Photochemistry of Bichromophoric Molecules. Norrish Type II Photodecomposition of 2-Ethoxyethyl Phenylacetate[1,2]

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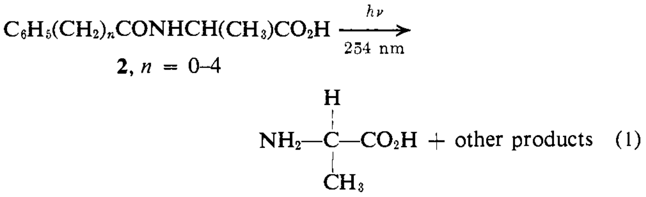
Abstract: The Norrish type II solution-phase photodecomposition of the title compound and selected homologs has been studied at 254 nm. For the generalized structure, $C_6H_5(CH_2)_nCO_2CH_2CH_2OCH_2CH_3$ (n = 0–4), only the phenylacetate (n = 1) shows appreciable photoreactivity ($\phi_{acid} = 0.098$). The 1- and 2-naphthylacetates are not photoreactive. Type II cleavage of the phenylacetate can be quenched by *cis*-piperylene but at a rate identical with that observed for fluorescence quenching at comparable ester concentrations. When compared with toluene, the phenylacetate shows a broadened primary band in its absorption spectrum and a qualitatively similar but quantitatively diminished fluorescence and phosphorescence emission (the ester singlet lifetime is likewise reduced). Mechanisms involving phenyl to ester singlet energy transfer and delocalized (whole-molecule) excitation are considered.

We have recently completed detailed investigations into the solution-phase photochemistry of several bichromophoric molecules, encompassing nonconjugated aryl olefin,[3–5] keto olefin,[6] and aryl ester[2,7] chromophores. In each case, the chemistry observed resulted from irradiation by light absorbed by the first member of a given pair. In this report, we concern ourselves with the third of the above-mentioned systems—specifically, Norrish type II photodecomposition of the title compound (**1**, n = 1) and its homologs (**1**, n = 0, 2, 3, 4) using 254-nm light.

$$C_6H_5(CH_2)_nCO_2CH_2CH_2OCH_2CH_3$$

1

Our reasons for choosing this specific system were primarily twofold. First, the much lower (*ca.* 83 kcal/mol)[8] triplet energy of the toluene chromophore, when compared with that of an ester (estimated at 103 kcal/mol, see Discussion), makes the aryl ester pair nicely complementary to the aryl olefin (where triplet energy transfer is exothermic)[3,4] and keto olefin (where triplet energy transfer, were it to occur, would be slightly endothermic)[6] systems. Secondly, we were intrigued by a fascinating report[9] on the photochemistry of a homologous series of amides **2**, in which the quantum efficiency for production of alanine was measured as a function of n (eq 1). A distinct maximum in the quantum efficiency for alanine formation was found at n = 3. Since no satisfactory explanation for this observation has, as yet, appeared, it was our hope that the somewhat analogous aryl ester series **1** might provide information useful toward this end.



$$C_6H_5(CH_2)_nCONHCH(CH_3)CO_2H \xrightarrow[254\text{ nm}]{h\nu} NH_2\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—}CO_2H + \text{other products} \quad (1)$$

2, n = 0–4

Our initial experiments thus centered on the irradiation of the series **1** with light (254 nm) primarily absorbed by the aromatic ring (see below), expecting that were excitation to be transferred into the ester moiety, type II cleavage would be observed. Such a reaction path for esters is well documented[10,11] (though not nearly so extensively as with ketones).

Results

A. Preparative Experiments. Irradiation of a solution (hexane, cyclohexane) of 2-ethoxyethyl phenylacetate (*ca.* 10^{-1} *M*) at room temperature, using 254-nm light, gave rise to two primary products. One, a solid, was identified as phenylacetic acid by comparison of physical and spectroscopic data with an authentic sample. The second was shown to be ethyl vinyl ether by direct glc analysis of the reaction mixture and by the conversion of argon-entrained vapor into acetaldehyde 2,4-dinitrophenylhydrazone.[12] Reactions in which loss of starting material exceeded *ca.* 10% also gave glc evidence of additional products, two of which were identified as bibenzyl and benzylcyclohexane. The phenylacetic acid was also identified by conversion to its methyl ester using diazomethone and glc analysis; the aryl acids formed from the other esters discussed below were isolated and identified as their methyl ester derivatives.

B. Quantum Efficiencies. The procedure used for the quantitative analysis of all ester photolyses was to convert product acids into methyl esters, and to analyze by glc against an added internal standard. All quan-

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[1] Organic Photochemistry. XIII. Part XII: R. Hoffman, P. Wells, and H. Morrison, *J. Org. Chem.*, **36**, 102 (1971).

[2] Abstracted from the doctoral dissertation of Robert Brainard, Purdue University, Aug 1970.

[3] R. Peiffer, Ph.D. Dissertation, Purdue University, 1969.

[4] (a) H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, in press; (b) H. Morrison and R. Peiffer, *ibid.*, **90**, 3428 (1968).

[5] (a) W. I. Ferree, Jr., Ph.D. Dissertation, Purdue University, Jan 1971; (b) H. Morrison and W. I. Ferree, Jr., *Chem. Commun.*, 268 (1969); (c) W. I. Ferree, Jr., J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, in press.

[6] (a) S. R. Kurowsky, Ph.D. Dissertation, Purdue University, Jan 1971; (b) Abstracts of the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14–18, 1969.

[7] For a preliminary communication, see H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968).

[8] D. F. Evans, *J. Chem. Soc.*, 2753 (1959); Y. Kanda and R. Shimada, *Spectrochim. Acta*, **17**, 279 (1961).

[9] (a) I. Mandl, B. Levy, and A. D. McLaren, *J. Amer. Chem. Soc.*, **72**, 1790 (1950); (b) A. D. McLaren and D. Shugar, "Photochemistry of Proteins and Nucleic Acids," Macmillan, New York, N. Y., 1964, pp 94–96.

[10] (a) P. Ausloos, *J. Amer. Chem. Soc.*, **80**, 1310 (1958); (b) R. Borkowski and P. Ausloos, *ibid.*, **83**, 1053 (1961); (c) P. Ausloos and R. E. Rebbert, *J. Phys. Chem.*, **67**, 163 (1963).

[11] J. E. Gano, *Tetrahedron Lett.*, 2549 (1969).

[12] Preliminary experiments using isobutyl phenylacetate indicated that this ester also decomposed to phenylacetic acid, but at a slower rate than the 2-ethoxyethyl derivative (D. Richardson, unpublished research).

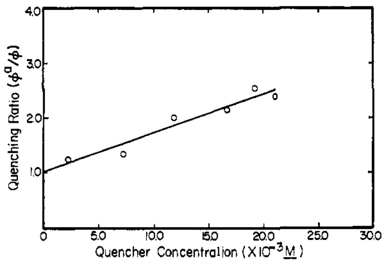

Figure 1. Stern–Volmer plot of the quenching by *cis*-piperylene of 2-ethoxyethyl phenylacetate Norrish type II decomposition.

titative runs were done at *ca.* 2 × 10^{-2} *M* ester in hexane, at 25°, to less than 10% conversion, unless otherwise noted.

