et al.[3] The latter **9a** was converted to 11-*O*-methanesulfonylerythromycin A enol ether **9b**, mp 122–131°, $[\alpha]^{23}\text{D}$ $-38°$, with methanesulfonic anhydride in pyridine followed by methanolysis of the 2′-*O*-acetyl and 4′′-*O*-formyl groups. Treatment of **9b** with DBU in refluxing benzene for 18 hr gave 11,12-epoxyerythromycin A enol ether **8** in 80% yield as a white foam, $[\alpha]^{26}\text{D}$ $-42°$.[4]

Treatment of 11,12-epoxyerythromycin A enol ether (**8**) with 1:1 acetic acid–water for 0.5 hr at room temperature gave a mixture from which were isolated 11,12-epoxyerythromycin A (**3**) (49%) and 8-*epi*-11,12-epoxyerythromycin A (**7**) (18%). Treatment of **8** with glacial acetic acid for 1 hr at room temperature yielded 20% of recovered starting material, 20% of the dienol ether **5**, and only 9% of 8-*epi*-11,12-epoxyerythromycin A (**7**). We believe the latter result proves that 11,12-epoxyerythromycin A enol ether **8** is not an intermediate in the C_8 epimerization of 11,12-epoxyerythromycin A (**3**) to 8-*epi*-11,12-epoxyerythromycin A (**7**) effected by glacial acetic acid, and that the epimerization proceeds *via* the 8-en-9-ol **10**.

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(4) A discussion of the contrast in the ease of 11,12-epoxide formation from 11-*O*-methanesulfonyl-2′-*O*-acetyl-4′′-*O*-formylerythromycin A and 11-*O*-methanesulfonylerythromycin A enol ether will be deferred to a complete paper.

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

Sir:

Recent studies of the photochemistry of esters and carboxylic acids have demonstrated the generality of the photodecarboxylation of benzyl- and phenyl-substituted derivatives.[1-6] A study of Meiggs and Miller[2] detailed the photochemistry of phenylacetic acid and methyl phenylacetate for which photodecarboxylation was a major pathway and the intermediacy of benzyl radicals was clearly demonstrated.

In our earlier report on the facile photodecarboxylation of benzyl esters and lactones,[6] we suggested a possible mechanism for these reactions (Scheme I)

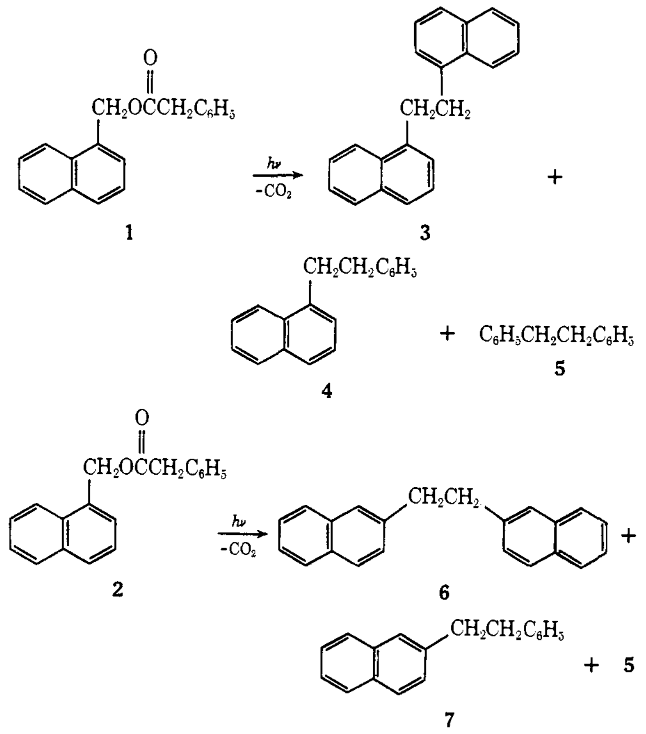
Scheme I. Proposed Mechanism for the Photodecarboxylation of Benzyl Esters and Lactones

