Woelm neutral, 7.5 (10.1); Woelm acidic, 4.5 (9.2); Woelm basic, 9.8 (10.3).

The crystalline structures of the aluminas (in standard alumina, this was predominately the γ form with a small amount of κ and χ aluminas) were determined by X-ray powder photographs using a Phillips camera and nickel-filtered Cu K_α radiation. After heating at 1250 °C, only lines for alumina were present.[4] Surface areas were determined by the multipoint BET method[14] using a Quanta-Sorb instrument with nitrogen as adsorbate. Standard alumina neutral (as well as 800 °C alumina) showed adsorption and desorption isotherms indicating capillary condensation and hysterisis (type IV);[15] this alumina is porous and most of the pore volume is in pores of radius about 23 Å, while most of the pores have radii between 18 and 27 Å. Alumina heated to 1250 °C showed type II behavior with no capillary condensation nor hysterisis; thus heating to 1250 °C has removed the porous texture of the catalyst. As shown by Electrozone Celloscope, the particle size distributions are little changed by heating; the mean particle diameters are 7.9 μm for standard alumina and 7.4 μm for 1250 °C alumina, with 99% of the diameters between 2.8 and 30 μm.

A sample was first evacuated at room temperature (for 48 h) to remove excess water adsorbed on the surface to test for the effect of CO_2 on standard alumina. Dry CO_2 was passed through a portion of the evacuated sample packed in a glass column for 24 h. The control sample was prepared by passing dry nitrogen through another portion of the evacuated sample for 24 h. The procedure was repeated with aluminas pyrolyzed at 800 °C and at 1250 °C. However, with these samples the controls were not treated with dry nitrogen since they were already free of adsorbed water. The activities were determined by stirring 1.6 g of each sample with 60 mL of 0.05 M glucose.

Tests of possible inhibition by pyridine were carried out by stirring 1.6 g of standard alumina with 10 mL of Me_2SO containing either 0.5 or 3.0 mmol of pyridine (or by direct addition of 3 mmol of pyridine to the alumina) before adding a solution of 0.54 g of glucose in 50 mL of Me_2SO. Tests of the effects of *n*-butylamine were carried out with 1.6 g of standard alumina in 10 mL of Me_2SO containing 0.03 mL (3×10^{-4} mol) of *n*-butylamine. After 150 min, 50 mL of Me_2SO containing 0.54 g of glucose was added and the kinetics followed. The overall (homo- and heterogeneous) rate constant at 25 min was 3.8×10^{-4} s^{-1}. Filtered samples from the reaction gave a rate constant for homogeneous catalysis by the *n*-butylamine remaining in solution of 0.28×10^{-4} s^{-1}; therefore, the rate constant for heterogenous catalysis is 3.5×10^{-4} s^{-1}. (Under similar conditions, but in the absence of any additive, 1.6 g of alumina showed a rate constant of 2.5×10^{-4} s^{-1}). From a separate measurement of the second-order rate constant for homogeneous catalysis by *n*-butylamine in Me_2SO, the amount of amine remaining in solution (0.8×10^{-4} mol) could be determined and the amount adsorbed on the alumina (2.2×10^{-4} mol) calculated. This corresponds to 1.4×10^{-4} mol of acid sites per gram of catalyst.

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Registry No. Me_2SO, 67-68-5; α-D-glucose, 26655-34-5; alumina, 1344-28-1.

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Bichromophoric Compounds. Photophysics and Photochemistry of (1-Naphthyl)alkyl Esters of Fumaric, Maleic, and Oxalic Acids

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Fumarate, maleate, and oxalate groups quench the excited singlet state of naphthalene. When the naphthalene chromophore is combined in the same molecule with one of these quenching groups, its fluorescence quantum yield is reduced to about 1% of that of the corresponding (1-naphthyl)alkyl acetate as a result of efficient electron transfer to the diester. No exciplex emission is observed from the bichromophoric compounds. Although the rate of quenching is only weakly dependent on the number of atoms linking the two groups, ground-state charge-transfer interactions between the two groups were observed only in the di-1-naphthyl esters and were absent when the groups were separated by longer chains. (1-Naphthyl)alkyl fumarates and maleates undergo photochemical cis-trans isomerization with quantum yields on the order of 0.04. This photoisomerization was shown to proceed via the electron-transfer pathway and not by direct triplet energy transfer from the naphthalene chromophore to the unsaturated diester. The 1-naphthylmethyl esters yield 1-naphthaldehyde with quantum yields of 0.001. Free-radical chain addition to the fumarate double bond occurs on prolonged irradiation in solvents containing abstractable H, particularly in the presence of acetophenone or radical sources such as *tert*-butyl hydroperoxide. Even in thoroughly degassed benzene oligomerization of the fumarate group leads to partial loss of the double bond at long irradiation times.

Bichromophoric compounds are currently the subject of considerable attention because excited-state interactions between the two functional groups frequently result in unexpected photophysics and photochemistry.[1] A number of processes can lead to perturbation of the excited-state behavior of a chromophore by a functional group separated by a considerable number of σ-bonds. These effects include singlet and triplet electronic energy transfer,[2] exciplex formation,[3] electron transfer,[4] and the formation of

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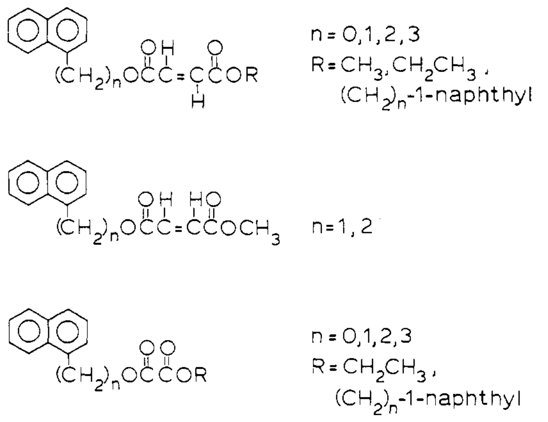
0022-3263/85/1950-0866$01.50/0

Chart I



ground-state charge-transfer complexes.[5]

Quenching of the luminescence of substituted naphthalene derivatives by both electron-rich and electron-deficient compounds is known.[6] Recently McCullough and his co-workers investigated intramolecular exciplex formation and photocycloaddition in compounds containing naphthonitrile and electron-rich olefin groups.[7] While several examples exist of photoreactions between electron-rich naphthalene derivatives and electron-deficient quenchers,[8] there do not seem to be any attempts to investigate intramolecular photoprocesses in the corresponding bichromophoric systems. The comparative lack of interest in this area may arise from an early observation by Schenck and co-workers that no photocycloadducts formed between naphthalene and maleic anhydride.[9]

In the course of a study of the photophysics of new naphthalene-containing polymers,[10] we encountered several examples of remarkably efficient intramolecular quenching of the naphthalene excited singlet by electron-withdrawing substituents. The present publication describes the mechanism and the chemical consequences of intra- and intermolecular quenching of the naphthalene chromophore by fumarate, maleate, and oxalate esters. Chart I shows the different compounds synthesized and used to investigate the structural requirements of the intramolecular electron-transfer process. Ground-state charge-transfer complexation of maleic anhydride with benzene and naphthalene derivatives is known,[11] and the formation of emitting exciplexes between phenanthrene and dimethyl fumarate has also been investigated.[12] In this context the intramolecular quenching of naphthalene by butenedioate esters is intriguing because this system is on the border line between interactions only in the excited state and interactions in both ground and excited states.

