a pipet and concentrated by fractional distillation. Capillary GC analysis (61-ft column, LAC-2R-446) of the reaction product and the reserved starting mixture gave peak areas of reactants (*cis*-**2** and **3**) and the internal standard (cyclohexyl acetate). From these values the rate-constant ratio for *cis*-**2** and **3** can be calculated with eq 2. This particular experiment gave a value of 0.31 for the rate of *cis*-**2** relative to **3**. Another experiment gave a value of 0.15. Thus the averaged rate for *cis*-**2** relative to **3** is 0.23 ± 0.11 as indicated in Chart I. The other values in Chart I are similarly averages of two or more independent experiments.

B. Proton NMR Analysis. In a typical experiment an ether solution of 163.4 mg (0.61 mmol) of **13**, 183.6 mg (0.97 mmol) of **11**, and 90.9 mg (0.64 mmol) of 1-methylnaphthalene was prepared as described above. This solution was cooled to 0 °C and added to a solution of 0.5 mmol of $LiCuMe_2$ in 5 mL ether at 0 °C. After being stirred 10 min, the reaction mixture was quenched with 0.5 mL of H_2O and centrifuged. The ether layer was dried (K_2CO_3), concentrated, and taken up in CCl_4 for NMR analysis. The peak areas for the acetyl methyl of **11**, the aromatic methyl of **13**, and the aromatic methyl of the internal standard (1-methylnaphthalene) for the reaction product and reserved starting mixture were determined with a planimeter. In this experiment a value of 1.51 was obtained for the **13**/**11** rate-constant ratio. Another experiment gave a value of 2.53. Thus the average rate of **13** relative to **11** is 1.9 ± 0.7 as indicated in Chart II. The other values in Chart II that were determined by this method are also average values of two or more independent experiments.

C. Deuterium NMR Analysis. In a typical experiment a mixture of 127.7 mg (0.97 mmol) of (*Z*)-**10**-d_3, 170.7 mg (1.20 mmol) of γ-D-**11**, and 78.9 mg (0.74 mmol) of cyclohexyl acetate-*1-d* in 3 mL of dry ether was prepared as described above. After thorough mixing, two-thirds of the solution was transferred to a small flask and the stirred solution was cooled to 0 °C. A prechilled solution of 0.1 M $LiCuMe_2$ (5 mL) was added rapidly to the stirred solution. After being stirred 10 min at 0 °C, the reaction was quenched with 0.5 mL of saturated aqueous NH_4Cl and the ether layer separated and concentrated by fractional distillation. Deuterium NMR analysis of the concentrated reaction product and the reserved starting mixture gave values for the areas (determined with a planimeter) of the reactants ((*Z*)-**10**-*d* and γ-D-**11**) relative to the internal standard (cyclohexyl acetate-*1-d*). From these values the rate-constant ratio of 0.86 for (*Z*)-**10** and **11** was obtained with eq 2.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8406480).

Photophysical Probes of Intramolecular Interactions Responsible for Asymmetric Induction

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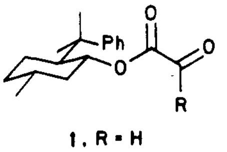
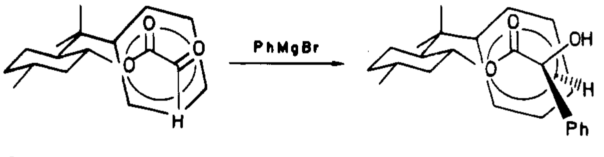
The study of fluorescence quantum yields and excited-state lifetimes for a family of α-carbonyl esters of 8-phenylmenthol reveals significant intramolecular quenching. The efficiency of the intramolecular quenching is conformationally dependent. Shifts in emission bands upon the addition of Lewis acid are consistent with excited-state charge-transfer interactions and with substantial HOMO–LUMO interactions. The observed unidirectional intramolecular quenching can be rationalized by a mechanism involving either electron or energy transfer from the excited arene to the proximate α-carbonyl ester.