Quantum efficiencies for aryl acid production (ϕ_{acid}) and ester disappearance (ϕ_{dis}) were measured at 254 nm using uranyl oxalate actinometry. The data are summarized in Table I, where "*n*" refers to the number of methylene units (*cf.* **1**). Quantum efficiencies were also measured for two substituted esters (2-ethoxyethyl *p*-methoxy- and *p*-bromophenylacetate) and the 2-ethoxyethyl 1- and 2-naphthylacetates. The data are shown in Table II.

Table I. Quantum Efficiencies for Acid Production and Ester Disappearance upon Photolysis of **1** (n = 0–4)

n	Acid formed	ϕ_{acid}	ϕ_{dis}
0	Benzoic	0.009	0.013
1	Phenylacetic	0.098	0.12
2	3-Phenylpropanoic	0.010	0.018
3	4-Phenylbutanoic	0.0014	0.007
4	5-Phenylpentanoic	0.0003	0.003

Table II. Quantum Efficiencies for Acid Production and Ester Disappearance upon Photolysis of Other Aryl Esters

Acid formed	ϕ_{acid}	ϕ_{dis}
p-Methoxyphenylacetic	0.001_5	0.29_5
p-Bromophenylacetic	0.002	0.88
1-Naphthylacetic	<0.001[a]	<0.02[a]
2-Naphthylacetic	<0.001[a]	0.06

[a] Too small to measure.

C. Quenching Experiments. *cis*-Piperylene proved to be an efficient quencher of phenylacetic acid production; the usual Stern–Volmer plot of quenching efficiency (ϕ_0/ϕ) *vs.* piperylene concentration is shown in Figure 1. The least-squares slope and intercept (with standard deviations) are 66 ± 13 M^{-1} and 1.05 ± 0.19.

Neither isopropyl alcohol (1.20 and 4.27 × 10^{-2} *M*) nor ethyl acetate (2.86 and 4.93 × 10^{-2} *M*) quenched the photodecomposition of the phenylacetate (*ca.* 10^{-2} *M*).

D. Quantum Efficiencies for Intersystem Crossing. The 2-phenylacetate sensitized cis–trans isomerization of *cis*-piperylene was studied, and the data were used to determine intersystem crossing efficiencies (ϕ_{ic}) by the method of Lamola and Hammond.[13] ϕ_{ic} values, obtained at various piperylene concentrations, are shown in Table III (no correction has been made for singlet quenching by piperylene; see Discussion).

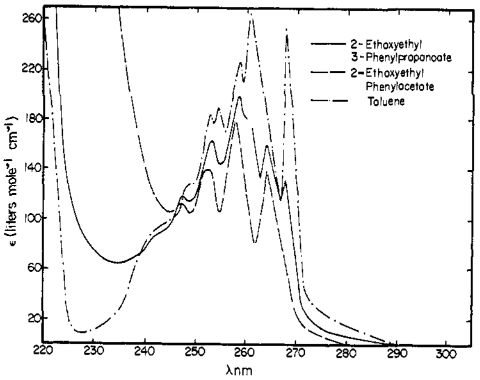

Figure 2. Ultraviolet absorption spectra of 2-ethoxyethyl phenylacetate, 2-ethoxyethyl 3-phenylpropanoate, and toluene, all in hexane solution.

Table III. Quantum Efficiencies of Intersystem Crossing for 2-Ethoxyethyl Phenylacetate as a Function of Piperylene Concentration

[*cis*-Piperylene] × 10^{-3} *M*	ϕ_{ic}
6.52	0.11
8.85	0.08
14.8	0.12
15.2	0.13
18.3	0.13

ϕ_{ic} values for methyl phenylacetate, phenylacetic acid, and 2-ethoxyethyl 3-phenylpropanoate were also obtained using 15 × 10^{-3} *M* piperylene; they are 0.18, 0.135 and 0.135, respectively.

The apparent invariance of the ethoxyethyl phenylacetate ϕ_{ic} (Table III) was confirmed in a second experiment using piperylene concentrations ranging from 2.76 × 10^{-3} *M* to 12.1 × 10^{-3} *M* (piperylene concentrations (× 10^{-3} *M*) and ϕ_{ic} values: 2.76 (0.17), 4.82 (0.23), 5.71 (0.22), 6.44 (0.20), 11.59 (0.24), 12.1 (0.17)). The ϕ_{ic} data unexplainably fall at somewhat higher values than those in Table III; the only known variable was the concentration of ester, which was raised from 2.29 × 10^{-2} *M* to 3.10 × 10^{-2} *M* (see also Fluorescence Quenching below).

E. Effect of Added Alcohol and Wavelength on the Phenylacetate Photolyses. All the studies described above were carried out in *n*-hexane. The photolysis was also studied in hexane containing 0.3 *M* *tert*-butyl alcohol and in neat *tert*-butyl alcohol. In both instances, the rates of acid formation and ester disappearance were comparable with controls run simultaneously in hexane.

ϕ_{acid} was also determined for the phenylacetate using a monochromator set to pass 261 ± 11 and 246 ± 11 nm light. The values measured were 0.07 and 0.08, respectively.

F. Absorption Spectra. Ultraviolet absorption spectra for 2-ethoxyethyl phenylacetate, 2-ethoxyethyl 3-phenylpropanoate, and toluene are displayed in Figure 2. A separate determination of the peak maxima for the primary (short wavelength) bands gave

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[13] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 3197 (1965).

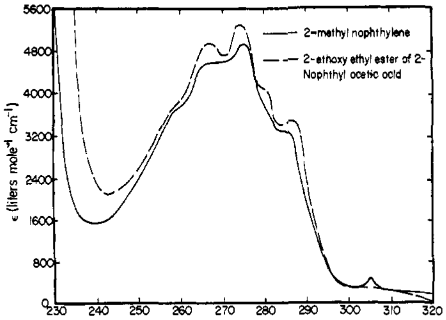

Figure 3. Ultraviolet absorption spectra of 2-ethoxyethyl 2-naphthylacetate and 2-methylnaphthalene, both in hexane solution.

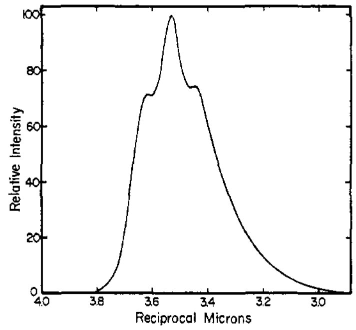

Figure 4. Corrected fluorescence spectrum for 2-ethoxyethyl phenylacetate at 25° in hexane solution.

λ_{max} for both toluene and the phenylacetate at 206 nm; the extinction coefficients were 7000 and 8000, respectively.