Experimental Section

General. Melting points were recorded on a Fisher Mel-Temp apparatus and are corrected. Infrared spectra were recorded on Beckman Acculab 10 or Perkin-Elmer 457 instruments. UV absorption spectra were measured with a Cary 118 spectrometer. Fourier transform ^{1}H NMR spectra were recorded using a Bruker WP-80 instrument with Me$_4$Si as internal reference. All gas chromatographic analyses were carried out on a Hewlett-Packard Model 5840 A instrument using a 6 ft × $^1/_8$ in. column packed with 5% OV-275 on Chromosorb W, N$_2$ carrier gas at 30 mL/min, and flame ionization detection. Elemental Analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario.

Materials. 1-Naphthaldehyde (Aldrich) was purified by high-vacuum distillation and was converted to 1-naphthylmethanol by reduction with NaBH$_4$ in refluxing ethanol.[13] The alcohol was purified by recrystallization from 1:1 benzene–cyclohexane. 1-Naphthylacetic acid (Aldrich) was reduced to 2-(1-naphthyl)ethanol with LiAlH$_4$ in refluxing ether.[14] 3-(1-Naphthyl)-1-propanol was prepared from 1-(bromomethyl)naphthalene via a malonic ester synthesis, followed by hydrolysis, decarboxylation, and a reduction with LiAlH$_4$, as described for the 2-naphthyl derivative in ref 14.

Fumaroyl dichloride was prepared from the acid and PCl$_5$ in CH$_2$Cl$_2$ and was distilled at reduced pressure. Methyl fumaroyl chloride and ethyl fumaroyl chloride were prepared by a literature method.[15] Ethyl oxalyl chloride and oxalyl dichloride were obtained from Aldrich. Dimethyl fumarate and dimethyl oxalate were purified from vacuum sublimation. Dimethyl maleate (Eastman) was fractionated at reduced pressure and contained 2.0% dimethyl fumarate by gas chromatography. Naphthalene and 1-naphthol were purified by high-vacuum sublimation.

For photochemical work benzene (J.T. Baker Photrex grade) and cyclohexane (Baker spectrograde) were used as received. Purification of benzene by distillation from P$_4$O$_{10}$ had no effect on the photochemistry. Tetrahydrofuran and 2-methyltetrahydrofuran were distilled from LiAlH$_4$ under dry nitrogen.

Bis[3-(1-naphthyl)propyl] Fumarate. A solution of 0.62 g of fumaroyl chloride in 5 mL of dry CH$_2$Cl$_2$ was added all at once to a stirred solution of 1.50 g of 3-(1-naphthyl)propanol in 10 mL of CH$_2$Cl$_2$. Stirring was continued while a solution of 1.05 g of *N,N*-dimethylaniline in 15 mL of CH$_2$Cl$_2$ was added over 30 min. This order of addition of reagents minimizes the formation of colored impurities. After overnight stirring at room temperature the total volume of solution was increased to 75 mL with CH$_2$Cl$_2$, and the solution was extracted with 1 M HCl, 2% NaHCO$_3$, and water and was dried over Na$_2$SO$_4$. Following evaporation of the solvent the product was dissolved in 25 mL of hot benzene and the solution was decolorized with activated charcoal. Large crystals formed when the filtered solution was mixed with 50 mL of absolute ethanol and allowed to evaporate slowly at room temperature. The yield of colorless crystals, mp 102–103 °C, was 1.19 g (65%): IR (Nujol) 1720, 1590, 1510 cm^{-1}; NMR (CDCl$_3$) δ 2.16 (m, 4 H), 3.20 (t, 4 H), 4.30 (t, 4 H), 6.87 (s, 2 H), 7.24–8.10 (complex m, 14 H); UV (THF) λ_{max} 319 nm (shoulder, ϵ 331 M^{-1} cm^{-1}), 314.5 (762), 308 (shoulder, 930), 296 (10800), 291 (shoulder, 11400), 284 (16900), 274 (15400), 266 (11200). Anal. Calcd for C$_{30}$H$_{28}$O$_4$: C, 79.62; H, 6.24. Found: C, 79.58; H, 6.25. Other symmetric diesters were prepared in the same way. The compounds bis(1-naphthylmethyl) oxalate and bis(1-naphthylmethyl) fumarate were available from previous work.[10]

Bis[2-(1-naphthyl)ethyl] fumarate: melting point 130.5–131.5 °C (recrystallized from ethanol); IR (Nujol) 1710, 1590,

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1510 cm^{-1}; NMR ($CDCl_3$) δ 3.44 (t, 4 H), 4.52 (t, 4 H), 6.73 (s, 2 H), 7.3–8.2 (m, 14 H); UV (THF) λ_{max} 319 nm (shoulder, ϵ 362 M^{-1} cm^{-1}), 315 (877), 308 (shoulder, 1050), 295 (10 700), 290.5 (10 800), 284 (16 000), 273.5 (13 700), 265 (shoulder, 9550). Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.23; H, 5.70. Found: C, 80.02; H, 5.06.

Bis[2-(1-naphthyl)ethyl] oxalate: melting point 113.5–114.5 °C (recrystallized from ethanol); IR (Nujol) 1750, 1590, 1510 cm^{-1}; NMR ($CDCl_3$) δ 3.51 (t, 4 H), 4.60 (t, 4 H), 7.3–8.2 (m, 14 H); UV (THF) λ_{max} 319 nm (shoulder, ϵ 292 M^{-1} cm^{-1}); 315 (785), 309 (shoulder, 894), 305 (shoulder, 2190), 294.5 (11600), 283.5 (17200), 273.5 (14500), 265 (shoulder, 9650). Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.56. Found: C, 78.94; H, 5.13.

Bis[3-(1-naphthyl)propyl] oxalate: melting point 116–117 °C (recrystallized by evaporation of a solution in 1:1 benzene–methanol); IR (Nujol) 1740, 1590, 1510 cm^{-1}; NMR ($CDCl_3$) δ 2.15 (m, 4 H), 3.22 (t, 4 H), 4.38 (t, 4 H), 7.24–8.08 (m, 14 H); UV (THF) λ_{max} 319.5 nm (shoulder, ϵ 316 M^{-1} cm^{-1}), 315.5 (761), 309 (shoulder, 870), 305 (shoulder, 1600), 296 (9460), 291 (9620), 284 (14 300), 274 (12 000). Anal. Calcd for $C_{28}H_{26}O_4$: C, 78.85; H, 6.14. Found: C, 78.80; H, 6.18.

Di-1-naphthyl fumarate: melting point 178.5–179.5 °C (four recrystallizations from benzene); IR (Nujol) 1715 cm^{-1}; NMR ($CDCl_3$) δ 7.52 (s, 2 H), 7.24–8.00 (m, 14 H); UV (THF) structureless absorption from 400 to 320 nm (ϵ 1100 M^{-1} cm^{-1} at 350 nm), 289 nm (11 000), 281.5 (13 000), 272 (11 800), 262.5 (shoulder, 8900). Anal. Calcd for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38. Found: C, 78.30; H, 4.42.