α-Carbonyl esters **1** and **2** of 8-phenylmenthol exhibit excellent degrees (90–99.4%) of asymmetric induction in ene reactions,[1] reductions,[2] and nucleophilic additions with Grignard reagents.[3] For example, addition of phenylmagnesium bromide to **1** gives the corresponding α-hydroxy ester in 90% chemical yield with 99.1% diastereomeric excess.[3] Such high levels of induction require both diastereoface selectivity and a fixed orientation of the carbonyl groups in the transition state. The configuration of the chiral centers generated in these reactions is consistent with addition from the front face of the glyoxylate ester as drawn in eq 1. The carbonyls are cis to one another, and the phenyl ring is positioned to block one face of the dicarbonyl, rendering the opposite face accessible to incoming reagents. This fixed orientation requires a stabilizing interaction between the phenyl and glyoxylate moieties as steric requirements would not favor close approach between the two groups. Such interaction could conceivably result from stabilizing overlap of the frontier molecular orbitals of the two functionalities. Through-space π–π overlap has also been invoked by Oppolzer[4] as an explanation for the asymmetric induction seen in Diels–Alder reactions of cyclopentadiene with 8-phenylmenthol acrylates and in Corey's observation of face selective reduction of α,β-unsaturated ketones in the prostaglandin series.[5]



1, R = H
2, R = Me



(1)

Molecular models reveal that the two carbonyls and the phenyl ring are quite well situated to facilitate HOMO–LUMO interaction. The frontier orbitals of the 1,2-dicarbonyl may be approximated as a butadiene system, and the frontier orbitals of the phenyl substituent may be

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[1] Whitesell, J. K.; Bhattacharya, A.; Aguilar, D. A.; Henke, K. *J. Chem. Soc., Chem. Commun.* **1982**, 989.

[2] Whitesell, J. K.; Deyo, D.; Bhattacharya, A. *J. Chem. Soc., Chem. Commun.* **1983**, 802.

[3] Whitesell, J. K.; Bhattacharya, A.; Henke, K. *J. Chem. Soc., Chem. Commun.* **1982**, 988.

[4] Oppolzer, W.; Kurth, M.; Reichlin, D.; Chapuis, C.; Mohnhaupt, M.; Moffatt, F. *Helv. Chim. Acta* **1981**, *64*, 2802.

[5] Corey, E. J.; Becker, K. B.; Varma, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 8616.

Table I. Ultraviolet Absorption Maxima and Relative Fluorescence Quantum Yields for 1–8[a]

compd	λ_{max}, nm	ϕ_{Frel}[b]	λ_{max}^{emiss}, nm	ϕ_{Frel}[c]	λ_{max}^{emiss}, nm
1	227, 258, tailing to 370	0.55	323	9.7	440[d]
2	228, tailing to 370	0.35	333	7.7	440[d]
3	229, 255, 355	0.01	325 (br)	8.0	435
4	258	1.00	354		*e*
5	259	0.32	346		*e*
6	230, 335	0.00		7.8	432
7	230, 350	0.00		7.1	434
8	330	0.00		1.0	418

[a] 1×10^{-3} M in CH_2Cl_2. [b] λ_{exc} = 285 nm. [c] λ_{exc} = 340 nm. [d] Emission spectrum is very broad and overlaps significantly with tailing π,π^* emission. [e] Only weak tailing emission.

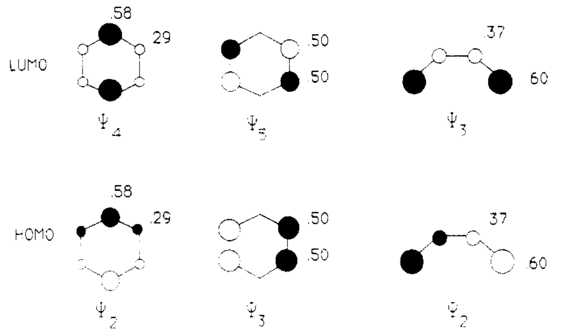


Figure 1. Molecular orbitals of benzene and butadiene.