$$\begin{tikzcd} C_6H_5CH_2CO_2CH_2C_6H_5 \arrow[r, "h\nu"] & {[C_6H_5CH_2CO_2CH_2C_6H_5]^*} \arrow[d, "\text{concerted or stepwise}"] \\ C_6H_5CH_2CH_2C_6H_5 & 2C_6H_5CH_2\cdot + CO_2 \arrow[l] \end{tikzcd}$$

which involved the excitation of the phenyl chromophore, homolytic cleavage of the ether oxygen–carbon bond with expulsion of CO_2 (either simultaneously or stepwise), and generation of a pair of radicals. We now present additional evidence for that mechanism and some interesting comparisons of the reactivity of α- and β-naphthyl esters.

Photodecarboxylation of α-naphthylmethyl phenylacetate (**1**) and β-naphthylmethyl phenylacetate (**2**) proceeded smoothly to yield the three products expected from the coupling of the naphthylmethyl radical and the benzyl radical (**3**, **4**, and **5** and **6**, **7**, and **5**, respectively). Interestingly, the ratios of the coupling products (1:10:1 for both esters) were not statistical but reflected a much higher cross coupling of the radicals. This probably resulted from a cage effect on the initially generated radical pair.[7] In a subsequent study, benzyl α- and β-naphthylacetates (**8** and **9**, respectively) were irradiated under identical conditions with those used for **1** and **2**. After very long reaction times, only a trace of product could be detected from photolysis of either **8** or **9** having a vpc retention time identical with that of the major isomer from irradiation of **1** or **2**, respectively.

Scheme II. Photodecarboxylation of α- and β-Naphthylmethyl Esters **1** and **2**



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(1) VIII. For part VII, see R. S. Givens and W. F. Oettle, *J. Org. Chem.*, in press.

(2) T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, **94**, 1989 (1972), and references therein.

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

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

(5) R. A. Finnegan and D. Knutson, *ibid.*, **89**, 1970 (1967), and references therein.

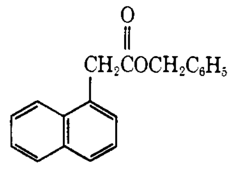
(6) R. S. Givens and W. F. Oettle, *ibid.*, **93**, 3301 (1971).

(7) This large deviation from statistical coupling is currently under investigation.

Table I. Quantum Yields and Relative Rates for Singlet Processes of α- and β-Naphthyl Esters

Ester	$10^{-3}\phi_r$[a]	k_r(rel)[b]	ϕ_f(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
2	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. [b] Relative values based on ester **2**. [c] Determined by 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 (N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 48). [e] Values obtained by oxygen quenching of the fluorescence in cyclohexane (T. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," 2nd ed, Academic Press, New York, N. Y., 1971).



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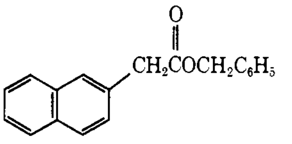

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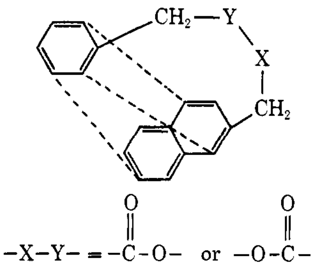
The efficiencies of these reactions were measured at 3000 Å and are recorded in Table I. Interestingly, the quantum yield for disappearance of ester shows that the efficiency for the β isomer is much greater than that of the α isomer. In an effort to assign the nature of the reactive excited state as singlet or triplet, quenching experiments of ester **2** and 1,3-pentadiene and cyclohexadiene were attempted. Although good Stern-Volmer quenching behavior was noted for product appearance, further investigation showed that this was due primarily to chemical reaction of the quencher with the starting ester.[8] Attempted sensitization with acetophenone or benzophenone was unsuccessful. We conclude that the singlet state is the reactive precursor to the homolytic bond cleavage step.