The uv absorption spectra of 2-ethoxyethyl 2-naphthylacetate and 2-methylnaphthalene are shown in Figure 3.

G. Fluorescence Spectra. The room-temperature fluorescence spectrum of 2-ethoxyethyl phenylacetate is shown in Figure 4. Its peak positions are identical with those of toluene but reduced in intensity; these relative intensity data are interesting in their own right and are summarized in Table IV. No fluorescence was observed for the benzoate or *p*-bromophenylacetate esters.

Table IV. Relative Fluorescence Intensities

Ester	Relative intensity, %
Toluene	100
3-Phenylpropanoate	87
p-Methoxyphenylacetate[a]	74
Phenylacetate	22
2-Naphthylacetate	70)[b]

[a] Fluorescence red-shifted with respect to toluene. [b] Value is given relative to 2-methylnaphthalene.

H. Fluorescence Quenching by ***cis*****-Piperylene.** The fluorescence emission of the phenylacetate could be readily quenched by piperylene, with a quenching efficiency linearly dependent on quencher concentration; see Figure 5. The slope of the Stern–Volmer plot was found to be a function of ester concentration; the data are 58.4 ± 4.6, 75.4 ± 1.9, and 91 ± 2 M^{-1} at 2.47 × 10^{-2}, 6.58 × 10^{-3}, and 9.29 × 10^{-4} *M* ester, respectively. All data are corrected for competitive light absorption by piperylene. The first cited slope above may be compared with the value of 66 ± 13 M^{-1} found for chemical quenching ([ester] = 2.4 × 10^{-2} *M*).

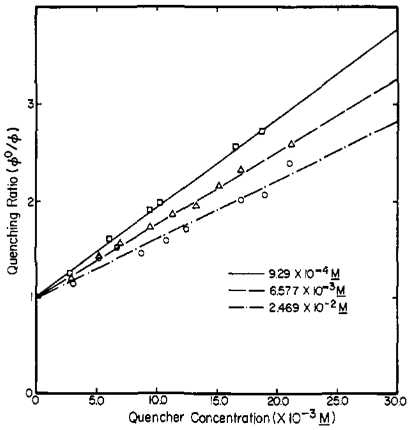

Figure 5. Stern–Volmer plot of the quenching by *cis*-piperylene of 2-ethoxyethyl phenylacetate fluorescence.

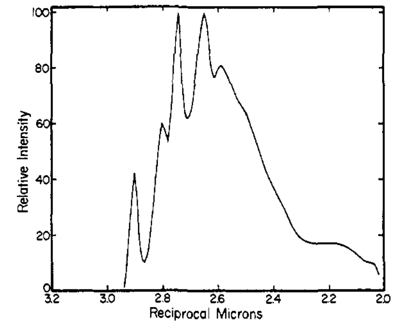

Figure 6. Corrected phosphorescence spectrum for 2-ethoxyethyl phenylacetate at 77 °K in an ethanol glass.

I. Singlet Lifetimes. All attempts to measure the fluorescence lifetime of the phenylacetate using a TRW Nanosecond Decay Time Fluorometer were unsuccessful.[14] As a result, the method of Berlman[15] was used, whereby fluorescence is partially quenched by saturation of the solution with oxygen and/or air. τ is then calculated from the usual expression, $\phi_0/\phi = 1 + k_q\tau(Q)$, where kq may be assumed to be diffusion controlled.[13] A value of 3 × 10^{10} M^{-1} sec^{-1} was calculated using[16,17] $kq \cong 8RT/2000\eta$ and η for hexane at 25° as 0.33 cP. The oxygen concentrations in hexane using air and oxygen saturation were taken as[18] 3.06 × 10^{-3} and 14.7 × 10^{-3} *M* (after correction for the observed barometric pressure).

The observed ϕ_0/ϕ values were 2.29 and 6.50 for air and oxygen saturation, giving a value of 12 nsec for τ; comparable data for toluene were ϕ_0/ϕ = 4.71 and 22.4, and τ = 47 nsec.[19] The lifetime of the ester is thus some 25% shorter than that of toluene.

J. Phosphorescence Emission. As with the fluorescence discussed above, the phosphorescence of the phenylacetate (77 °K) is similar to that of toluene but reduced in intensity. In this case, the ester emission is *ca.* 40% that observed for toluene (see Figure 6).

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(14) We are grateful to Dr. F. Lytle for the use of this instrument.

(15) I. B. Berlman, "Handbook of Fuorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, pp 35–37.

(16) A. D. Osborne and G. Porter, *Proc. Roy. Soc., Ser. A*, **284**, 9 (1965).

(17) E. W. Washburn, Ed., "International Critical Tables," Vol. VII, McGraw-Hill, New York, N. Y., 1930, p 218.

(18) J. C. Gjaldback, *Acta Chem. Scand.*, **6**, 623 (1952).

(19) The absolute values will depend on the concentrations used in the calculations, method of degassing, etc. Berlman[15] reports a value of 34 nsec for toluene.

Discussion

The most striking aspect of these data is the pronounced dependence of ϕ_{acid} on the number of methylene units separating the ester and phenyl moieties (*cf.* Table I); there is a clear maximum with the phenylacetate, *i.e.*, **1**, $n = 1$, and it is this substrate which became the subject of most of our studies. As mentioned in the introductory statement, one of our objectives was to compare our observations with those previously reported for the series **2** and it is obvious that the ester series does *not* mirror the amides, where maximum efficiency occurs at $n = 3$.

Of equal interest is the lack of reactivity noted for the 2-ethoxyethyl 1- and 2-naphthylacetates (*cf.* Table II); the high efficiency for $n = 1$ in **1** is apparently restricted to the *phenyl* ester system. It is perhaps more than coincidental that this lack of reactivity for the naphthyl derivatives is accompanied by a considerable diminution in the perturbation[20] one observes for the phenylacetate uv absorption spectrum; compare Figures 2 and 3. This feature will be further discussed below. The *p*-bromo- and *p*-methoxyphenylacetates also show little type II cleavage, but in these cases, the reason seems to be very facile photodecomposition by alternate routes (Table I). Although we made no intensive effort to study their photochemistry in detail, it is interesting that the base peak in the mass spectrum of the methoxy derivatives is *m/e* 121 (corresponding to benzylic (type I) cleavage) whereas the base peak of the phenylacetate itself is *m/e* 72 (*i.e.*, the radical cation of ethyl vinyl ether). Surprisingly, the *p*-bromo substrate's base peak is also at *m/e* 72—we expect its primary mode of photodecomposition is loss of the halogen atom.[21]

Having observed the facile type II cleavage of the phenylacetate, we addressed ourselves to the identification of the multiplicity of the reacting state. Unfortunately, little is known about the reacting species in simple aliphatic esters. It has been suggested[10c] that a triplet state might be responsible for the formation of ethylene from ethyl acetate; on the other hand, both Barltrop[22] and Jorgenson[23] have proposed that a singlet precursor is responsible for deconjugation of α,β-unsaturated esters (a reaction which, as with type II cleavage, can be viewed as the abstraction of a hydrogen atom through a six-membered transition state). Earlier evidence from our laboratories demonstrated that the phenylacetate decomposition could be efficiently quenched by *cis*-piperylene (*cf.* Figure 1); however, more recent studies[3,4a,5a] have shown that the fluorescence of benzenoid aromatics is likewise quenched by *cis*-piperylene with remarkable efficiency. In fact, when comparable concentrations of the ester are utilized,[24] essentially identical slopes (66 ± 13, 58 ± 5 M^{-1}) for chemical and fluorescence quenching are observed (compare Figures 1 and 5). The efficiency of this singlet quenching may be estimated by assuming τ for the ester is 12 nsec (see Results) and taking the slope (for a comparable ester concentration) of 75 M^{-1}. The rate constant, kq, is then $\sim 6 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$.

