di-*p*-anisylmethylamine and on the other side with 43.0 mg (0.195 mmol) of dioxygenyl hexafluoroarsenate. The tube was capped, removed from the glovebox, and attached to a high-vacuum line where it was evacuated. Chlorodifluoromethane (1.7 mL) was vacuum transferred into the side containing the amine. With the tube at −130 °C, the break-seal was broken. A green color developed instantly and darkened upon stirring. After 25 min, the solvent was removed in vacuo, and the apparatus was allowed to warm to room temperature. The green solid that remained was dissolved in 20 mL of a 1:6 acetonitrile/methylene chloride solution and, under nitrogen, the solution was equally divided into six septum-capped test tubes. Diethyl ether (6.2 mL) was mixed into each tube, and an additional 5.4 mL of ether was layered on top of the mixed solutions. The test tubes were placed in a −20 °C freezer. After 14 h, purple, metallic-looking needles formed. The mother liquor was removed using a Teflon-needled syringe, and the crystals were rinsed with two 2-mL portions of diethyl ether. The solvent was removed in vacuo. Yield: 57.5 mg (70.4%). MP: 90–95 °C dec. Anal. Calcd for $C_{15}H_{17}NO_2AsF_6$: C, 41.68; H, 3.96; N, 3.24. Found: C, 41.51; H, 3.93; N, 3.17. A degassed EPR sample was prepared in methylene chloride (10^{-4} M). EPR (CH_2Cl_2): a_N = 9.97 G, a_{CH_3} = 10.46 G, a_o = 2.49 G, a_m = 0.50 G, a_p = 1.00 G (lit.[11] EPR (CH_3CN): a_N = 9.77 G, a_{CH_3} = 10.27 G, a_o = 2.42 G, a_m = 0.48 G, a_p = 0.97 G).

Preparation of *N*-[(Di-*p*-anisylamino)methyl]quinuclidinium Tetrafluoroborate (1). A solution of 35.0 mg (0.144 mmol) of di-*p*-anisylmethylamine in 1.0 mL of acetonitrile was added dropwise to a solution of 46.3 mg (0.140 mmol) of triphenylcarbenium tetrafluoroborate in 1.0 mL of acetonitrile under a nitrogen atmosphere. After stirring for 30 min, 10.0 mL of carbon tetrachloride was added and a light green oil separated. The solvents were evaporated to give a light green solid. The solid was rinsed with six 1-mL portions of carbon tetrachloride to remove triphenylmethane (36 mg). The remaining solid was analyzed by NMR. ^{1}H NMR ($CDCl_3$): δ 8.24 (s, 1.94 H), 7.48 (d, J = 9.0 Hz, 4.04 H), 7.02 (d, J = 9.0 Hz, 3.92 H), 3.87 (s, 6.10 H). The solid was then dissolved in 2 mL of methylene chloride, and a solution of quinuclidine (17.9 mg, 0.161 mmol) in 2 mL of methylene chloride was added. After 5 min a flocculent precipitate formed. The solvent was removed by rotary evaporation to give an off-white solid. ^{1}H NMR (CD_3CN): δ 7.08 (d, J = 7.0 Hz, 4.01), 6.90 (d, J = 7.0 Hz, 3.97 H), 5.09 (s, 1.98 H), 3.78 (s, 5.85 H), 3.40 (m, 6.06 H), 2.17 (m, 1.04 H), 1.98 (m, 6.10 H).

Reaction of Di-*p*-anisylmethylaminium Hexafluoroarsenate with Quinuclidine in Acetonitrile. A solution of di-*p*-anisylmethylaminium hexafluoroarsenate (3.0 mg, 0.012 mmol) in 1.5 mL of acetonitrile was added via syringe over 2 min to a solution containing 13.5 mg (0.121 mmol) of quinuclidine in 1.5 mL of acetonitrile. The aminium ion solution decolorized immediately upon addition. After 10 min, the solvent and excess quinuclidine were removed in vacuo. ^{1}H NMR analysis showed three products, *N*-[(di-*p*-anisylamino)methyl]quinuclidinium hexafluoroarsenate (**1**), di-*p*-anisylmethylamine, and quinuclidinium hexafluoroarsenate. The first two products were identified by comparison with authentic spectra. The quinuclidinium hexafluoroarsenate was identified by addition of a small quantity of quinuclidinium chloride, which increased the peak intensities at δ 3.12 (br t, J = 8.1 Hz), 2.00 (sept, J = 3.23 Hz), and 1.79 (br dt). The yields of *N*-[(di-*p*-anisylamino)methyl]quinuclidinium hexafluoroarsenate (**1**) (48%) and di-*p*-anisylmethylamine (49%) were determined by ^{1}H NMR integration against an internal standard (fluorenone).