To check that the relative efficiencies of these four reactions were measures of the relative reactivities of the esters, the relative fluorescence quantum yields and the fluorescence rate constants were determined. All four esters had similar fluorescence yields and fluorescent lifetimes which allowed us to compare the efficiencies of the four reactions in terms of either their quantum yields or excited state reactivities (k_r) as obtained by the following expressions[9]

$$\frac{k_r}{k_r'} = \left(\frac{\phi_r}{\phi_r'}\right)\left(\frac{\phi_f'}{\phi_f}\right)\left(\frac{\tau_0'}{\tau_0}\right) = \left(\frac{\phi_r}{\phi_r'}\right)\left(\frac{\tau_s'}{\tau_s}\right)$$

where k_r is the rate constant for reaction, τ_0 is the intrinsic lifetime, and τ_s is the natural fluorescent lifetime.

The excited state reactivities are in variance with expectations based on the relative stabilities of the ground-state radicals for α- and β-naphthylmethyl.[10] This reversal of ground-state and excited-state reactivities has been noted in several photosolvolysis reactions[11] and may have its origin in the electron density changes in going from ground state to excited state.[12] The lack of reactivity of **8** and **9** clearly demonstrated the requirement that the excited chromophore be adjacent to the ether C–O bond. Furthermore, this result rules out any significant complex or chromophore interaction in the excited state leading to homolytic cleavage, *i.e.*, "bichromophoric" interactions.[13] If such an interaction were present, *e.g.*, **10**, the relative orientation of the CO_2 group should not greatly alter the reactivity of the molecule. We conclude that the excitation energy remains principally in the naphthyl moiety and that C–OCO bond rupture is clearly favored over C–CO_2 bond cleavage.[14]



$$-X-Y- = -\overset{\overset{O}{\|}}{C}-O- \text{ or } -O-\overset{\overset{O}{\|}}{C}-$$

10

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(8) A small fraction of the quenching by 1,3-pentadiene was due to singlet quenching detected by the diminished fluorescence at high 1,3-pentadiene concentrations. Less than one-third of the observed quenching can be attributed to singlet quenching.

(9) These expressions are alternative forms of the equation for relative rates of singlet reactivities given in a communication by S. Hixon, *J. Amer. Chem. Soc.*, **94**, 2507 (1972).

(10) (a) Gleicher (J. D. Unruh and C. J. Gleicher, *ibid.*, **93**, 2008 (1971)) has found that the rate of hydrogen abstraction by trichloromethyl radicals from 2-methylnaphthalene is about 0.68 times the rate of abstraction from 1-methylnaphthalene. Furthermore, he has obtained an excellent correlation of this finding with the differences in the π-bonding energies (ΔE_π) between the naphthylmethyl radicals and the parent hydrocarbons. Since ΔE_π can be directly correlated with the ground-state energies of the intermediate radical, the results confirm the greater stability of the α-naphthylmethyl radical relative to the β-naphthylmethyl radical. (b) Alternative explanations are possible. For example, the restricted rotation of the α-substituted ester by peri interactions could reduce the photochemically effective conformation which aligns the C–O bond with the excited π system. Such a restriction is lessened in the β-substituted ester.

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

(12) (a) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963); (b) H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

(13) R. Brainard and H. Morrison, *ibid.*, **93**, 2685 (1971). Several alternative mechanisms are suggested in this article. Our findings would favor localized excitation energy in the naphthyl moiety for the decarboxylation reaction.

(14) Interestingly, bond strength arguments would favor the opposite order of reactivity. Thus, the CH_2–CO_2 bond is weaker [estimated as 55 kcal/mol for $C_6H_5CH_2$–CO_2H (M. H. Back and A. H. Sehon, *Can. J. Chem.*, **38**, 1261 (1960))] than the CH_2–OCO bond [estimated as 68 kcal/mol for $C_6H_5CH_2$–$OCOCH_3$ from 83 kcal/mol for $CH_3CH_2CO_2$–CH_3 and allowing 15 kcal/mol for benzyl resonance (J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, pp 824–825)].

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(17) NDEA Title IV Fellow, 1971–present.

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