It is particularly significant that the quenching of the photoreaction is not *greater* than that observed for fluorescence since analogy with ketones[25] would suggest that a triplet precursor might be efficiently quenched (assuming of course that τ's for the two systems were comparable). The quenching of ethylene formation from ethyl acetate by biacetyl is reported[10c] and ascribed (rather tenuously) to quenching of the triplet state. Thus, to the extent that intersystem crossing and fluorescence in the aryl ester are competitive (see below), the *observed* efficiency for quenching a triplet photoreaction would be the sum of the fluorescence and actual triplet quenching slopes.

The above considerations suggest that we are dealing with a singlet derived type II process and that chemical quenching occurs by intercepting a precursor common to both fluorescence and reaction. Further evidence that chemical quenching originates at the singlet level comes from the piperylene isomerization data summarized in Table III. It is clear that the phenylacetate-sensitized isomerization of the diene remains at a constant value even though the piperylene concentration is varied over a range spanning the quencher concentrations used in Figure 1. Were the progressively increasing quenching displayed in Figure 1 a consequence of triplet–triplet energy transfer (*i.e.*, triplet quenching), a concomitant increase in acceptor (piperylene) isomerization should have been observed. (What is surprising is that ϕ_{ic} should be invariant even as fluorescence quenching increases; see below.)

Another experiment pertinent to the question of multiplicity involves the effect of added alcohol on the photolysis. It has been shown that polar solvents markedly increase triplet (but not singlet) type II cleavage of ketones, presumably *via* stabilization of an intermediate hydroxy biradical.[26] Although there is evidence that aliphatic esters decompose *via* a similar intermediate,[27] we find the phenylacetate reaction to be insensitive to the presence of *tert*-butyl alcohol. Unfortunately, the obvious implications to be drawn here must be qualified by the possibility that formation of the ester intermediate is not reversible,[27] and its stabilization by alcoholic solvents therefore not reflected in reaction efficiency.

A final, and particularly strong, piece of evidence in favor of phenylacetate decomposition *via* the singlet state is the predominantly stereospecific type II decomposition observed by Gano[28] for *threo*- and *erythro*-1,2-dimethylbutyl phenylacetate. These results contrast sharply with data previously obtained for a simple

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[20] The red shift in the end absorption of the phenylacetate is neither a consequence of an increased extinction coefficient nor a change in position of the primary band (206 nm) maximum (see Results). The band is simply much broader than that of toluene.

[21] For example, see: W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *J. Amer. Chem. Soc.*, **91**, 6049 (1969); J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Lett.*, 1267 (1969).

[22] J. A. Barltrop and J. Wills, *ibid.*, 4987 (1968).

[23] M. J. Jorgenson and L. Gundel, *ibid.*, 4991 (1968); M. J. Jorgenson and S. Patumevapibal, *ibid.*, 489 (1970).

[24] The slope for fluorescence quenching diminishes as the concentration of ester increases (Figure 5), suggesting that an efficient self-quenching mechanism is shortening the ester lifetime at higher concentrations. Curiously, one measurement of ϕ_{acid} at higher ester concentration gave a larger value than those observed under standard conditions. Finally, two series of measurements of ϕ_{ic} for the phenylacetate at two different ester concentrations gave somewhat different results (see Results). The reproducibility and possible relationship of these data are under study.

[25] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

[26] P. J. Wagner, *ibid.*, **89**, 5898 (1967).

[27] J. E. Gano, *Tetrahedron Lett.*, 2549 (1969).

[28] J. E. Gano, submitted for publication. Professor Gano has suggested the likelihood of singlet-derived type II cleavage for this system; we are grateful to Professor Gano for making his results known to us prior to publication.

aliphatic ester,[27] and suggest a singlet process is operative in arylacetate type II cleavage.

It now remains to be ascertained as to just how the 254-nm excitation energy becomes localized in the ester moiety. The extinction coefficient at this wavelength is essentially zero for simple aliphatic esters and the secondary (*ca.* 260 nm) band of the phenylacetate has, if anything, a somewhat lower extinction coefficient at 254 nm than toluene (*cf.* Figure 2). The lack of reactivity of the naphthyl derivatives and the sharp decline in ϕ_{acid} for the propanoate argues against vibrational energy being transmitted across the methylene bridge (keeping in mind the dangers of oversimplifying the extension to a conjugated benzoate, it is still interesting that this system, too, is much less reactive). We at one time[7] entertained the possibility of triplet energy transfer from the aryl T_2 state (estimated at 100 kcal/mol assuming the same T_2–T_1 gap as in benzene[29]) to the ester T_1 level (estimated at *ca.* 103 kcal/mol assuming 260 nm as an approximate location for the 0–0 transition of a simple ester, and assuming 6–8 kcal/mol for the S_1–T_1 gap[30]). Since the evidence presented above points to a reaction from a singlet species, we now tend to discount the possibility of such transfer for this compound.

An alternative mode of excitation transfer is suggested by the spectroscopic data in hand. We note, for example, that although the aryl ester fluorescence is qualitatively similar to that of toluene, the intensity is reduced by a factor of about 4 (Table IV);[31] such a reduction in intensity is *not* characteristic of the unreactive propanoate or naphthylacetate. Furthermore, the singlet lifetime which we estimate for the phenylacetate (12 nsec) is also a factor of 4 smaller than that measured for toluene.[19] Some competing mode of radiationless decay[32] would thus seem to be operative in the phenylacetate, and it is tempting to postulate a correlation with the unique photoreactivity which characterizes this compound. This can be done by invoking singlet–singlet energy transfer as the mechanism by which excitation becomes localized in the ester, *i.e.*, eq 2–4,

$$\text{phenyl ester} \xrightarrow{h\nu} {}^1\text{phenyl* ester} \tag{2}$$

$$^1\text{phenyl* ester} \xrightarrow[\text{transfer}]{\text{energy}} \text{phenyl } {}^1\text{ester*} \tag{3}$$

$$\text{phenyl } {}^1\text{ester*} \longrightarrow \begin{array}{c}\text{phenylacetic acid}\\ + \\ \text{ethyl vinyl ether}\end{array} \tag{4}$$

where ^{1}phenyl* ester and phenyl ^{1}ester* denote the acetate with excitation localized in the phenyl and ester moieties, respectively. The 0–0 transition for toluene (267-nm vapor phase[33]) is in the same region as one might estimate for an ester (see above), with the unusually sharp drop in reactivity upon lengthening the methylene chain a possible indication of endothermic transfer or the need for a specific steric relationship.[34] One positive aspect of such a mechanism would be the opportunity to rationalize the inefficiency shown by naphthalene derivatives; the naphthalene singlet state is too low in energy (90 kcal/mol)[35] for such transfer to take place.