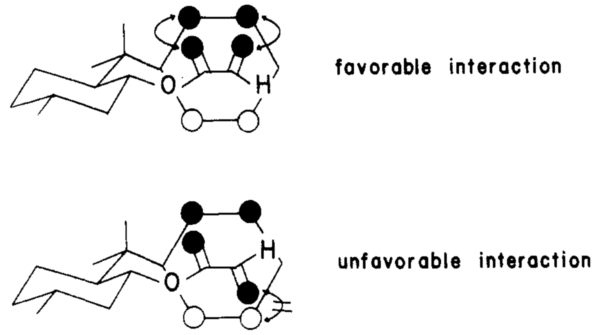
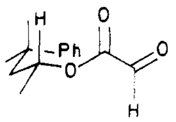


Figure 2. HOMO–LUMO interactions for cis and trans carbonyl configurations.

derived from benzene (Figure 1). The nodal properties of the ψ_3 HOMO of benzene and the ψ_3 LUMO of butadiene are favorable for a stabilizing interaction provided the carbonyls are in a cis orientation; a trans conformation leads to unfavorable orbital overlap (Figure 2). (The ψ_2 HOMO of benzene has been omitted to a first approximation as the eigenvalues on the carbons of interest are too small to create significant interaction.)

Excited-state lifetimes and emission efficiencies have proven useful in numerous studies to evaluate electronic interaction in bifunctional molecules.[6–9] In this study the photophysics of **1** and **2** as well as appropriate models **3–8** were studied to determine the extent of HOMO–LUMO interaction.



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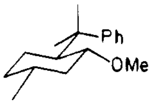

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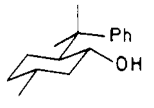

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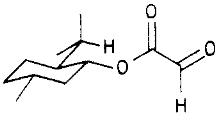

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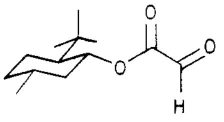

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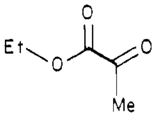

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Results and Discussion

Ultraviolet Spectra. Ultraviolet spectral data for each of the compounds is shown in Table I. The molecules with aryl moieties (**1–5**) show the typical π,π^* aromatic absorption between 250 and 260 nm. All of the α-keto esters show an absorption of low extinction coefficient in the 300–350-nm region characteristic of the carbonyl n,π^* transition.[10] Esters **1–3**, **6**, and **7** exhibit a distinctive band at about 230 nm, which can be assigned to the π,π^* transition of the carbonyl.

Emission Efficiency. The relative fluorescence quantum yields and emission maxima for excitation at 285 and 340 nm are given in Table I. Excitation at 285 nm of the model phenyl fluorophore, compound **4**, gives fluorescence at 354 nm resulting from the π,π^* singlet excited state of the aromatic ring while ethyl pyruvate (**8**) containing only the α-keto ester chromophore shows little activity upon similar excitation.

The α-keto ester fluorophore **8** emits strongly at 418 nm upon irradiation into the n,π^* band (340 nm). By analogy to biacetyl (which fluoresces at 460 nm and phosphoresces at 520 nm),[11a] the emission of compound **8** probably originates from the n,π^* singlet state of the α-keto ester. Exciting compound **4** at 340 nm gives a weak emission spectrum with no well-defined maximum. This spectrum probably results from excitation of the tailing phenyl absorption into the 340-nm region.

The phenyl-substituted glyoxylate esters (**1–3**) show emission maxima in the region from 323 to 333 nm upon excitation of the phenyl group (see Table I). As anticipated, those esters without a phenyl substituent (**6–8**) show no appreciable emission upon excitation at 285 nm.

All of the phenylglyoxylate esters show a decreased fluorescence quantum yield relative to the monofunctional compound **4** indicative of fluorescence quenching of the excited aryl fluorophore by the diketo group. The very low fluorescence efficiency of **3** may be the result of the sterically unconstrained approach of the two chromophores, facilitating more efficient electronic interaction. In addition, the observed result is consistent with the well-known enhancement of fluorescence upon increasing molecular rigidity.[11b]

A more dramatic quenching of the phenyl fluorescence is noted upon addition of an equimolar amount of tin(IV) tetrachloride ($SnCl_4$), a Lewis acid necessary for high levels of stereochemical control in the ene reaction of **1**.[1] A

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[6] Breen, D. E.; Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1935.

