the naphthyl derivatives, it would appear correct based on our observations that *cis*- and *trans*-α,β-diphenyl-γ-butyrolactones do not interconvert during photodecarboxylation.[6,7]

(29) Melting points were obtained on a hot-stage apparatus calibrated with known samples, unless otherwise noted. Boiling points were uncorrected. The following spectrometers were used: nmr, Varian A-60; ir, Beckman IR-8; uv, Cary 14; mass, Varian MAT CH-5; spectrofluorimeter, Aminco-Kurs.

Scheme I

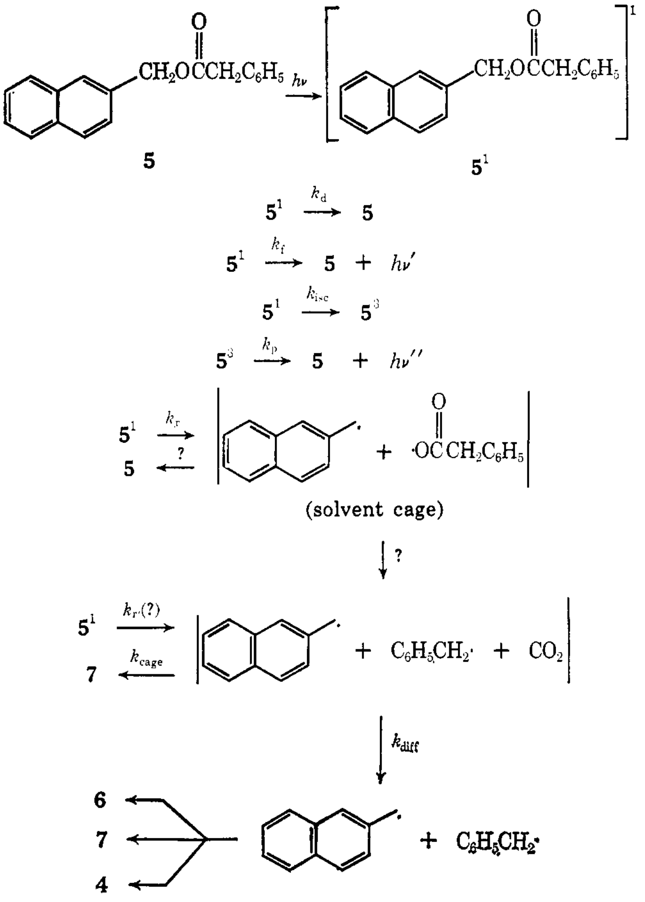

Table IV. Spectra Properties of Esters[a] **1**, **5**, and **8–10**

Compd	Nmr (CCl_4)	Ir (CCl_4), μ	Uv[b] (log ε), nm
1	7.1–7.7 (m, 12), 5.45 (s, 2), 3.50 (s, 2)	3.28, 5.78, 8.17, 8.81, 10.30, 14.44	318 (2.40), 314 (2.55), 293 (3.68), 288 (3.70), 283 (3.86), 272 (3.80), 263 (3.62)
5	7.2–7.8 (m, 12), 5.22 (s, 2), 3.58 (s, 2)	3.29, 5.79, 8.15, 8.90, 14.45	320 (2.39), 305 (2.65), 285 (3.61), 275 (2.76), 266 (3.75), 252 (3.71)
8	7.0–7.8 (m, 12), 4.99 (s, 2), 3.92 (s, 2)	3.29, 5.79, 8.62, 8.85, 10.30, 13.76, 14.46[c]	315 (2.56), 293 (3.71), 283 (3.87), 273 (3.79)
9	7.2–7.8 (m, 12), 5.08 (s, 2), 3.70 (s, 2)	3.29, 5.79, 8.95, 10.50, 13.67, 14.46[c]	319 (2.31), 314 (2.42), 305 (2.64), 287 (3.59), 278 (3.75), 269 (3.72), 251 (3.68)
10	7.15 8.02 (m, 14), 5.32 (s, 2), 3.83 (s, 2)	3.28, 5.75, 7.53, 8.44, 8.62, 12.19, 12.94, 13.79[d]	318 (2.52), 313 (2.62), 304 (2.83), 285 (3.83), 276 (3.99), 268 (3.96), 227 (5.21)