Stopped-Flow Kinetics. The reaction kinetics were performed on freshly prepared solutions, which were stored under a nitrogen atmosphere. Both the aminium ion and the base solutions contained tetra-*n*-butylammonium hexafluoroarsenate (3.5 mM). The disappearance of aminium ion was followed at 734 nm. During temperature-dependent runs, the instrument was allowed to equilibrate for at least 1 h after reaching the desired temperature.

Acknowledgment. We thank J. L. Goodman for assistance in the photoacoustic measurements, I. R. Gould for the quantum yield determinations, W. D. Jones for help in the X-ray structure analysis, and W. H. Saunders, Jr., for the use of his stopped-flow spectrophotometer. Research support was provided by the National Science Foundation (Grant CHE86-10404) and by the National Institutes of Health (Grant S07 RR07069-23).

Supplementary Material Available: Tables of X-ray data for *p*-$An_2NCH_3^{\bullet+}$ AsF_6^- including listings of intramolecular bond angles and bond distances, intermolecular distances, least-squares planes, torsion and conformation angles, and positional and thermal parameters (7 pages); listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

Lewis Acid Catalysis of Photochemical Reactions. 8. Photodimerization and Cross-Cycloaddition of Coumarin[1]

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Abstract: The effect of Lewis acid complexation upon the electronic structure and photochemical behavior of coumarin has been investigated. Changes in IR and ^{1}H NMR spectra upon complexation of coumarin with BF_3 or $EtAlCl_2$ are indicative of 1:1 complexation of the Lewis acid with the carbonyl oxygen. Changes in the UV spectrum and the observation of room-temperature fluorescence from the coumarin–BF_3 complex are attributed to increased energy of the n,π* singlet state relative to the fluorescent π,π* singlet state. Dimerization is found to occur via the reaction of either the singlet or triplet complex with ground-state coumarin. The singlet-state reaction selectively yields the syn head-to-tail dimer while the triplet-state reaction yields the anti head-to-head dimer. The singlet- and triplet-state complexes also react with simple alkenes. Addition of the singlet complex with the isomeric 2-butenes occurs with retention of configuration. The enhanced reactivity of complexed vs uncomplexed coumarin is attributed to its increased singlet-state lifetime and electrophilicity.

The photophysical and photochemical behavior of coumarin and its derivatives have been the subject of numerous investigations. Direct irradiation of the parent unsubstituted coumarin in solution results in highly inefficient photodimerization and cross-cycloaddition with simple alkenes, whereas triplet sensitization results in more efficient reactions.[2-9] These observations are consistent with the absence of fluorescence and low efficiency of intersystem crossing from the short-lived singlet state in non-

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Table I. Infrared Data for Coumarin and Its Lewis Acid Complexes

	ν(C=O)	ν(C-C)	ν(C-O)	ν(C-O-C)
coumarin	1700 (s)	1255 (m)	1175 (m)	1105 (m)
coumarin-BF_3[a]	1670, 1600 (vs)	1280 (m)	1200 (m)	
coumarin-$EtAlCl_2$[b]	1640, 1570 (vs)	1290 (m)	1200 (s)	1135 (m)

[a] Examined as Nujol mull of the crystalline complex. [b] Examined as oil after evaporation of solvent (CH_2Cl_2).