[7] Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, 393.

[8] (a) Scaiano, J. C. *Can. J. Chem.* **1984**, 628. (b) Scaiano, J. C.; Perkins, M. J.; Sheppard, J. W.; Platz, M. S.; Barcus, R. L. *J. Photochem.* **1983**, *21*, 137. (c) Whitten, D. G.; Punch, W. E. *Mol. Photochem.* **1970**, *2*, 77. (d) Wagner, P. J.; Kelso, P. A. *Mol. Photochem.* **1970**, *2*, 81.

[9] Wagner, P. J.; Siebert, E. J. *J. Am. Chem. Soc.* **1981**, *103*, 7335.

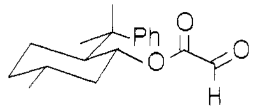
[10] Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1967; Chapter 4.

[11] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin Cummings: Menlo Park, CA, 1978; pp (a) 117, (b) 113, 148.

Table II. Excited-State Lifetimes for 1–4[a]

compd	lifetime(s) in CH_2Cl_2, ns ± 0.5 ns: aerated[b]	lifetime(s) in CH_2Cl_2, ns ± 0.5 ns: deaerated[b]	lifetime(s) in MeTHF, ns ± 0.5 ns: deaerated[b]	lifetime(s) in MeTHF, ns ± 0.5 ns: glass[c]
1	3.1	2.9	4.4	2.1, 6.8
2	1.1, 5.3	0.9, 3.5	0.8, 6.2	1.4, 6.2
3	1.1, 3.4	1.2, 1.9	2.9, 9.0	2.5, 21
4			4.1	2.8, 17

[a] λ_{exc} = 265 nm; substrate concentration = 1×10^{-4} M. [b] 25 °C. [c] 77 K.



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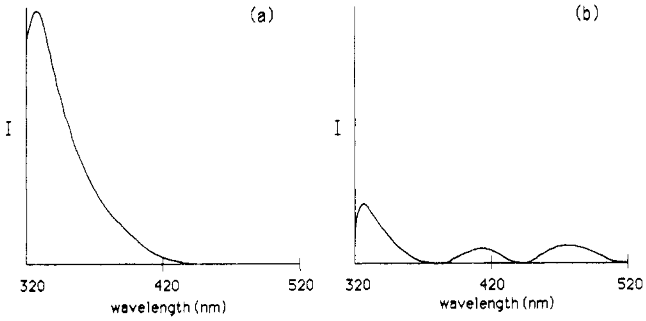


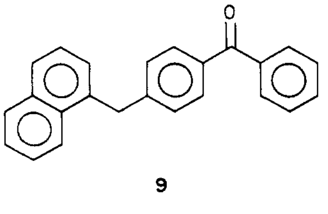
Figure 3. Effect of Lewis acid on the emission spectrum of 1: (a) no $SnCl_4$ added; (b) an equimolar amount of $SnCl_4$ present.

fivefold decrease in the emission intensity from the π,π^* excited state of 1 accompanies the addition of $SnCl_4$ as does the appearance of two new emission bands at 417 and 478 nm (Figure 3). The 417-nm band appears at the same position as that of a $SnCl_4$ complex of 8, while that at the longer wavelength duplicates the spectrum of a charge-transfer complex of this species. In the conformationally unrestricted phenylglyoxylate model 3, the relative intensity of the n,π^* emission grew at the expense of the π,π^* emission upon adding Lewis acid, but no new charge-transfer bands could be seen.

In contrast, addition of $SnCl_4$ to dichloromethane solutions of 4, our phenyl emission model, caused no decrease in the fluorescence yield from the π,π^* state. Neither did any additional long wavelength bands appear.

These results can be understood if Lewis acid complexation enhances electronic interaction of the aromatic donor and the dicarbonyl acceptor. Tin(IV) tetrachloride is known to function as an oxygen complexing agent, increasing the electrophilic character of the α-carbonyl ester and enhancing the relevant interaction. A stronger phenyl–dicarbonyl interaction is evidenced by an increase in the fluorescence efficiency of dicarbonyl chromophore concomitant with a decrease in the emission of the arene. With 1, but not with 3, a stable donor–acceptor complex capable of emission is apparently formed in the presence of Lewis acid.