[a] Esters **1**, **5**, **8**, and **9** had mass spectral parent peaks of *m/e* 276. Ester **10** had a mass spectral parent peak of *m/e* 326. [b] In 95% ethanol. [c] In CS_2. [d] KBr.

on Chromosorb W) showed three main products in a ratio of 1 :10 :1. The solvent was removed *in vacuo* to give 1.061 g of residue which was chromatographed on silica gel. Eluting with hexane gave 235 mg of a hydrocarbon mixture; eluting with (96:4) hexane–ether gave 266 mg of **1**; eluting with ether gave 278 mg of an oil which upon analysis had characteristic nmr and ir bands for solvent derived coupling products; eluting with ethyl acetate gave 48 mg of a yellow polymeric material. Rechromatography of 151 mg of the hydrocarbon mixture on Woelm alumina (activity I) gave 5.1 mg (3.4%) of dibenzyl (**4**, 1% benzene–hexane), 100 mg (66%) of 1-phenyl-2-(α-naphthyl)ethane (**3**, 4% benzene–hexane), and 6.9 mg (4.6%) of di-α-naphthylethane, mp 161–162° (**2**, 10% benzene–hexane). The ratio of **2**:**3**:**4** from isolated yields was *ca.* 1:15:1. Dibenzyl (**4**) and di-α-naphthylethane (**2**) were identified by comparison of their physical and spectral properties with known compounds. Assignment of the third product (**3**) as α-phenyl-2-(α-naphthyl)ethane was made from the nmr and ir spectra: nmr (CCl_4) δ 7.96–7.07 (m, 12 H, arom), 3.17 (s, 2 H, CH_2), 3.05 (s, 2 H, CH_2); ir (CS_2) 3.39, 14.12, 14.42 μ; mass spectrum, *m/e* 232. *Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.86; H, 6.89.

Preparative Photolysis of β-Naphthalenemethyl Phenylacetate (5). A solution of 1.046 g (3.8 mmol) of ester **5** was dissolved in 120 ml of dioxane and placed in eight quartz tubes, degassed, and irradiated for 47 hr in a merry-go-round apparatus using 15 RPR-2537-Å lamps. The solvent was removed *in vacuo* to give 0.829 g of a yellow oil which was chromatographed on silica gel. Eluting with hexane gave 276 mg of a mixture of hydrocarbons; eluting with 4% ether–hexane gave 316 mg of the starting ester **5**; eluting with ether and with ethyl acetate gave 230 mg of polymeric material. The mixture of hydrocarbons was rechromatographed on Woelm alumina (activity I) to give 25 mg of a mixture of β-methylnaphthylene and dibenzyl (1% benzene–hexane) as a solid and 3.4 mg of 1,2-di-β-naphthylethane (**6**) as a solid. Vpc analysis of the crude reaction mixture indicated the presence of toluene (by coinjection). These hydrogen abstraction products (toluene and β-methylnaphthylene) were absent when the photolysis was carried in benzene at 3000 Å.

The structures of **6** and **7** were assigned on the basis of their spectra. For **7**, nmr (CCl_4) δ 7.74–7.13 (m, 12 H), 3.02 (s, 4 H); ir (CS_2) 3.49, 13.97, and 14.45 μ; mass spectrum *m/e* 232; mp 96.5–97.5° after sublimation. *Anal.* Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.04; H, 6.65.

For **6**, the ir (CS_2) showed absorptions at 3.28, 3.30, 3.39, 3.42 (m), 3.51 (s), 12.22, 12.34, 13.53 (s) μ; mass spectrum *m/e* 282.1410, calcd 282.1408 by peak matching.

Photolysis of Benzyl α-Naphthylacetate (8) and Benzyl β-Naphthylacetate (9). Irradiation of **8** and **9** gave only a trace of product by vpc after very long irradiation times (40 hr at 2537 Å in dioxane). The retention times of the products were identical by coinjection with those from **1** and **5**, respectively.