Di-1-naphthyl oxalate: melting point 165–166.5 °C (three recrystallizations from benzene); IR (Nujol) 1770 cm^{-1}; NMR ($CDCl_3$) δ 7.4–8.2 (complex m); UV (THF) structureless absorption from 380 to 320 nm (ϵ 163 M^{-1} cm^{-1} at 350 nm), 292 nm (11 000), 289 (11 300), 282 (12 500), 273 (11 400), 263 (shoulder, 7320). Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.35; H, 4.11.

Methyl 1-Naphthylmethyl Fumarate. To a stirred room-temperature solution of 6.0 g of 1-naphthylmethanol and 3.1 g of pyridine in 50 mL of dry benzene was added 5.95 g of methyl fumaroyl chloride over 1 h. After 2 days of stirring at room temperature the solution was washed with 1 M HCl, 5% $NaHCO_3$, and saturated NaCl solution and was dried over Na_2SO_4. Following evaporation of the solvent the product was purified by short-path distillation under high vacuum. The solid product (5.65 g, 55% yield) was purified further for fluorescence measurements by two recrystallizations from hot cyclohexane and had melting point 76–77 °C: IR (Nujol) 1720, 1590, 1510 cm^{-1}; NMR ($CDCl_3$) δ 3.77 (s, 3 H), 5.70 (s, 2 H), 6.89 (s, 2 H), 7.2–8.1 (m, 7 H); UV (THF) λ_{max} 318 nm (ϵ 258 M^{-1} cm^{-1}), 314 (459), 308 (shoulder, 570), 294 (5310), 289 (shoulder, 5340), 283 (7890), 273 (6780), 264 (shoulder, 4720). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.17; H, 5.29. Other unsymmetrical fumarates and oxalates were prepared similarly. For fluorescence work liquid fumarate esters were chromatographed on neutral alumina, eluting with benzene containing 1% THF. The unsymmetrical oxalates decomposed on attempted purification by column chromatography; so they were distilled under high vacuum through a short insulated column.

Methyl 2-(1-naphthyl)ethyl fumarate: melting point 60–61 °C; IR (melt) 1720, 1590 cm^{-1}; NMR ($CDCl_3$) δ 3.46 (t, 2 H), 3.80 (s, 3 H), 4.55 (t, 2 H), 6.84 (s, 2 H), 7.25–8.15 (m, 7 H); UV (THF) λ_{max} 319 nm (shoulder, ϵ 182 M^{-1} cm^{-1}) 315 (451), 309 (shoulder, 533), 295.2 (5240), 291 (5285), 284 (7850), 274 (6710), 265 (shoulder, 4630). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.50; H, 5.54.

Ethyl 1-naphthylmethyl fumarate: oil, $n^{20}{}_D$ 1.5775; IR (neat) 1720, 1600 cm^{-1}; NMR ($CDCl_3$) δ. 1.25 (t, 3 H), 4.22 (quartet, 2 H), 5.69 (s, 2 H), 6.88 (s, 2 H), 7.2–8.2 (m, 7 H); UV (THF) λ_{max} 318 nm (ϵ 270 M^{-1} cm^{-1}), 314 (475), 308 (shoulder, 610), 305 (shoulder, 950), 294 (5350), 290 (shoulder, 5430), 283 (7910), 273 (6830), 264 (shoulder, 4750). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.82; H, 5.67. Found: C, 72.23; H, 5.86.

Ethyl 1-naphthylmethyl oxalate: needles from cyclohexane, mp 43.5–44.5 °C; IR (Nujol) 1740, 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (t, 3 H), 4.16 (quartet, 2 H), 5.63 (s, 2 H), 7.2–8.1 (m, 7 H); UV (cyclohexane) λ_{max} 318.5 nm (ϵ 160 M^{-1} cm^{-1}), 314.5 (283), 294 (4170), 290 (shoulder, 4220), 283 (6440), 272.5 (5540), 264 (shoulder, 4330). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.76; H, 5.46. Found: C, 69.75; H, 5.45.

Ethyl 2-(1-naphthyl)ethyl oxalate: oil, $n^{20}{}_D$ 1.5658; IR (neat) 1760, 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.28 (t, 3 H), 3.52 (t, 2 H), 4.39 (quartet, 2 H), 4.65 (t, 2 H), 7.2–8.1 (m, 7 H); UV (THF) λ_{max} 320 nm (shoulder ϵ, 135 M^{-1} cm^{-1}), 316 (364), 309 (shoulder, 413), 305 (shoulder, 810), 295 (5090), 291 (5060), 284 (7600), 274 (6360), 265 (shoulder, 4210). Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.83; H, 5.85.

(1-Naphthylmethyl)maleic Acid.[16] A mixture of 10.0 g of 1-naphthylmethanol and 6.25 g of maleic anhydride was melted on a water bath and stirred at 70 °C for 5 h. Recrystallization of the cooled product from 75 mL of hot benzene gave 9.6 g (59%) of well-formed crystals, mp 91.5–95 °C. Cooling the benzene filtrate yielded additional product: IR (Nujol) 3000 (br), 1715, 1685, 1630, 1590, 1510 cm^{-1}; NMR (C_6D_6) δ 5.28 (s, 2 H), 5.41 (d, 1 H), 5.71 (d, 1 H), 7.0–7.9 (m, 7 H), 8.4 (br s, 1 H). In a similar manner [2-(1-naphthyl)ethyl]maleic acid, mp 97.5–99 °C, was obtained.

Methyl 1-Naphthylmethyl Maleate. The above acid (3.0 g) was treated with excess diazomethane in ether at 0 °C. Following removal of the solvent the product was chromatographed on neutral alumina, eluting with benzene (100 mL) followed by benzene containing 2% THF. The compound was eluted in the mixed fractions and was freed of all traces of solvent by storage under high vacuum. The yield of a colourless oil, $n^{20}{}_D$ 1.5846, was 1.3 g (31%): IR (neat) 1720, 1590, 1505 cm^{-1}; NMR ($CDCl_3$) δ 3.58 (s, 3 H), 5.68 (s, 2 H), 6.25 (s, 2 H), 7.25–8.15 (m, 7 H); UV (THF) λ_{max} 318 nm (ϵ 187 M^{-1} cm^{-1}), 314.5 (360), 308 (shoulder, 435), 294 (4950), 289.5 (4920), 283 (7320), 273 (6130), 264.5 (shoulder, 4020). Anal. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 70.10; H, 5.03.

Methyl 2-(1-naphthyl)ethyl maleate: oil, $n^{20}{}_D$ 1.5765; IR (neat) 1720, 1640, 1590, 1510 cm^{-1}; NMR ($CDCl_3$) δ 3.47 (t, 2 H), 3.75 (s, 3 H), 4.54 (t, 2 H), 6.24 (s, 2 H), 7.3–8.2 (m, 7 H); UV (THF) λ_{max} 319.5 nm (shoulder, ϵ 141 M^{-1} cm^{-1}), 315.5 (370), 309.5 (shoulder, 407), 305 (shoulder, 770), 296 (4990), 291 (5000), 284 (7570), 274 (6570), 265 (4790). Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.97. Found: C, 71.90; H, 5.65.