That such donor–acceptor interactions can be highly efficient is well documented. In 9, for example, intramolecular singlet energy transfer from the naphthyl moiety to the benzophenone portion occurs with 90% efficiency.[12]



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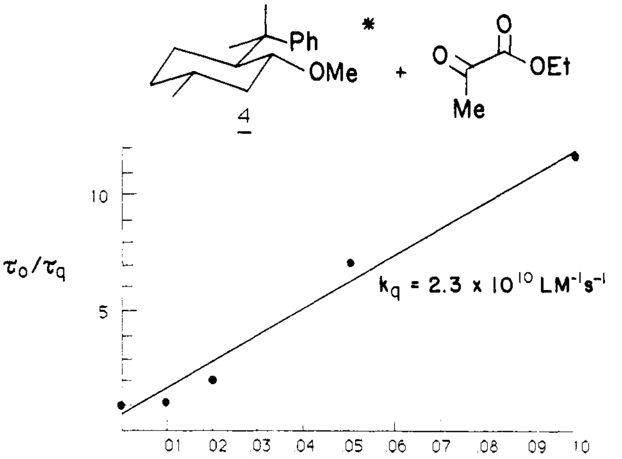

Figure 4. A Stern–Volmer plot for the quenching of fluorescence of ether 4 by ethyl pyruvate (8).

Population of the n,π^* excited state of the dicarbonyl was accomplished by excitation at 340 nm (Table I). Fluorescence emission maxima in the 430–440-nm region are observed in each ester 1–3 and 6–8. The fluorescence spectra of 1 and 2 show tailing of the 8-phenyl emission with a shoulder that was presumed to arise from the α-carbonyl ester moiety. Accurate measurement of the wavelength of maximum intensity for 1 and 2 was not possible. All of the glyoxylate esters show enhanced emission relative to the parent 8. Furthermore, the relative quantum yields do not vary greatly in this series irrespective of the presence or absence of the phenyl substituent. (Compare 1 and 7, for example). This insensitivity implies that the n,π^* excited state is incapable of energy transfer to phenyl, because of either steric or energetic factors, and that it does not participate efficiently in intramolecular electron exchange via a charge-transfer electronic interaction.

Excited-State Lifetimes. The fluorescence at 320 nm of a solution of ether 4 in spectral grade methylene chloride was monitored as quantities of ethyl pyruvate (8) were incrementally added (0–0.1 M). A linear plot of the fluorescence lifetime ratio (t_0/t_q) of 4 against the concentration of 8 was obtained, indicating quenching of the phenyl fluorophore by the α-dicarbonyl moiety (Figure 4). From this plot, a diffusion-controlled quenching rate constant (2.3×10^{10} L M^{-1} s^{-1}) was derived. This highly efficient quenching is consistent with our observation of the contrasting behavior of the relative fluorescence quantum yields in the presence and absence of an intramolecular arene quencher.

The excited-state lifetimes of several of the phenyl-containing compounds were measured at room temperature in methylene chloride and in 2-methyltetrahydrofuran (MeTHF) and in a frozen MeTHF glass at 77 K, to give

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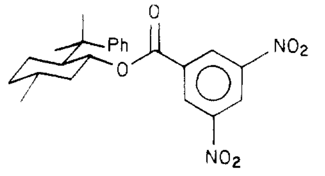
(12) Lamola, A. A.; Leermakers, P. A.; Byris, G. W.; Hammond, G. W. *J. Am. Chem. Soc.* **1965**, *87*, 2322.

the results shown in Table II. For many of these samples, two lifetimes are seen for gas chromatographically pure (>99.9%) substrates. The fluorophores are assumed to be singlets since triplet lifetimes for arenes are usually significantly longer than observed here and should be much more sensitive to the presence of oxygen.