Equations 2–4 do, of course, incorporate the assumption that the aryl and ester moieties may be treated as separate, independent chromophores. Although such an assumption seems justified in other bichromophoric systems we have studied,[3–6] it is particularly hazardous here in view of the large perturbation evident in the uv absorption spectrum, a perturbation that we have elsewhere noted[7] seems to be peculiar to the reactive phenylacetate (at least with respect to order of magnitude; *cf.* Figures 2 and 3). The obvious alternative to such an assumption is to consider the two moieties as one chromophoric group, whereby the absorption of light would involve a delocalized excitation process which directly activates the ester. There are difficulties with such a picture—for example, it is difficult to explain the toluene-like emission of the phenylacetate or the lack of such delocalization in the naphthalene series. Nevertheless, delocalized or "whole-molecule" excitation must continue to be considered a possible source of phenylacetate reactivity.

Finally, there remains the problem of the invariance of ϕ_{ic} (Table III) as a function of piperylene concentration, even while changes in the diene concentration lead to progressively increased amounts of fluorescence quenching. Certainly this is difficult to reconcile with the usual picture of intersystem crossing and fluorescence in competition at the lowest vibrational level of the singlet state. One explanation would be that a different species is responsible for each of the two processes; for example, one conformational isomer of the phenylacetate as the source of fluorescence and chemical reaction, and another as the source of intersystem crossing.[36] Alternatively, intersystem crossing may occur prior to the occupation of the lowest vibrational level;[37] further speculation will have to await the conclusion of studies now in progress on model systems.

Experimental Section

Materials. Phenylacetic acid (Eastman, Matheson Coleman and Bell), hydrocinnamic acid (Eastman), 4-phenylbutanoic acid, 5-phenylpentanoic acid, 1-naphthylacetic acid, 2-naphthylacetic acid (all Aldrich), *p*-bromophenylacetic acid (K & K), 4-methoxyphenylacetic acid (Aldrich), and benzoic acid (Baker) were used as received. 2-Ethoxyethanol (Eastman), diphenyl ether (Matheson Coleman and Bell), and *cis*-piperylene (Chemical Sample Co.)

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(29) S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, **43**, 2661 (1965); J. P. Doering, *ibid.*, **51**, 2866 (1969).

(30) The real value is probably at a slightly shorter wavelength but the dependence of the $n \rightarrow \pi^*$ peak maximum on the steric bulk of the alcohol moiety leads us to choose 260 nm as an upper wavelength limit; *cf.* W. D. Closson and P. Hang, *J. Amer. Chem. Soc.*, **86**, 2384 (1964). An estimate of T_1 as approaching 105 kcal/mol has been ventured by R. Simonaitis and J. N. Pitts, Jr., *ibid.*, **90**, 1389 (1968).

(31) A better model for purposes of comparison might be a long-chain alkylbenzene: *i.e.*, hexylbenzene has a fluorescence efficiency about 87% that of toluene (P. Froehlich, unpublished results). It is also interesting that a comparable reduction in fluorescence intensity has been noted for phenylacetic acid: V. M. Berenfel'd and V. A. Krongauz, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **32**, 1575 (1968).

(32) This mode does not seem to be enhanced intersystem crossing, since the phenylacetate phosphorescence is reduced by an amount comparable to that observed for fluorescence, and the ϕ_{ic} data are not unusually large.

(33) C. S. Burton and W. A. Noyes, Jr., *J. Chem. Phys.*, **49**, 1705 (1968).

(34) Were endothermic energy transfer involved, one would expect the extent of vibrational excitation to be critical to the overall reaction efficiency; in fact, we see no pronounced change in ϕ_{acid} upon varying the excitation wavelength.

(35) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 297.

(36) It is interesting that no marked increase in ϕ_{ic} is detected for the propanoate relative to the acetate.

(37) We have elsewhere been forced to consider the same possibility upon observing that 1-phenyl-2-butene's photoisomerization is less efficiently quenched than is its fluorescence emission.[4a] See ref 31 where a proposal to this effect has been made.

were distilled before use. Toluene (Baker Analyzed Reagent grade) and Benzene (Mallinckrodt spectrophotometric grade) were used as received. Stockroom isopropyl alcohol was distilled from calcium hydride; ethyl acetate (Matheson Coleman and Bell, 99.5% anhydrous) was dried over molecular sieves and distilled. *n*-Hexane and *n*-pentane were Burdick and Jackson spectral grade (OD less than 1.0 at 200 nm), *tert*-butyl alcohol (Baker) was distilled from calcium hydride, isopentane (Phillips instrument grade) was chromatographed twice through silica (uv clean above 230 nm), and ethanol was dried[38] and distilled prior to use.

Spectral and Physical Data. Infrared spectra were taken either neat between salt plates or in carbon tetrachloride solution on a Beckman IR-8. Ultraviolet spectra were determined in hexane solution on a Cary Model 14. Nmr spectra were taken in carbon tetrachloride solution on a Varian A-60. Mass spectra were recorded on a Hitachi Perkin-Elmer RMV-6A. Fluorescence spectra were recorded on a homemade,[2] right-angle instrument using an Oriel Optics low-pressure mercury lamp (C-13-63) with an Oriel power supply (C-73-16), an Oriel interference filter (G-521-2537), a modified Aminco-Bowman sample chamber, a Jarell-Ash 0.25-m Ebert monochromator (82-410), and an EMI 9558-OB photomultiplier housed in a Products for Research thermoelectrically cooled housing (TE-104). The tube output was amplified by a Hewlett-Packard vacuum tube voltmeter (412A) and recorded on a Sargent SR recorder. Excitation spectra were taken on the same instrument but with a 150-W xenon arc (Hanovia 901-C) coupled to a Bausch and Lamb monochromator (33-86-25-05) as the source. Phosphorescence spectra were recorded as described for fluorescence but using an Aminco-Bowman phosphorescence sample chamber and a quartz dewar flask (Aminco B28-62140). All emission spectra were corrected[2] by suitable calibration of the light source and detector system[39-41] with the data corrected, printed out, and integrated using appropriate computer programs.[2]

Elemental analyses were by Dr. C. S. Yeh of this department. Gas–liquid chromatography (glc) was done using a Varian-Aerograph Model 90-P3 or Model 1200 chromatograph, each with attached Disc Integrator.