Table II. ^1H NMR Data for Coumarin and Its Lewis Acid Complexes[a]

		chemical shift, ppm			
Lewis acid	equiv	H_α	$\Delta\delta_\alpha$	H_β	$\Delta\delta_\beta$
none		7.73		6.38	
BF_3[b]	1.0	8.58	0.85	7.13	0.75
BF_3·OEt_2	1.0	7.96	0.23	6.58	0.20
$EtAlCl_2$	0.5	8.01	0.28	6.59	0.21
	0.75	8.18	0.45	6.81	0.43
	1.0	8.42	0.69	6.96	0.58
	1.25	8.55	0.82	7.22	0.84

[a] Chemical shifts for 0.1 M coumarin in CD_2Cl_2 vs TMS. [b] Solution prepared from 1:1 crystalline complex.

hydroxylic solvents.[4] We have observed that complexation of coumarin with the strong Lewis acid BF_3 results in enhanced fluorescence and stereoselective photodimerization to yield the syn head-to-head dimer, a minor product of direct irradiation.[10] Dimerization was proposed to occur via the reaction of the complexed coumarin singlet state with noncomplexed ground-state coumarin. Support for this mechanism was provided by a subsequent investigation by Shim et al.[11]

The occurrence of stereoselective Lewis acid catalyzed photodimerization encouraged us to investigate the effects of Lewis acids upon cross-cycloaddition reactions with simple alkenes. It was hoped that these reactions would occur with retention of olefin stereochemistry, thus providing an attractive alternative to nonconcerted, triplet-sensitized cross-cycloaddition.[7] We report herein the results of our investigation of the BF_3- and $EtAlCl_2$-catalyzed photochemical cross-cycloaddition reactions of coumarin with (*E*)- and (*Z*)-**2**-butene and several nonisomerizable olefins. The stereoselectivity of addition to the isomeric butenes increases with butene concentration, indicative of the occurrence of both concerted (singlet-state) and nonconcerted (triplet-state) reactions. These results prompted a reinvestigation of the Lewis acid catalyzed photodimerization reaction, which was also found to occur via both singlet and triplet mechanisms.

Results and Discussion

Spectra and Structure. IR spectroscopic data for coumarin and its 1:1 complexes with BF_3 and $EtAlCl_2$ are presented in Table I. The most notable change observed upon complex formation is a shift of the C=O stretch to lower frequency and its splitting into two broadened maxima. The C-C and C-O stretch and the C-O-C bend are all shifted to higher frequency. Similar frequency shifts have previously been reported for the 1:1 complexes of coumarin with several other boron and aluminum halides and are attributed to complexation of the Lewis acid with the carbonyl oxygen.[12]

^1H NMR data for coumarin and its BF_3 and $EtAlCl_2$ complexes are summarized in Table II. Large downfield shifts are observed for the vinyl protons, as previously observed for the Lewis acid complexes of α,β-unsaturated ketones and esters.[13] Significantly larger shifts are observed for a 0.1 M solution of the crystalline coumarin-BF_3 complex than for a solution of 0.1 M coumarin with 1 equiv of BF_3·OEt_2. Evidently, only partial complexation is obtained in the latter case, and the time averaged signal for complexed and uncomplexed coumarin is observed. Similarly, addition of 0.25-equiv aliquots of $EtAlCl_2$ resulted in progressive downfield shifts until ca. 1.25 equiv had been added. Addition of more $EtAlCl_2$ resulted in no further shift of the vinyl protons, indicating the formation of a 1:1 complex with chemical shifts similar to those for the BF_3 complex. However, a second set of vinyl resonances at lower field was observed at higher concentrations of $EtAlCl_2$ (>1.5 equiv), possibly indicating the formation of a 1:2 complex, which is not in equilibrium with the 1:1 complex on the NMR time scale.[14] An equilibrium constant of 140 M^{-1} for formation of the coumarin-$EtAlCl_2$ complex in CD_2Cl_2 was determined from NMR chemical shift data for 0.05-0.25 M solutions using the method of progressive dilution developed by Bouquant and Chuche.[15] This value is within the range of values obtained for cinnamic ester-BF_3 complexes (K = 80-860 M) from absorption spectral data.[13]