The two emissive species may be the two separate chromophores (in **1**–**3**), emission from the lowest and some higher lying singlet, or emission from two conformations of a single excited state. The observation of two emissions from **4** argues against separate emissive fluorophores for the entire series, since this species lacks bifunctionality. Emission from upper excited states, while not unknown, is rare.[12] The third possibility, conformationally dependent lifetimes, has been observed relatively frequently[13] and may be important here. X-ray crystallographic analysis of functionally analogous compounds has shown that the position of the phenyl, as for example in molecules **10**[14] and **11**,[15] may either be close to or remote from the carbonyl group. However, in fluid solution, the aldehydic proton in **1** is shifted upfield by approximately half of the magnitude of the shift observed in a similar, but rigid, system **12** where the phenyl is held proximate to the α-dicarbonyl moiety.[16] The significantly longer lifetimes observed here for **3** and **4**, but not for **1** and **2**, in frozen MeTHF glasses compared with fluid solution may be indicative of such conformational equilibration.



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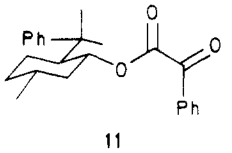

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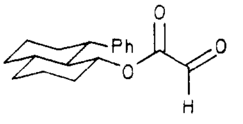

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That bimolecular interaction may be responsible for the biexponential decay can be excluded, for quencher concentrations greater than 0.1 M would be required to compete with the natural decay of these short-lived transients.

Several mechanisms for electronic energy transfer have been documented in fluorescence quenching of photoexcited aromatics by carbonyl compounds including energy transfer by a charge-transfer stabilized exciplex.[11d,17,18] We consider two: intramolecular electron transfer in the spatially proximate donor–acceptor pair and Förster energy transfer between these groups.

The efficiency of excited-state electron transfer for donor–acceptor systems can be estimated from the relative positions of the highest occupied and lowest unoccupied molecular orbitals of the reactants (Figure 5). For example, the free energy for electron transfer from an excited donor to a ground-state acceptor can be calculated from the Weller equation,[19]

$$\Delta G = (23.06\ \text{kcal mol}^{-1}\ \text{V}^{-1}) \times (E(\text{D}^+/\text{D}) - \text{E}(\text{A}/\text{A}^-) - \text{e}^2/ar - E_{0,0})$$

where E(D$^+$/D) is the oxidation potential of the donor, E(A/A$^-$) is the reduction potential of the electron acceptor, e^2/*ar* is a coulombic term determining the energy gained by bringing two opposite charges together, and $E_{0,0}$ is the excited state energy of the donor or acceptor. The coulombic term has a value of 0.06 eV for a large number of donors in acetonitrile.[19]

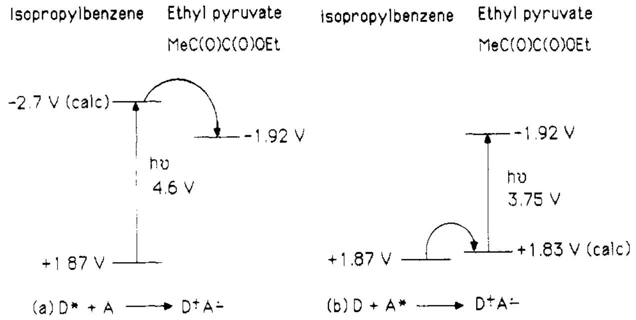

Figure 5. Electron transfer from excited donors or acceptors.

We first consider the electron transfer from excited arene to dicarbonyl. Oxidation and reduction potentials can be estimated from model compounds: E(D/D$^+$) for isopropylbenzene = 1.87 V;[20] E(A/A$^-$) for ethyl pyruvate (**10**) = −1.92 V.[21] The singlet excitation energy can be estimated from the absorption spectrum: $E_{0,0}$ for isopropylbenzene = 4.6 V (268 nm).[22] The free energy for electron transfer from excited isopropylbenzene (and of its modeled congeners here) to ethyl pyruvate (and its modeled substrates) is thus calculated to be −20 kcal mol^{-1}. Such an exothermic exchange can be confidently predicted to occur at rates approaching the diffusion controlled limit.[19]