Photochemical Apparatus. For all experiments except the wavelength-dependence study, a Hanovia low-pressure mercury arc (688A-45) in a Vycor housing was used. The wavelength dependence experiments utilized a Hanovia 200-W mercury–xenon compact arc (901-B) housed in a Bausch and Lamb "high intensity" source-monochromator combination (33-86-25-05). The uv grating (33-86-01) with a dispersion of 3.2 nm/mm was used. All experiments with the mercury arc employed a rotating turntable holding Vycor test tubes which was immersed in a constant temperature (25 ± 1°) bath.

Synthesis of the Esters. The general procedure was as follows. The acid corresponding to the ester desired (0.1 mol) was added to a 100-ml round-bottomed flask followed by about 0.3 mol of 2-ethoxyethanol (27 g) and a few crystals of *p*-toluenesulfonic acid. The flask was then filled with benzene, attached to a reflux condenser fitted with a Dean–Stark trap, and allowed to reflux overnight on a steam bath. The crude ester–benzene solution was washed first with water several times to remove the excess 2-ethoxyethanol and then with a saturated solution of sodium bicarbonate until the wash water was basic. The benzene solution was dried over sodium sulfate, and when dry the benzene was removed on a rotary evaporator. The resulting crude ester was vacuum distilled through a Vigreux column. The esters were routinely microdistilled immediately before use. The yields for all esters were 90–95%.

2-Ethoxyethyl Phenylacetate. This ester is a thick oily liquid: bp 104° (0.1 mm); $\lambda_{\max}^{\text{film}}$ 3.35 and 3.49 (doublet), 5.78 (s), 8.0, and 8.9. The nmr spectrum (δ) was observed in carbon tetrachloride: 7.2 (singlet, 5 H), 4.2–3.3 (multiplet, 8 H), 1.2 (triplet, 3 H). Mass spectral analysis gave a parent peak at *m/e* 208.

Anal. Calcd for $C_{12}H_{15}O_3$: C, 69.21; H, 7.74. Found: C, 69.42; H, 7.82.

2-Ethoxyethyl 3-Phenylpropanoate. This ester is a clear oily liquid: bp 115° (0.1 mm); $\lambda_{\max}^{\text{film}}$ 3.4 and 3.55 (doublet), 5.9 (s), 8.9 (b), 13.5, and 14.5. The nmr spectrum (δ) was observed in carbon tetrachloride: 7.1 (singlet, 5 H), 4.2–2.5 (multiplet, 10 H), 1.1 (triplet, 3 H). Mass spectral analysis gave a parent peak at *m/e* 222.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.54; H, 8.37.

2-Ethoxyethyl 4-Phenylbutanoate. This ester is a clear oily liquid: bp 140° (1.6 mm); $\lambda_{\max}^{\text{film}}$ 3.35 and 3.50 (doublet), 3.4 (doublet), 5.75 (s), 8.9 (vw), 13.4 (s), and 14.3 (s). The nmr spectrum (δ) was observed in carbon tetrachloride: 7.3 (singlet, 5 H), 4.2, 3.5, 1.8–2.8 (multiplet, 13 H), 1.1 (triplet, 3 H). Mass spectral analysis gave a parent peak at *m/e* 236.

Anal. Calcd for $C_{14}H_2O_3$: C, 71.16; H, 8.53. Found: C, 71.34; H, 8.61.

2-Ethoxyethyl Benzoate. This ester is a clear liquid: bp 104° (1 mm); $\lambda_{\max}^{\text{film}}$ 3.35 and 3.50 (doublet), 5.80, 6.90, 7.90, 8.0, 8.75, 14.1. The nmr spectrum (δ) was observed in carbon tetrachloride: 8.1–7.5 (multiplet, 5 H), 4.4 (multiplet, 2 H), 3.6 (multiplet, 2 H), 1.2 (triplet, 3 H). Mass spectral analysis gave no parent peak.

Anal. Calcd for $C_{11}H_{14}O_3$: C, 69.1; H, 7.1. Found: C, 68.25; H, 7.23.

2-Ethoxyethyl 1-Naphthylacetate. This ester is a very thick oily liquid: bp ≃155° (0.25 mm); $\lambda_{\max}^{\text{film}}$ 3.41 and 3.55 (doublet), 5.95 (s), 9.0, 13.0. The nmr spectrum (δ) was observed in carbon tetrachloride: 7.0–8.0 (multiplet, 7 H), 4.0 (multiplet, 4 H), 3.2 (multiplet, 4 H), 1.0 (triplet, 3 H). Mass spectral analysis gave a parent peak at *m/e* 258.

Anal. Calcd for $C_{16}H_{18}O_3$: C, 74.39; H, 7.02. Found: C, 74.18; H, 7.09.

2-Ethoxyethyl *p*-Bromophenylacetate. This ester is a thick oily liquid: bp ≃150° (0.1 mm). The nmr spectrum (δ) was observed in carbon tetrachloride: 7.3 (quartet, 4 H), 4.2 (triplet, 2.1 H), 3.5 (multiplet, 3.9 H), 1.2 (triplet, 3 H). Mass spectral analysis gave a parent peak at 286 mass units and a p + 2 peak at *m/e* 288.

Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.79; H, 7.87.

2-Ethoxyethyl 5-Phenylpentanoate. This ester is a clear thick oily liquid: bp ≃143° (0.55 mm); $\lambda_{\max}^{\text{film}}$ 3.42 and 3.55 (doublet), 5.9 (s), 9.0 (b), 12.7. The nmr spectrum (δ) was observed in carbon tetrachloride: 7.2 (singlet, 5 H), 4.2, 3.4, 2.7, 2.3, 1.7 (complex, 14 H), 1.1 (triplet, 3 H). Mass spectral analysis gave a parent peak at *m/e* 250.

Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.16; H, 9.01.

Preparative Photolysis. In order to provide preliminary data on the reaction, several irradiations were made of the 2-ethoxyethyl ester of phenylacetic acid in *n*-hexane solution. About 4–6 g of the ester in 300 ml of cyclohexane was added to a Pyrex photolysis vessel in which a quartz immersion well was inserted. The solution was deoxygenated by bubbling with argon for 30–45 min and then irradiated from 2 to 8 hr with the low-pressure mercury arc. After irradiation the photolysis solution was concentrated on the rotary evaporator and extracted with saturated sodium bicarbonate solution. The aqueous sodium barcarbonate solution was then acidified with concentrated hydrochloric acid and extracted with ether. The ether was dried and evaporated leaving phenylacetic acid (0.6–1.2 g) which was identified by comparison of its melting point and ir spectrum with an authentic sample. Ethyl vinyl ether was identified as a product of the reaction by bubbling the exit gas of the photolysis vessel through a solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl. The ethyl vinyl ether was hydrolyzed by the acid to acetaldehyde which was precipitated as the 2,4-dinitrophenylhydrazone. When cyclohexane was used as solvent, benzyl cyclohexane and bibenzyl could be identified in the tar and oils of the non-bicarbonate-soluble fraction by overlaying the glc peaks with authentic samples.