1-Naphthylmethyl Acetate. Treatment of 1-naphthylmethanol with excess of acetic anhydride in pyridine gave the crude product, which was purified by high-vacuum distillation. A colorless oil, $n^{20}{}_D$ 1.5912, was obtained having satisfactory NMR and IR spectra. UV (THF) λ_{max} 319 nm (ϵ 171 M^{-1} cm^{-1}), 315 (340), 308.5 (shoulder, 407), 304.5 (shoulder, 910), 294 (5150), 289.5 (5130), 282.5 (7570), 272.5 (6470), 264 (shoulder, 4320). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.29; H, 5.84. Similar procedures yielded the following compounds: 2-(1-naphthyl)ethyl acetate [mp 50–51 °C; UV (THF) λ_{max} 319 nm (shoulder, ϵ 141 M^{-1} cm^{-1}), 315 (373), 309 (shoulder, 411), 305 (shoulder, 760), 295 (4970), 291 (4970), 284 (7480), 273.5 (6250), 265 (shoulder, 4040). Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 79.04; H. 6.51] and 3-(1-naphthyl)propyl acetate [$n^{20}{}_D$ 1.5753; UV (THF) λ_{max} 319 nm (ϵ 167 M^{-1} cm^{-1}), 315 (398), 309 (shoulder, 446), 305 (shoulder, 930), 296 (4990), 291 (5050), 285 (7380), 274.5 (6270), 266 (shoulder, 4100). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.01; H, 7.50].

Photochemical Studies. Dilute solutions of compounds in deoxygenated or degassed benzene were irradiated through Pyrex in a Rayonet RPR-100 photochemical reactor with light from 16 3000-Å lamps. The reaction temperature was 35 °C.

Preparative Irradiations. In a typical experiment a solution of 1.5 g methyl 1-naphthylmethyl fumarate in 20 mL of benzene was degassed by four freeze–pump–thaw cycles and sealed under high vacuum in a heavy-walled Pyrex tube. The solution was then irradiated at 300 nm for 24 h, during which time it turned pale yellow. An NMR of the crude product mixture in $CDCl_3$ shows conversion of the starting ester to a 65/35 mixture of cis and trans isomers. There is a trace of 1-naphthaldehyde, identified by comparison with the NMR of an authentic sample (CHO singlet at δ 10.3, one aromatic ring H doublet shifted to δ 9.2). A considerable shortage of olefinic signals corresponds to approximately 30% conversion to oligomeric products. Following removal of the solvent the product mixture was chromatographed on neutral alumina, eluting first with benzene, then with benzene containing

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[16] Kasper, F.; Trefflich, F. *Z. Chem.* 1975, *15*, 185–186.

increasing amounts of THF, and finally with CH_2Cl_2 containing 5% anhydrous ethanol. Fractions were analyzed by TLC and IR and NMR spectroscopy. The first compound to emerge was 1-naphthaldehyde, identified by comparison of its spectra with those of an authentic sample. An oily mixture of staring material and methyl 1-naphthylmethyl maleate emerged in the mixed benzene–THF fractions. Finally the dichloromethane–ethanol solvent system eluted a mixture of oligomers (broad signals at δ 2.9–4.4 and 5.2–5.5) and 1-naphthylmethanol (singlets at δ 2.12 and 5.09, IR OH band at 3350 cm^{-1}). The alcohol is formed by ester interchange on the column and is not one of the photolysis products. The oligomers show the retention of the naphthalene ring system, the loss of the δ 6.2 and 6.9 singlets of the cis and trans butenedioate ester groups, and a complete absence of other olefinic signals.

Quantum Yield Measurements. (a) Analysis by Gas Chromatography. For the determination of quantum yields of cis–trans photoisomerization, solutions of 0.01 g of a naphthalene compound in 1.00 mL of benzene were deoxygenated with a pair of syringe needles and irradiated in Pyrex NMR tubes in a Rayonet merry-go-round assembly in the photoreactor. The solutions were concentrated on a rotary evaporator, dissolved in 0.1 mL of acetone and analyzed by GC (column temperature 210–220 °C). In studies of the intermolecularly sensitized photoisomerization of dimethyl maleate and dimethyl fumarate, solutions of 0.006 g of 1-methylnaphthalene and 0.01 g of diester in 1 mL of benzene were irradiated as above. The solutions were concentrated by evaporation, taken up in acetone, and analyzed with a column temperature of 100 °C programmed to rise to 190 °C at 15 °C/min after 6 min. In both sets of experiments the relative responses of the detector to the cis and trans isomers were determined by analyzing mixtures of known composition under the same conditions. The estimated accuracy of the GC method of analysis is ±15% at 4% conversion.

(b) Analysis by NMR. For the determination of quantum yields of cis–trans photoisomerization and 1-naphthaldehyde formation, solutions of 0.01 g of a naphthalene compound in 1.00 mL of benzene-d_6 were deoxygenated and irradiated in Pyrex NMR tubes. The extent of cis–trans isomerization was determined from the relative strengths of the olefinic signals at δ 5.6 (cis) and 6.9 (trans) in the ^1H NMR spectrum of the irradiated solution. The yield of 1-naphthaldehyde was determined from the intensity of the signal from the aldehyde proton at δ 10.21. In order to maximize the precision of the NMR method of analysis, solutions were irradiated to 10–15% conversion and correction for reverse photoisomerization was subsequently made using the cis/trans composition of the photostationary state. Since the accuracy of quantum yield measurements by this method was about ±30% method (a) was used where the thermal stability of the maleates was sufficient to prevent decomposition on the GC column.

Actinometry. The use of 2-undecanone as an actinometer at 300 nm[17] was convenient because the long-wavelength absorption of the neat ketone is very similar to that of a dilute solution of naphthylalkyl ester, as shown in Figure 1. Solution concentrations were adjusted to give an optical density of about 3 at 300 nm and quantum yields were adjusted for the small systematic error caused by differences in the absorption above 320 nm. 2-Undecanone (Aldrich) was purified by vacuum distillation from P_4O_{10} and was of 99% purity by gas chromatography. One milliliter aliquots of the ketone in NMR tubes were deoxygenated and irradiated simultaneously with the naphthalene compounds. Irradiated samples were analyzed by GC (50 °C column temperature programmed to rise to 140 °C at 10 °C/min). The concentration of 1-octene in the sample was determined by the standard addition method. The incident light intensity was calculated using a value of 0.20 for the quantum yield of 1-octene formation by the Norrish Type II reaction.[17] Typical measured light intensities were 2×10^{-7} einstein mL^{-1} s^{-1} with a reproducibility of ±2%.