Similarly, the thermicity of electron transfer from isopropylbenzene to excited ethyl pyruvate can be estimated as the difference between the oxidation potentials of the donor and acceptor, corrected by the same coulombic term, Figure 5. Although the oxidation potential of ethyl pyruvate in neutral solution is not known, it can be estimated by subtraction of its singlet energy (−3.75 V at 330 nm) from its reduction potential. Thus, electron transfer from arene to excited pyruvate should be approximately thermoneutral or in fact endothermic (if the calculations are to be regarded as quantitatively reliable) by about 2.3 kcal mol^{-1}. Without a significant thermodynamic driving force, such electron transfers would be expected to encounter a significant barrier. It is reasonable to expect, therefore, that the operation of a substantial donor–acceptor interaction as the mechanism for fluorescence quenching in **1**–**3** would proceed through specific glyoxylate quenching of the arene fluorescence without concomitant arene quenching of the glyoxylate fluorescence. A comparison of the relative fluorescence quantum yields in Table I indicate that this expectation is certainly met.

Unfortunately, this observation does not unambiguously establish the occurrence of a strong HOMO–LUMO photophysical interaction as the mechanism for intramolecular fluorescence quenching in this series, although our results are consistent with this interpretation. Förster singlet energy transfer would also predict unidirectional quenching by the arene, for its singlet energy (from absorption data)

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(13) Wagner, P. J. *Acc. Chem. Res.* **1983**, *16*, 461.

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(15) James, D. K. Ph.D. Dissertation, University of Texas, 1984.

(16) Chen, H. H. Ph.D. Dissertation, University of Texas, 1984.

(17) Lamola, A. A.; Turro, N. J. "Energy Transfer and Organic Photochemistry"; Interscience; New York, 1969; chapter 3.

(18) Busch, D.; Dahm, L.; Siwiche, B.; Ricci, R. W. *Tetrahedron Lett.* 1977, *18*, 4489.

(19) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

(20) Bard, A. J.; Lund, H. "Encyclopedia of Electrochemistry of the Elements"; Marcel Dekker: New York, 1973; Vol. 11, p 44.

(21) This potential was determined by cyclic voltammetry at a platinum disk electrode in acetonitrile on a Bioanalytical Systems Model 100 electrochemical analyzer.

(22) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

lies approximately 20 kcal/mol higher than the glyoxylate (268 vs. 330 nm).

We can say, however, that the intramolecular quenching observed here does require close approach of the phenyl and glyoxylate functionalities within several nanoseconds of what is probably a vertical absorptive transition. Furthermore, the quenching efficiency is dramatically enhanced by Lewis acids, as would be expected if the operative quenching mechanism involved electron transfer, i.e., a strong donor–acceptor interaction. In fact, the observation of excited-state charge-transfer emission bands for **1** in the presence of Lewis acid requires a substantial HOMO–LUMO interaction in the excited-state geometry of this substrate when complexed with tin tetrachloride.

Experimental Section

Equipment. UV absorption spectra were obtained on a Cary 17 spectrophotometer. Emission spectra were obtained on a Spex Fluorolog fluorimeter Model 1902 with double monochromators for excitation and emission. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at ambient probe temperature on a Varian EM 390 90-MHz spectrometer with chemical shifts reported in parts per million downfield from tetramethylsilane as an internal standard. A Waters chromatograph equipped with a refractive index detector and a μ-Porasil 26859 semipreparative column was used for purification of **4**. Cyclic voltammetry was conducted on a BAS-100 electrochemical analyzer with a Houston Instruments DMP-40 digital plotter. A standard three-compartment cell was used. The solution was 0.1 M in tetra-*n*-butylammonium perchlorate and was deaerated and kept under a positive pressure of N_2 during the run. Silver–silver nitrate (0.1 M in acetonitrile) served as the reference electrode, and a platinum disk and coil were the working and counter electrodes, respectively.

Materials. 2-Methyltetrahydrofuran (Aldrich) was passed through a 30-cm column of alumina (Spectrum, 80–325 mesh), refluxed over $LiAlH_4$, and distilled immediately prior to use. Methylene chloride (Fisher, reagent grade) was purified by stirring over H_2SO_4 followed by $NaHCO_3$. Distillation from P_2O_5 afforded pure solvent. After this purification, no extraneous absorptive or emissive bands could be detected.