Quantitative Photolyses. For the quantitative analysis of the photolysis solutions, quantum yields, and chemical quenching studies, the deoxygenated ester solutions ($1–2 \times 10^{-2}$ *M* unless otherwise noted) were irradiated (typically 45–55 min) in 50-ml Vycor tubes on a turntable apparatus (25 ± 1°, intensity $\sim 1 \times 10^{17}$ photons/sec). Ethereal diazomethane (EXR-101) was added to irradiated tubes to convert the free acid to the methyl ester for analysis by glc. After an excess of diazomethane was added to the tubes, they were allowed to stand overnight at room temperature. The next morning a weighed amount of the internal standard, diphenyl ether, was added to each tube. For quantum yield determinations, actinometer tubes (uranyl oxalate)[42] were irradiated in parallel with the ester.

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(38) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956.

(39) R. F. Chen, *Anal. Biochem.*, **20**, 339 (1967).

(40) W. H. Melhuish, *J. Opt. Soc. Amer.*, **52**, 1256 (1962).

(41) C. A. Parker, "Photoluminescence of Solutions," W. A. Benjamin, New York, N. Y., 1967, p 253.

(42) G. S. Forbes and L. J. Heidt, *J. Amer. Chem. Soc.*, **56**, 2363 (1934).

For irradiation of the less reactive esters, the actinometer tubes were changed either after 2 hr of irradiation or screened with 40 mesh copper screen to reduce the light intensity to 37% of the unscreened value. For the first series of reactions the Vycor tubes were masked; however, the same quantum yields were obtained with unmasked tubes.

The amount of methyl phenylacetate and the 2-ethoxyethyl ester of phenylacetic acid in the tubes was determined by glc with a 10 ft × $^{1}/_{4}$ in. column of 12% DEGS (diethylene glycol succinate) with a Varian A-90-P3 chromatograph. Synthetic mixtures of the internal standard, diphenyl ether, and the two esters of phenylacetic acid were analyzed. From this analysis a calibration curve was prepared comparing the weight ratios of the esters to internal standards with the ratio of the areas under their glc peaks. The calibration factor (k) is defined by the relationship (weight of ester)/(weight of standard) = k[(area ester)/(area standard)]. The calibration factor, 1.04, was found to be the same, within experimental error, for both the methyl and 2-ethoxyethyl esters of phenylacetic and 3-phenylpropanoic acids. For the methyl and 2-ethoxyethyl esters of 4-phenylbutanoic and 5-phenylpentanoic acids the 2 ethoxyethyl ester of phenylacetic acid was used as the internal standard with a factor of 1.0.

Sample Deoxygenation. All photolysis solutions used to obtain the results presented in this thesis, unless otherwise noted, were deoxygenated by bubbling with argon for at least 45 min before being capped and irradiated. In those solutions containing added quenchers, the quencher was either added to the solution before degassing or, in the case of volatile quenchers such as *cis*-piperylene, injection through the rubber stopple used to seal the tube following deoxygenation. Some solvent was lost during the deoxygenation of most solutions and as a result, all solutions were diluted to the desired volume with additional deoxygenated solvent.

Solutions for fluorescence were degassed for 12 min by bubbling with argon in a specially modified fluorescence cell which was fitted with a Teflon stopcock. Solutions for phosphorescence were degassed by four or more freeze–pump–thaw cycles (<1 μ) on a cell fitted with a vacuum stopcock and Teflon o-ring seal.

Quantum Yields. Typically, 0.2–0.3 g of the ester was dissolved in 50 ml of *n*-hexane, placed in the Vycor tubes, and deoxygenated with argon for 45 min. Irradiations were conducted on the turntable apparatus, to conversions of 10% or less for the majority of analyses. Work-up was as described above. Results are shown in Table V.

Table V. Quantum Yields for Phenylacetate Photoreaction

Concn (× 10^{-2} M)	ϕ_{acid}	ϕ_{dis}
1.23	0.096	0.12
1.23	0.097	
1.46	0.096	
3.2	0.10	0.12
3.2		0.13
7.6	0.19	

Analyses of the methyl *p*-bromo- and *p*-methoxyphenylacetates were performed on the Varian 1200 chromatograph with a $^{1}/_{8}$ in. × 20 ft column of 5% SF-96. 2-Ethoxyethyl phenylacetate was used as the internal standard for the *p*-methoxy ester (k = 1.03) and 2-ethoxyethyl 3-phenylpropanoate was used as the standard for the *p*-bromo ester (k = 1.31). Results are shown in Table VI.

Table VI. Quantum Yields for *p*-Bromo- and *p*-Methoxyphenylacetates[a]

Ester	Concn (× 10^{-2} M)	ϕ_{acid}	ϕ_{dis}
p-Bromo	3.02	0.0023	
p-Bromo	3.02	0.0016	
p-Bromo	3.02		0.98
p-Bromo	3.02		0.78
p-Methoxy	2.56	0.0022	
p-Methoxy	2.56	0.0010	
p-Methoxy	2.56		0.25
p-Methoxy	2.56		0.43

[a] Quantum yields for other esters are given in the Results.

Quenching of the Photoreaction. For these experiments, various amounts of the quenching agents were weighed and injected through the rubber stopples capping the Vycor tubes into deoxygenated ester solutions. The relative quantum yields of the tubes with quencher were determined by comparison with two ester solutions which had no quencher and were irradiated in the same turntable simultaneously. Work-up and analysis were as described. Results with *cis*-piperylene are given in Table VII.

Table VII. Chemical Quenching of 2-Ethoxyethyl Phenylacetate by *cis*-Piperylene[a]

[Q] (× 10^{-3} M)	ϕ_0/ϕ
2.3	1.24
7.3	1.34
11.8	2.00
17.0	2.15
19.2	2.54
21.0	2.20

[a] Ester concentration at $\simeq 2.4 \times 10^{-2}$ M.

Isopropyl alcohol (1.2 and 4.27 × 10^{-2} M) and ethyl acetate (2.86 and 4.93 × 10^{-2} M) produced no observable quenching. When *tert*-butyl alcohol was used in the solvent (either neat or 0.3 M in hexane), no change in reaction rate was observed.

Photolysis of 2-Ethoxyethyl Phenylacetate as a Function of Wavelength. These experiments were performed with the Bausch and Lomb "High Intensity" monochromator using the uv grating and a Hanovia 901-B 200-W Hg–Xe arc. The exit slit was set at 3.4 mm so as to give a band pass of 11 nm. Phenylacetate (1.38 × 10^{-2} M; 60 ml) was deoxygenated for 1 hr and photolyzed in a 5-cm pathlength, water-jacketed cell maintained at 25 ± 0.1°. Photolyses were conducted at 246 (35 hr) and 261 nm (54 hr) giving 5.0 and 4.5 mg of methyl ester. Light intensities, measured by uranyl oxalate actinometry before and after each photolysis, were: 1.05 × 10^{16} and 7.83 × 10^{14} photons/sec (246 nm) and 1.46 × 10^{15} and 1.25 × 10^{15} photons/sec (261 nm); ϕ_{acid} (246 nm) = 0.08; ϕ_{acid}' (261 nm) = 0.07.