Quantum Yield Determination. General Procedure. A solution of the ester and cyclodecane (as an internal standard) in 15 ml of benzene in a Pyrex tube was degassed, placed in a merry-go-round apparatus, and irradiated at 40° with 15 RPR-3000-Å lamps. Light output was monitored by potassium ferrioxalate actinometry using the method of Hatchard and Parker.[30] Samples were withdrawn at intervals and analyzed directly by vpc. In some experiments, especially for the most photoreactive ester **5**, an optical bench (Bausch and Lomb 250 high intensity monochromator, Osram 200-W high-pressure mercury lamp, three 10-cm path length cells, fitted with mechanical stirring and N_2 degassing) was used similar to the procedure described by Zimmerman.[31] Results are given in Table I.

Sensitization and Quenching Experiments. Sensitizers and quenchers were purified before use. Sensitization experiments with benzophenone and acetophenone were performed at 350 nm (merry-go-round, 15 RPR lamps) in benzene; quenching experiments with piperylene and 1,3-cyclohexadiene were performed at 300 nm (15 RPR-3000-Å lamps) in benzene. Sensitizer concentrations were sufficient to capture >99% of the incident light. Samples of 0.27 mmol in 15 ml of solvent with and without sensitizers were degassed and irradiated simultaneously. Quencher concentrations, given in Figure 1, were adjusted so that capture of incident light was less than 5%. Product and ester concentrations were followed by vpc using cyclodecane as an internal standard. Results are given in Table I and Figure 1.

Comparative Runs for Esters 1, 5, 8, and 9. (1) The esters **1** (25.0 mg, 0.091 mmol), **5** (24.5 mg, 0.089 mmol), **8** (68.7 mg, 0.249 mmol), and **9** (70.0 mg, 0.254 mmol), each in 15 ml of dioxane, were degassed and irradiated simultaneously in a merry-go-round apparatus with 15 RPR-2537-Å lamps. After 4 hr of irradiation 30% of ester **1** had disappeared to give **3** as a main product (7%) and several minor products (not determined). About 65% of ester **5** disappeared and the main product (**7**) was formed in about 35% yield. Esters **8** and **9** were stable to irradiation for 38.5 hr and their

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(30) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

(31) H. E. Zimmerman, *Mol. Photochem.*, **3**, 281 (1971).

products (**3** and **7**) were formed in only trace amounts, **7** slightly greater than **3**.

(2) The esters **1** (53.7 mg, 0.195 mmol), **5** (52.4 mg, 0.190 mmol), **8** (53.0 mg, 0.192 mmol), and **9** (50.1 mg, 0.182 mmol), each in 15 ml of benzene in Pyrex tubes, were degassed and irradiated simultaneously in a merry-go-round apparatus with 15 RPR-3000-Å lamps. After 5.5 hr of irradiation **1** disappeared very slowly (4%) and its main product **3** was formed (1%). The ester **5** disappeared much faster (20%) and the main product **7** was formed in 10% yield while the other two products **6** and **4** appeared in about 1% yield. After 31.1 hr 5% of **1** and about 60% of **5** had disappeared. After 43.7 hr no significant changes of esters **8** and **9** could be observed. The products **3** and **7** were formed only in trace amounts (much smaller yields than in the irradiations at 2537 Å).

Fluorescence Measurements for Esters 1, 5, 8, and 9. Fluorescence emission spectra were determined with an Aminco-Bowman spectrofluorimeter using the IP 28 photomultiplier with an excitation wavelength of 313 nm. The uv spectra of the esters in dioxane and cyclohexane were identical in shape and absorbance, thus indicating a lack of solvent effect for the four esters' uv absorptions and permitting direct comparison of the fluorescence and absorption results for the two solvent systems.