Steady-State Fluorescence Measurements. Fluorescence spectra were recorded on two instruments, a Hitachi–Perkin-Elmer MPF-2A and an SLM spectrofluorimeter. With the SLM instrument (500 W Xe arc excitation) problems were encountered with the buildup of intensely emitting photoproducts in the irradiated volume of the solution. This increase in emission intensity occurred in as little as 30 s and distorted the spectra by increasing the intensity of the long-wavelength emission in scans from low to high wavelength. Using a narrow excitation bandwidth of 2 nm on the Perkin-Elmer instrument (150 W arc source), no such difficulties were encountered. For quantum yield measurements THF solutions of naphthalene compounds were prepared having optical densities of 0.2 in a 1-cm cell. The total emission intensities on 280-nm excitation were compared with that of 1-naphthol in deoxygenated cyclohexane, which has a quantum yield of 0.21.[18] Considerable care was needed to prevent contamination of the weakly emitting bichromophoric compounds by more intensely emitting impurities such as the (1-naphthyl)alkyl acetate or 1-naphthol. Spectra of 0.001 M samples in 77 K 2-MeTHF glasses were recorded using the low-temperature accessories of the MPF-2A, as described in a previous publication.[10]

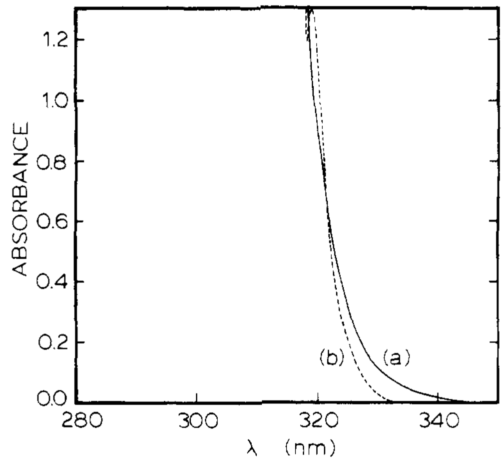

Figure 1. UV absorption spectra of (a) neat 2-undecanone and (b) bis(1-naphthylmethyl) oxalate (2.78×10^{-2} M in benzene), 1-mm path length.

Stern–Volmer Quenching Studies. A 1 cm square fluorescence cuvette with a 6 cm stem (Hellma) was used for all measurements. THF solutions containing 5×10^{-3} M naphthalene compound were deoxygenated using a pair of syringe needles. Samples were excited at 310 nm to avoid screening by added quencher. The quencher was injected through the septum as a 0.2–2.0 M solution in THF, taking care to avoid the presence of air bubbles in the syringe. Concentrations of quencher solution were adjusted so that the maximum amounts added caused no more than a 1% dilution. Agreement of Stern–Volmer quenching constants determined by this very rapid method with those obtained by the much slower procedure of making up a large number of solutions and deoxygenating each one separately was very good, with the rapid procedure giving much higher precision.

Fluorescence Lifetime Measurements. Fluorescence decays were measured using a Photochemical Research Associates System 2000 fluorescence lifetime instrument. Details of the instrument and the general techniques have appeared in previous publications.[10,19,20] Samples were excited at 280 nm through a monochromator and emission was detected at 340 nm either with a second monochromator or an interference filter. In the case of weakly emitting samples a Schott KG-3 filter (300–900-nm band-pass) was used to give adequate counting rates. Decay times were computed on an IBM-PCXT by the technique of iterative reconvolution with minimization of the reduced sum of squares of the residuals.[21] In several cases a sum of two exponentials was used as the trial function. The decrease of the preexponential factor of one of the terms to a negligible value during iteration

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Table I. Fluorescence Quantum Yields of (1-Naphthyl)alkyl Acetates $ROCOCH_3$ in Deoxygenated THF at 28 °C

R	ϕ_f
1-naphthylmethyl	0.123
2-(1-naphthyl)ethyl	0.166
3-(1-naphthyl)propyl	0.183

Table II. Fluorescence Quantum Yields ϕ_f and Quantum Yields of Photoreaction ϕ of (1-Naphthyl)alkyl Esters of Fumaric Acid (*trans*-$R_1OCOCH{=}CHCOOR_2$), Maleic Acid (*cis*-$R_1OCOCH{=}CHCOOR_2$), and Oxalic Acid ($R_1OCOCOOR_2$)

R_1	R_2	ϕ_f[a] × 10^3	ϕ
fumarates			(trans → cis)
1-$C_{10}H_7$	1-$C_{10}H_7$	0.3	nd[b]
1-$C_{10}H_7CH_2$	Me	1.5	0.029[c]
1-$C_{10}H_7CH_2$	Et	0.9	0.039[d]
1-$C_{10}H_7CH_2$	1-$C_{10}H_7CH_2$	0.4	0.033[d]
1-$C_{10}H_7(CH_2)_2$	Me	0.9	0.049[c]
1-$C_{10}H_7(CH_2)_2$	1-$C_{10}H_7(CH_2)_2$	0.5	0.044[d]
1-$C_{10}H_7(CH_2)_3$	1-$C_{10}H_7(CH_2)_3$	0.5	0.067[d]
maleates			(cis → trans)
1-$C_{10}H_7CH_2$	H	0.5	0.042[d]
1-$C_{10}H_7CH_2$	Me	0.8	0.051[c]
1-$C_{10}H_7(CH_2)_2$	Me	0.9	0.058[c]
oxalates			(aldehyde)
1-$C_{10}H_7$	1-$C_{10}H_7$	1.7	nd
1-$C_{10}H_7CH_2$	Et	0.7	0.0008[d]
1-$C_{10}H_7CH_2$	1-$C_{10}H_7CH_2$	0.6	0.0011[d]
1-$C_{10}H_7(CH_2)_2$	Et	1.7	nd
1-$C_{10}H_7(CH_2)_2$	1-$C_{10}H_7(CH_2)_2$	1.0	nd
1-$C_{10}H_7(CH_2)_3$	1-$C_{10}H_7(CH_2)_3$	2.8	nd

[a] In THF at 28 °C. [b] None detected. [c] In benzene at 35 °C; GC analysis; ±15%. [d] In benzene-d_6 at 35 °C; NMR analysis; ±30%.

constituted evidence that the experimental decay was actually single exponential.

Results and Discussion

Intramolecular Fluorescence Quenching. In compounds containing the naphthalene chromophore and a fumarate, maleate, or oxalate ester group the naphthalene fluorescence is only 1% as intense as in the corresponding naphthylalkyl acetate. No new bands are observed in the very weak fluorescence spectra of the bichromophoric compounds in room-temperature solution which could be attributed to exciplex emission. Tables I and II compare the fluorescence quantum yields of the acetates with those of the bifunctional compounds. Several features are apparent. Quenching by all three functional groups is of comparable efficiency. The fluorescence quantum yields are nearly the same in compounds containing one or two naphthalene chromophores, so that the involvement of the naphthalene excimer can be ruled out. Furthermore, the efficiency of the intramolecular quenching process is insensitive to the length of the chain linking the two groups. The absence of a marked chain-length dependence is in contrast to the well-defined geometrical requirements for excimer and exciplex formation which give rise to the "$n = 3$" rule observed for phenyl-[22] and many naphthalene-containing systems,[7,23] where excited-state complexes are most easily achieved when the chromophores are linked by a flexible three-atom chain.