Photosensitized Isomerization of *cis*-Piperylene. These experiments were run with pentane as solvent and without any attempt to analyze for ester photoproduct. Analysis of the *cis*- and *trans*-piperylene was performed on the Varian 1200 chromatograph using a 30% β,β'-oxidipropionitrile on Varaport 30 column maintained at ice temperature. Retention times are *ca.* 38 min for the trans diene and 41 min for the cis isomer. The trans isomer was mea-

Table VIII. Fluorescence Quenching of 2-Ethoxyethyl Phenylacetate by *cis*-Piperylene

[Ester]	[*cis*-Piperylene] × 10^{-3} M	ϕ_0/ϕ
9.29 × 10^{-4}	2.79	1.23
	6.09	1.60
	9.50	1.89
	10.47	1.97
	16.76	2.55
	18.97	2.71
6.57 × 10^{-3}	2.93	1.20
	5.28	1.42
	7.05	1.56
	9.54	1.72
	11.45	1.84
	13.36	1.96
	15.26	2.18
	17.17	2.32
	21.28	2.59
2.47 × 10^{-2}	3.08	1.13
	5.28	1.38
	6.75	1.51
	8.81	1.44
	10.86	1.56
	12.48	1.70
	17.02	1.98
	18.94	2.04
	21.14	2.33

sured relative to the cis and corrected for the back reaction[43] and for the amount of isomerization produced by light absorbed by the piperylene ($\phi_{cis \rightarrow trans} = 0.09$).[6a] Light intensities were measured by uranyl oxalate actinometry and were typically 1.2×10^{17} photons/sec. Optimum data were obtained with piperylene isomerization of 5–15%. The ϕ_{ic} values are shown in the Results.

Emission Spectra. All solutions for fluorescence studies were degassed by bubbling with argon for 12 min; such solutions were found to be equivalent to four freeze–pump–thaw cycles at vacuum of less than 1 μ. Studies were made with *n*-hexane as solvent at 25°. Phosphorescence spectra were determined in ethanol glasses at 77°K. The cell was a 3 or 4 mm (i.d.) quartz tube attached by epoxy resin to an O-ring seal; a second O-ring seal was attached to a Kel-F high-vacuum stopcock and the two pieces joined by a Teflon O-ring. Samples were deoxygenated by four freeze–pump–thaw cycles to a vacuum of less than 1 μ. It was found that with this diameter quartz tube, relative intensities could be measured to 10–20% reproducibility.

Fluorescence Quenching by Piperylene. Solutions of the phenylacetate and varied amounts of piperylene were deoxygenated and relative fluorescence intensities determined. The data are collected in Table VIII.

Acknowledgments. We are grateful to the Public Health Service (Grant No. CA-10733, National Cancer Institute) and the National Science Foundation (Grant No. GP 7463 and GP 12650) for the generous support of this research. We also are grateful for the assistance of Professor F. Lytle in the construction and calibration of the fluorometer and P. Froehlich for obtaining some of the fluorescence quenching data.

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(43) A. A. Lamola, Ph.D. Thesis, California Institute of Technology, Calif., 1965, p 41.

The Effect of Polar Substituents on the Barrier to Rotation about the Sulfenyl Sulfur–Nitrogen Bond in *N*-Alkyl-*N*-arenesulfonylarenesulfenamides[1,2]

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Abstract: An investigation of the effect of polar substituents on torsional barriers in *N*-isopropyl-*N*-arenesulfonylarenesulfenamides was undertaken using the methods of Hammett analysis. The results provide additional confirmation that chemical-shift nonequivalence in these compounds derives from a torsional barrier about the N–S bond. Polar substituents attached to the sulfenyl phenyl ring increase the torsional barrier. The effect of substituents in the para position is more dramatic than that of those in the meta position indicating that conjugation with the aromatic π system is important. The effect of polar substituents attached to the sulfonyl phenyl ring is quite different. When the sulfenyl phenyl ring does not have polar substituents, substitution in the sulfonyl phenyl ring has no effect on the torsional barrier. However, when the sulfenyl phenyl ring is substituted with electron-withdrawing groups, the effect of electronegative substituents in the sulfonyl phenyl ring is to lower the torsional barrier. The data are best accommodated by postulating three contributors to the sulfenamide torsional barrier: (a) overlap repulsion between nonbonding electrons on sulfur and nitrogen; (b) steric hindrance at the transition state; (c) dependence of the S–N bond strength on dihedral angle. The dihedral angle dependence of the bond strength is related to partial multiple bonding which most likely involves sulfur d orbitals.

Nuclear magnetic resonance (nmr) spectroscopy has proved to be a powerful tool for the study of the stereochemistry of trivalent nitrogen bonded to heteroatoms bearing nonbonding valence shell electrons. Compounds containing trivalent nitrogen bonded to nitrogen, oxygen, sulfur, or phosphorus have been observed to exhibit chemical-shift nonequivalence of diastereotopic substituents.[4] The coalescence of signals of diastereotopic groups has been associated with either of two conformational processes: inversion of the nitrogen pyramid or rotation about the nitrogen–heteroatom bond. Indeed, several studies have been devoted to determining which of the two, torsion or inversion, represents the slow step in the "topomerization,"[5] the conformational interchange corresponding to coalescence. In the sulfenamide system, where the heteroatom is divalent sulfur, the rate-determining step has been firmly established as rotation about the N–S formal single bond.[4a]

Among the largest torsional barriers in compounds of this type are those in sulfenamides, ranging from 12 to 20 kcal/mol. As such, sulfenamides represent useful substrates for studying the influence of structural

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(1) Stereochemistry at Trivalent Nitrogen. XI. Part X: M. Raban and E. H. Carlson, *J. Amer. Chem. Soc.*, **93**, 685 (1971).

(2) (a) This work was supported in part by the National Science Foundation under Grant No. GP-17092 and by the Petroleum Research Fund, administered by the American Chemical Society, under Grant No. 1139-G. (b) Abstracted from the Ph.D. Thesis of F. B. J., Wayne State University, 1970. (c) A portion of this work has appeared in preliminary form: M. Raban and F. B. Jones Jr., *J. Amer. Chem. Soc.*, **91**, 2180 (1969).

(3) Holder of a University Fellowship at Wayne State University, 1969–1970.

(4) For leading references in this area see: (a) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **91**, 6677 (1969); (b) H. Kessler, *Angew. Chem.*, **82**, 237 (1970); *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); (c) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(5) Topomerization has been suggested as a useful term to describe degenerate processes which alter the time-averaged stereochemical relationships of groups in molecules.[4b] This includes processes by which diastereotopic groups are rendered enantiotopic or equivalent on the nmr time scale. Often, as in the present instance, topomerization may be effected by degenerate racemization, the interconversion of two enantiomers in a racemic modification.