Methyl iodide (Spectrum) was distilled prior to use. *n*-Butyllithium in hexane (Aldrich) was standardized by titration with diphenylacetic acid. Hexamethylphosphoramide (HMPA) was obtained from Aldrich and used without further purification.

The preparation of all compounds studied except for **4** will be detailed in a separate manuscript to be published in this journal.

Synthesis of 8-Phenylmenthyl Methyl Ether (4). Phenylmenthol **5** (1 mmol) was stirred with 1 equiv of *n*-butyllithium, 2 mL of THF, and 0.5 mL of HMPA at −78 °C under argon. The solution was warmed to 0 °C, and 3 equiv of methyl iodide was syringed into the reaction mixture. The mixture having been stirred for 15 h, 20 mL of ether was added. The ethereal solution was extracted 3 × 10 mL with water and dried over $MgSO_4$. The methylated product was purified by HPLC (6:1 hexane–EtOAc, 5 mL/min) to give a yellow oil in 70% yield: ^{1}H NMR δ 0.85 (d, 3 H; J = 6 Hz), 1.30 (s, 3 H), 1.40 (s, 3 H), 2.90 (d of t, 1 H, J = 4 Hz, J = 9 Hz), 3.10 (s, 3 H), 7.20 (m, 5 H); ^{13}C NMR δ 150.8, 127.5, 125.8, 124.8, 81.9, 54.5, 52.0, 40.3, 39.9, 34.9, 31.2, 29.5, 27.1, 24.9, 21.9; MS, m/e (M^+) calcd 246.198354, obsd 246.199130.

Determination of Relative Quantum Yields of Fluorescence. The area under the emission curve was determined by multiplying the peak height by the width at half-height. Dividing the curve area by the optical density at the excitation wavelength and correcting for the instrumental sensitivity setting gave the relative quantum yields reported in Table I.

Fluorescence Quenching of 8-Phenylmenthyl Methyl Ether with Ethyl Pyruvate. Dichloromethane solutions (10^{-3} M in ether **4**) were prepared with gradually increasing concentrations (0, 0.01, 0.02, 0.05, 0.1 M) of ethyl pyruvate. Lifetimes were determined by monitoring the emission decay at 320 nm.

Determination of Excited-State Lifetimes. The excitation source for these experiments was a picosecond mode-locked Nd:YAG laser operated at the fourth harmonic (266 nm). Emission intensities were monitored at right angles to the excitation beam blazed at 320 nm. For room-temperature experiments, the sample was contained in a 5-mm cuvette fixed in a holder to ensure reproducible excitation and emission geometry. The runs at 77 K were conducted by suspending a 1-cm cell in a quartz Dewar flask filled with liquid nitrogen. The output waveforms were displayed on a Tektronix 7912 fast digitizer and transferred to a computer for data analysis.[23] The excited-state lifetimes were obtained by fitting the decay curves to single or double exponential functions including a deconvolution routine to minimize the effect of the laser pulse.

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Merostabilization vs. Linnett Stabilization in the Control of Regioselectivity of Pyrrole Formation by (4 + 2) Cyclization

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On the assumption that spin-paired diradical intermediates are formed in the reactions of hydrofluoroborate salts of open-chain analogues of Reissert compounds with alkynes, we present evidence that merostabilization is more effective than Linnett stabilization in controlling the regioselectivity of these (4 + 2) cyclization reactions.

We have recently provided data in support of the concept of merostabilization of biradicaloid intermediates as a factor in determining rates and regioselectivity in (4 + 2) cycloaddition reactions of Reissert hydrofluoroborate salts with alkenes and alkynes.[1] Since, in other 1,3-dipolar addition reactions, Linnett[2] stabilization of spin-paired diradical intermediates also seems to play a major role in determining rates and regioselectivity,[3] we became interested in trying to determine the relative effectiveness of merostabilization and Linnett stabilization in controlling

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