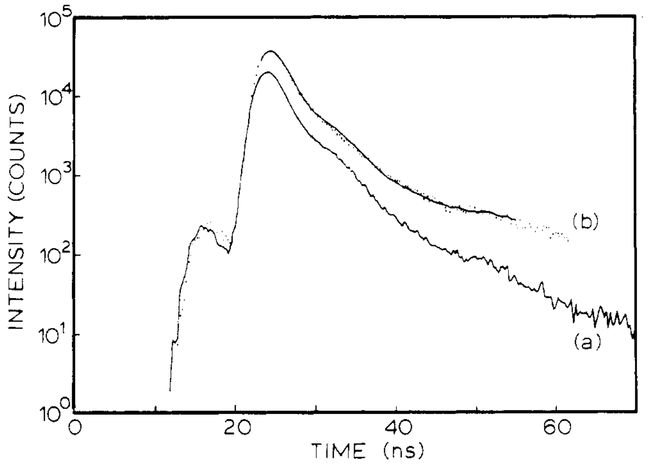

Figure 2. Fluorescence decay of ethyl 1-naphthylmethyl oxalate in nitrogenated THF at 25 °C. (a) Excitation pulse profile, (b) decay at 330–370 nm. The solid line is the convolution of a single-exponential fitting function ($\tau = 0.45$ ns) with the excitation profile.

Table III. Fluorescence Lifetimes of Some Naphthalene-Containing Compounds in Nitrogenated THF at 25 °C.

compd	τ, ns
naphthalene	64.8
1-naphthylmethyl acetate	41.7
2-(1-naphthyl)ethyl acetate	59.5
3-(1-naphthyl)propyl acetate	64.0
ethyl 1-naphthylmethyl oxalate	0.45
ethyl 2-(1-naphthyl)ethyl oxalate	0.64
bis[3-(1-naphthyl)propyl] oxalate	1.27
methyl 2-(1-naphthyl)ethyl fumarate	0.59
bis[2-(1-naphthyl)ethyl] fumarate	0.51
bis[3-(1-naphthyl)propyl] fumarate	1.21

Since the fluorescence quantum yields of the bichromophoric compounds are low, the emission spectra are particularly sensitive to the presence of more intensely emitting impurities, including photoproducts and unesterified alcohols. The question arises whether the residual fluorescence itself comes from impurities. This is unlikely to be the case, since the fluorescence quantum yields listed in Table II are of the same magnitude for a variety of compounds prepared and purified by several methods. Furthermore, the fluorescence decays of the freshly purified compounds are exponential, as illustrated in Figure 2, with very short lifetimes (Table III) consistent within experimental error with their steady-state fluorescence quantum yields:

$$\tau/\tau_{\text{acetate}} = \phi/\phi_{\text{acetate}} \tag{1}$$

After prolonged storage the samples show an additional, much weaker fluorescence decay component with a considerably longer decay time. This is attributed to the formation of traces of ω-(1-naphthyl)alkanols by hydrolysis and not to a feedback step such as dissociation of a long-lived exciplex.

The absence of exciplex emission in these bichromophoric compounds simplifies kinetic analysis. If k_1 is the unimolecular rate constant for fluorescence quenching, then k_1 is readily obtained from steady-state data by using

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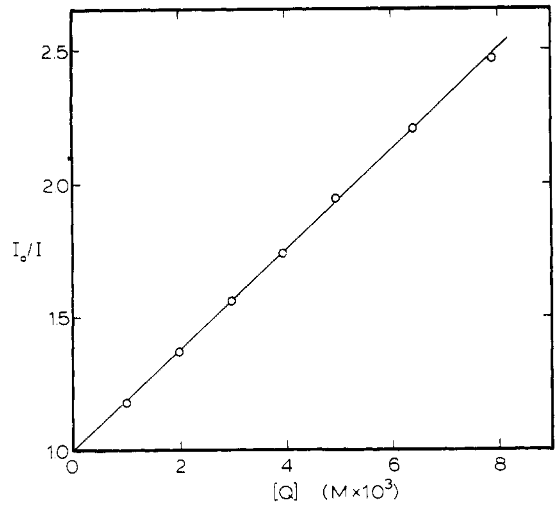

Figure 3. Stern–Volmer plot of the quenching of naphthalene fluorescence by dimethyl oxalate in deoxygenated THF.

Table IV. Rate Constants for Quenching of Fluorescence of Naphthalene Compounds in Nitrogenated THF at 28 °C

	k_Q (M^{-1} s^{-1} × 10^{-9}) for the following quenchers:		
fluorophore	dimethyl oxalate	dimethyl maleate	dimethyl fumarate
naphthalene	2.9	8.2	23
1-naphthylmethyl acetate	4.2	7.2	19
3-(1-naphthyl)propyl acetate	5.8	8.0	17

eq 2. The values of ϕ_f listed in Table II correspond to values of k_1 of (1–7) × 10^9 s^{-1}.

$$\phi_{\text{acetate}}/\phi = 1 + k_1\tau_{\text{acetate}} \qquad (2)$$

Comparison with Intermolecular Quenching. Intermolecular quenching of the fluorescence of naphthalene-containing compounds by dimethyl fumarate, maleate, and oxalate obeys the Stern–Volmer equation:

$$I_0/I = 1 + k_Q\tau_0[Q] \qquad (3)$$

No exciplex emission is observed, even in nonpolar solvents such as cyclohexane. Figure 3 illustrates typical quenching behavior. By combination of quenching constants $k_Q\tau_0$ with fluorescence lifetimes obtained in the absence of quencher (Table III), rate constants k_Q for bimolecular quenching were calculated and are listed in Table IV. These range from an order of magnitude less than diffusion controlled for quenching by dimethyl oxalate to completely diffusion controlled in the case of quenching by dimethyl fumarate. Table V lists quenching rate constants calculated from the Weller equation[24] for electron-transfer quenching using literature values for the oxidation potentials of related naphthalene compounds and the reduction potentials of the three esters in aprotic solvents.[25] Experimental and calculated quenching rate constants agree within a factor of 2 and respond in the same way to changes in donor oxidation and acceptor reduction potentials. These model-compound studies therefore establish that the quenching of the naphthalene singlet occurs by partial electron transfer to the diester acceptor.

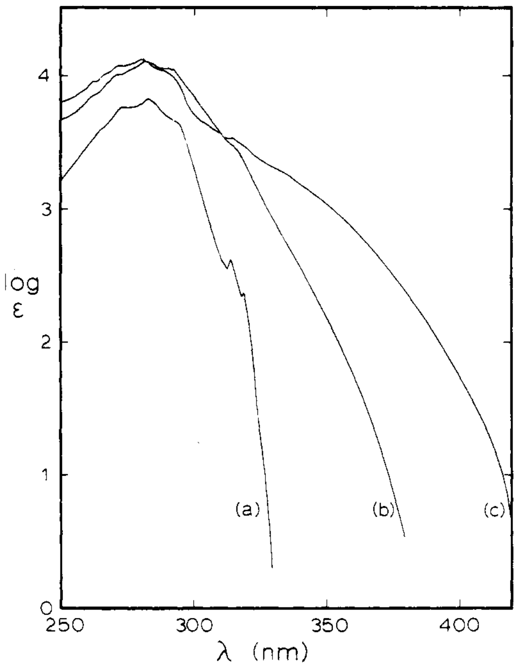

Figure 4. UV absorption spectra of (a) 1-naphthyl pivalate, (b) di-1-naphthyl oxalate, and (c) di-1-naphthyl fumarate in THF.