Fluorescence Quantum Yields (Φ_f). The measured fluorescence intensities (I_f) at 336 nm were used to calculate the relative quantum yields (Φ_f) using ester **5** as the standard. The absorbance values (A) were obtained at 313 nm using more concentrated solutions (×10). The quantum yields were then calculated according to the following expression[32]

$$\frac{\Phi_f}{\Phi_f'} = \frac{I_f(1 - 10^{-A'})}{I_f'(1 - 10^{-A})}$$

Natural Lifetimes (τ_0). The natural radiative singlet lifetimes (τ_0) were determined for the four esters by integration of the uv absorption band and using the following expression[19]

$$\tau_0 = \frac{3.5 \times 10^8}{\bar{\nu}_m{}^2 \epsilon_m \Delta\bar{\nu}_{1/2}}$$

where $\bar{\nu}$ is the mean wavelength in reciprocal centimeters, ϵ_m is the extinction coefficient at λ max, and $\bar{\nu}_{1/2}$ is the half-width of the band in reciprocal centimeters.

Fluorescence Decay Time (τ_s). The fluorescence decay times were calculated from the Stern–Volmer relationship for oxygen quenching of the fluorescence emission in cyclohexane[20] according to the following expression

$$L_0/L = 1 + \tau_s k_q[\mathrm{Q}']$$

where L and L_0 are the fluorescence intensities with and without air, τ_s is the mean decay time of the deaerated solution, k_q is the quenching rate constant for oxygen, and [Q'] is the concentration of dissolved oxygen.

The value of $k_q[\mathrm{Q}']$ was taken as 6×10^7 sec^{-1}.[20] The fluorescence intensity measurements were first obtained with samples saturated with air and then repeated after argon or nitrogen degassing to give the L and L_0 values.

Phosphorescence Measurements of Esters 1, 5, and 8–10. Phosphorescence emission spectra were determined in methylcyclohexane–isopentane (1:3) glass at 77°K using 280-nm excitation wavelength. All esters (10^{-4} M) showed the characteristic three-band emission; the observed 0,0 bands were at 470 (**1**), 475 (**5**), 475 (**8**), 485 (**9**), and 475 nm (**10**). Essentially the same spectra were obtained when the glass was a 5:2:2 mixture of ether–isopentane–ethanol.

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Conformation of Cyclic β-Adenosine 3',5'-Phosphate in Solution Using the Lanthanide Shift Technique[1a]

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Abstract: The preferred conformation of cyclic β-adenosine 3',5'-phosphate in aqueous solution has been determined from shifts of proton magnetic resonance signals caused by lanthanide ions. The conformation of the ribose and phosphate groups is consistent with the structure in the crystalline state. At pD 5.3, the purine base is in the syn conformation, with the best agreement ($R = 0.048$) of calculated and observed shifts at a glycosyl torsion angle of 86°. Reasonable error limits for the torsion angle determination are ±22°. Experiments were performed over a pD range of 2.2–5.3 with a nucleotide concentration range of 0.02–0.072 M, and a lanthanide nucleotide ratio ranging from 0 to 15, without significant changes in the association constant of the lanthanide–nucleotide complexes. K_{eq} at pD 5.3, 13.0 ± 1.7, and at pD 2.2, $K_{eq} = 14.2 \pm 2.9$.

A very versatile hormonal messenger is cyclic β-adenosine 3',5'-phosphate (3',5'-AMP).[2] The crystal structure of 3',5'-AMP shows two molecules in the asymmetric unit which have very different orientations of the purine about the glycosyl bond.[3] In one molecule, the torsion angle is "anti" (−50°), while in the other it is "syn" (102°). The activation energy for rotation about the glycosyl bond may be sufficiently low that the orientation in the crystal may be determined by crystal packing forces and hydrogen bonding considerations rather than the intrinsic lowest energy orientation of the base as is more probable in solution. The structure of the molecule in solution is of interest in determining the intimate mechanism of action of the molecule and in comparing solution structures of the cyclic nucleotides with those of the noncyclic nucleo-

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(1) (a) Presented in part at the 29th Southwest Regional Meeting of the American Chemical Society, El Paso, Texas, Dec 1973. (b) Colorado State University. (c) Los Alamos Scientific Laboratory.

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