Table V. Rate Constants for Electron Transfer in THF Calculated from the Weller Equation[a]

donor	E_{D/D^+},[b] V vs. SCE	acceptor	$E_{A^-/A}$,[c] V vs. SCE	k_Q, M^{-1} s^{-1} × 10^{-9}
naphthalene	1.54[d]	dimethyl fumarate	−1.51[e]	14.5
naphthalene		dimethyl maleate	−1.87[e]	13.5
naphthalene		diethyl oxalate	−2.54[f]	1.5
1-methylnaphthalene	1.43[d]	dimethyl fumarate		14.6
1-methylnaphthalene		dimethyl maleate		13.8
1-methylnaphthalene		diethyl oxalate		3.7

[a] Assumed ion-pair separation of 0.4 nm. [b] Donor oxidation potential in CH_3CN. [c] Acceptor reduction potential in CH_3CN. [d] Reference 25a. [e] Reference 25b. [f] Reference 25c.

Tests for Ground-State Interaction. The differences in quenching efficiencies between the three esters observed in the intermolecular case are much less marked in the intramolecular case. One explanation is that strong ground-state interactions in the bichromophoric 1-naphthylalkyl compounds cause them to adopt conformations that place the naphthalene and ester groups close together. Several experiments served to rule out this possibility. Careful UV measurements showed that the long-wavelength absorption spectra of the 1-naphthylalkyl diesters were the same within experimental error as those of the corresponding acetates. Furthermore, the absorption spectrum of naphthalene in THF containing high concentrations of added dimethyl ester showed no new long-wavelength absorption which could be attributed to ground-state charge transfer (CT) complexation. In addition the intermolecular fluorescence quenching described in the preceding section obeys Stern–Volmer kinetics over a wide range of concentrations of the naphthalene donor.

When the separation between naphthalene and diester groups is made still smaller, as in the di-1-naphthyl esters whose absorption spectra are shown in Figure 4, perturbations in the long-wavelength absorption are observed as a result of ground-state interactions. For the 1-naphthylalkyl esters, however, the strength of the

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Table VI. Limiting Quantum Yields of Sensitized Cis-Trans Photoisomerization

compd	sensitizer	$\phi_{c \leftrightarrow t}$
dimethyl maleate	naphthalene	0.030[a]
dimethyl fumarate	1-methylnaphthalene	0.036[b]
dimethyl maleate	1-methylnaphthalene	0.039[b]

[a] In benzene-d_6 at 35 °C; 300-nm irradiation; analysis by NMR; ±30%. [b] In benzene at 35 °C; 300-nm irradiation; analysis by GC; ±15%.

ground-state CT interaction appears too small to produce the large observed changes in the photophysics of the naphthalene chromophore.

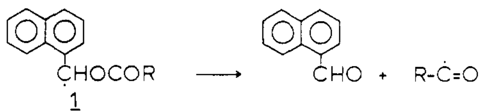
Measurements of fluorescence of the bichromophoric compounds in low-temperature glasses provide useful information on the degree of interaction between the two groups in their lowest energy conformations. These compounds show only naphthalene monomer fluorescence in 2-MeTHF solution at 77 K, with no long-wavelength emission which could be attributed to an exciplex. Bis(1-naphthylmethyl) oxalate shows intense fluorescence at 77 K with a decay time of 88 ns, comparable to that of other naphthalene derivatives not containing quenching groups.[10] This result indicates minimal interaction between the naphthalene singlet and the oxalate group at 77 K. On the other hand the fluorescence intensities of bis(1-naphthylmethyl) fumarate and methyl 1-naphthylmethyl fumarate are less than 10% of that of bis(1-naphthylmethyl) succinate at the same concentration. This suggests that quenching by fumarates occurs over greater distances than quenching by oxalates and is able to deactivate the naphthalene excited singlet in the ground-state conformation to the fumarates at 77 K.

Photochemical Studies. Singlet quenching of the naphthalene fluorescence by maleate and fumarate esters is accompanied by cis–trans isomerization of the double bond of the unsaturated ester. Table II lists the quantum yields of photoisomerization sensitized by intramolecular electron transfer. Although the electron-transfer process deactivates almost all of the naphthalene singlets, photoisomerization is inefficient. The quantum yields of isomerization remain around 0.04 for both maleates and fumarates with little dependence on the separation between naphthalene and ester groups. The inefficiency of photoisomerization suggests that reverse electron transfer to give ground-state reactants is rapid in comparison with isomerization.

In a comparison study quantum yields of sensitized cis–trans photoisomerization of dimethyl maleate and dimethyl fumarate were measured at concentrations where the ester quenches over 97% of the naphthalene singlet. These quantum yields, listed in Table VI, are of the same magnitude as those of the intramolecular reaction and are some 20% lower if the reaction is carried out in aerated solution. Since cis–trans isomerization of the radical anions of the *cis* and *trans*-butenedioate esters is known from the electrochemical work to be comparatively slow ($k = 2\ \text{s}^{-1}$),[26] isomerization involving a fully separated ion pair can be ruled out. Isomerization within a singlet exciplex is unlikely because the absence of emission from this state implies that its lifetime is unusually short. Photoisomerization via triplet energy transfer from naphthalene to the unsaturated ester is unlikely, first because the rate of intersystem crossing of the naphthalene chromophore is slow relative to the rate of singlet quenching in the bichromophoric compounds and second because triplet energy transfer from naphthalene to both maleates and fumarates is endothermic.[27] In addition, direct triplet transfer from naphthalene to the unsaturated ester would be expected to reveal much more pronounced differences in $\phi_{c \leftrightarrow t}$ between maleates and fumarates in light of the known differences in the triplet levels of the two isomers.[27] As in the case of the phenanthrene–dimethyl fumarate system,[12] it is proposed that a nonemitting singlet exciplex undergoes intersystem crossing to a triplet exciplex, and cis–trans isomerization occurs subsequently from this state.

On prolonged 300-nm irradiation the 1-naphthylmethyl esters give 1-naphthaldehyde. With carefully purified esters in thoroughly deoxygenated solvents resistant to H-atom abstraction this reaction is inefficient, as the quantum yields of Table II show. Higher chemical yields of the aldehyde result if acetophenone, *tert*-butyl hydroperoxide, or AIBN are present in the reaction mixture. The apparent quantum yield of naphthaldehyde increased with increasing irradiation time. No naphthaldehyde was detected on irradiation of degassed benzene solutions of 1-naphthylmethyl acetate.

Taken together these results suggest that there is a slight tendency for the bichromophoric compounds to undergo C–O bond scission on direct irradiation, but the major source of 1-naphthaldehyde is via β-scission of the free radical **1** formed through H atom abstraction by radicals generated during the photolysis of trace impurities (eq 4).



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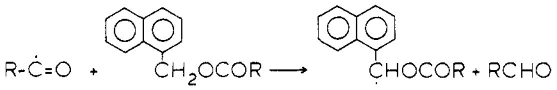
(4)



(5)

Equations 4 and 5 constitute a free-radical chain reaction initiated photochemically either by impurities or by the aldehydes themselves.

This mode of scission is completely different from that observed in the pyrolysis of dinaphthylmethyl oxalate,[28] which yields predominantly 1,2-dinaphthylethane by expulsion of 2 mol of CO_2. In further contrast to the naphthalene-containing compounds described here, the photochemistry of dibenzyl oxalate is very similar to its thermal chemistry, with toluene and diphenylethane being the major products in both cases.[29]

In preliminary work it was observed that the major products of the photolysis of bis((1-naphthyl)alkyl) fumarates in THF, CH_2Cl_2, or $CHCl_3$ were the products of free-radical addition of solvent across the double bond. This reaction is therefore similar to the acetophenone-initiated addition of THF and other cyclic ethers to dimethyl maleate described by Rosenthal and Elad.[30] Prolonged irradiation of benzene solutions of the fumarate esters resulted in complete disappearance of the cis and trans double bonds. We were unable to detect either cycloadducts of the fumarate double bond with the aromatic ring, cyclobutane dimers, or noncyclic dimers such as those formed on electrochemical reduction of fumarate diesters.[26,31] Instead the products are a mixture of oligomers

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(26) Yeh, L.-S.; Bard, A. J. *J. Electrochem. Soc.* **1977**, *124*, 189–195.

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formed by free-radical chain addition to the fumarate double bond. The removal of the quenching group through this free-radical reaction also explains the rapid increase in fluorescence intensity observed when THF solutions of the fumarates are irradiated with an intense arc source.

Conclusions

Compounds incorporating the naphthalene chromophore and a diester with a low reduction potential exhibit particularly fast photosensitized electron transfer, even though the two groups do not interact in the ground state. Singlet quenching by electron transfer occurs over sufficiently long distances that geometric requirements for quenching are largely removed. Photosensitized cis–trans isomerization of fumarate and maleate esters accompanies electron-transfer quenching. This photoreaction was shown to be preceded by the electron-transfer process and not to involve direct triplet energy transfer from naphthalene to the unsaturated diester. The degradation of naphthylalkyl fumarates and maleates by free-radical side reactions suggests that polymers incorporating the two groups may have useful photosensitivity at wavelengths below 300 nm.

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Registry No. 1-$C_{10}H_7CH_2OCOCH_3$, 13098-88-9; 1-$C_{10}H_7$-$(CH_2)_2OCOCH_3$, 26157-05-1; 1-$C_{10}H_7(CH_2)_3OCOCH_3$, 27653-23-2; (*E*)-1-$C_{10}H_7OCOCH{=}CHCOOC_{10}H_7$-1, 31263-12-4; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOOMe$, 94644-77-6; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOEt$, 94644-78-7; (*E*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOCH_2C_{10}H_7$-1, 83561-71-1; (*E*)-1-$C_{10}H_7(CH_2)_2OCOCH{=}CHCOOMe$, 94644-79-8; (*E*)-1-$C_{10}H_7$-$(CH_2)_2OCOCH{=}CHCOO(CH_2)_2C_{10}H_7$-1, 94644-80-1; (*E*)-1-$C_{10}H_7(CH_2)_3OCOCH{=}CHCOO(CH_2)_3C_{10}H_7$-1, 94644-81-2; (*Z*)-1-$C_{10}H_7CH_2OCOCH{=}CHCO_2H$, 94644-82-3; (*Z*)-1-$C_{10}H_7CH_2OCOCH{=}CHCOOMe$, 94644-83-4; (*Z*)-1-$C_{10}H_7$-$(CH_2)_2OCOCH{=}CHCOOMe$, 94644-84-5; 1-$C_{10}H_7OCOCOOC_{10}H_7$-1, 94644-74-3; 1-$C_{10}H_7CH_2OCOCOOEt$, 94644-85-6; 1-$C_{10}H_7CH_2OCOCOOCH_2C_{10}H_7$-1, 19829-49-3; 1-$C_{10}H_7(CH_2)_2OCOCOOEt$, 94644-75-4; 1-$C_{10}H_7(CH_2)_2OCOCOO$-$(CH_2)_2C_{10}H_7$-1, 82160-12-1; 1-$C_{10}H_7(CH_2)_3OCOCOO(CH_2)_3C_{10}H_7$-1, 94644-76-5; $C_{10}H_8$, 91-20-3; MeOCOCOOMe, 553-90-2; (*Z*)-MeOCOCH=CHCOOMe, 624-48-6; (*E*)-MeOCOCH=CHCOOMe, 624-49-7; 1-$C_{10}H_7CH_3$, 90-12-0; (*E*)-$HO_2CCH{=}CHCO_2H$, 110-17-8; (*E*)-ClCOCH=CHCOCl, 627-63-4; 1-$C_{10}H_7$-$(CH_2)_3OH$, 27653-22-1; 1-$C_{10}H_7CH_2OH$, 4780-79-4; (*E*)-MeOCOCH=CHCOCl, 17081-97-9; $(CH_3CO)_2O$, 108-24-7; 1-$C_{10}H_7CHO$, 66-77-3; maleic anhydride, 108-31-6.

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Conversion of α,β-Unsaturated Esters to Their β,γ-Unsaturated Isomers by Photochemical Deconjugation[1]

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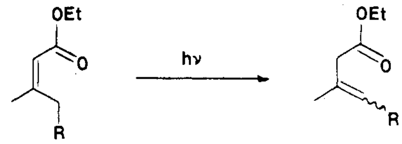
It is shown that the α,β-unsaturated esters **1**, **2**, **4**, **5**, **6**, **16**, and **18**, which have been reported to be inert to photochemical deconjugation or to undergo the reaction inefficiently, can be converted to their β,γ-unsaturated isomers in good yield if the irradiation is performed in the presence of a catalytic amount of a weak base such as 1,2-dimethylimidazole. It is also shown that addition of catalytic amounts of base can alter the product distribution in cases such as **11**, **23**, and **26** where more than one isomer can be formed.

Introduction

Irradiation of suitably substituted α,β-unsaturated esters with UV light results in the formation of their thermodynamically less stable β,γ-unsaturated isomers in high yield[2-10] (Scheme I). However, the reaction is not general and is efficient only if the esters possess substituents in the γ-position; in the absence of such substituents the esters are either photochemically unreactive (e.g., **1**[10]) or undergo the reaction slowly to give deconjugated products in low yield. For example, extended irradiation of ethyl 2,3-dimethyl-2-butenoate, **2**, results in incomplete conversion to ethyl 2,3-dimethyl-3-butenoate, **3**, in only 7% yield,[10] while the cyclopentylidene and cycloheptylidene esters **4** and **5** are reported to yield the β,γ-unsaturated isomers in "inferior" yield.[8] Similarly ethyl *trans*-butenoate, **6**, is converted to **7**, but incompletely and at a much slower rate than its higher homologues possessing an alkyl substituent in the γ-position.[2,11] With some esters the deconjugation reaction is sufficiently inefficient for alternative photochemistry to compete effectively. Examples are esters **8**,[12] **9**,[12] **10**,[12] and **11**.[9,13] The esters **8**, **9**, and **10**

Scheme I



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