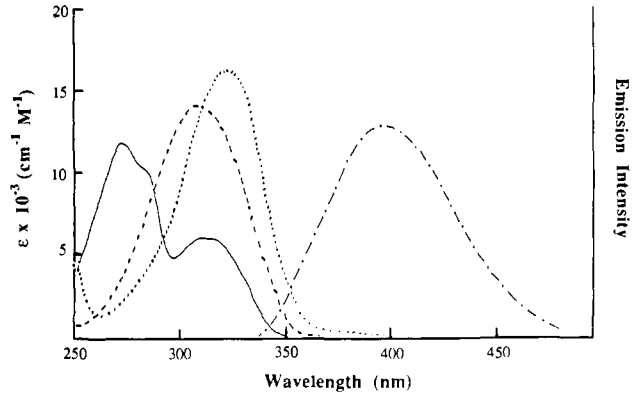

Figure 1. UV absorption spectra of coumarin (—), coumarin-BF_3 (---), coumarin-$EtAlCl_2$ (···), and fluorescence spectrum of coumarin-BF_3 (-·-) in dichloromethane solution.

The structure of the coumarin-$HgCl_2$ complex has been determined by X-ray crystallography.[16] Hg is coordinated to the carbonyl oxygen and lies in the coumarin plane syn to the ring oxygen. Analysis of NMR data for coumarin-Eu(fod)$_3$ and coumarin-Yb(dpm)$_3$ using a two-site model indicates that both syn and anti conformations are present in solution, the anti being favored.[17] The existence of both syn and anti conformers could account for the observation of two peaks in the C=O stretching region of coumarin-BF_3 and coumarin-$EtAlCl_2$.

Absorption spectra for dichloromethane solutions of 5×10^{-4} M coumarin and its Lewis acid complexes recorded in a 2-mm-path-length cell are shown in Figure 1. The spectrum of the BF_3 complex was obtained after purging a coumarin solution with BF_3 gas, while the $EtAlCl_2$ spectrum was obtained using >20 equiv of $EtAlCl_2$. The use of <20 equiv of BF_3·OEt_2 or $EtAlCl_2$ results in spectra intermediate in appearance between those of free and fully complexed coumarin shown in Figure 1. Using the value of K_{eq} = 140 M^{-1} obtained from NMR dilution studies, we calculate that 1 equiv of $EtAlCl_2$ will complex only 2% of the coumarin present at UV concentrations. At typical photolysis concentrations (0.02 M coumarin), approximately 70% of the coumarin is complexed by 1 equiv of $EtAlCl_2$. Attempts to determine

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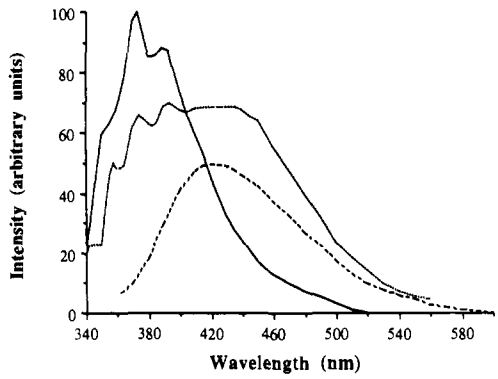

Figure 2. Total emission spectra of coumarin (—), coumarin-BF_3 (---), and coumarin-$EtAlCl_2$ (···) in a methylcyclohexane glass at 77 K.

Table III. Frontier Orbital Energies (Hartrees)

orbital	coumarin	coumarin-H^+	orbital	coumarin	coumarin-H^+
LUMO	0.160	−0.072	SHOMO	−0.280	−0.462
HOMO	−0.230	−0.448	n_0	−0.328	−0.613

equilibrium constants from absorption spectral data failed to yield linear Benesi-Hildebrand plots.

Whereas coumarin is nonfluorescent at room temperature in non-hydroxylic solvents,[5,18] its BF_3 complex is strongly fluorescent (Figure 1).[10] Broad, structureless fluorescence is observed from dichloromethane solutions of 10^{-4} M coumarin containing as little as 1 equiv of $BF_3{\cdot}OEt_2$. The fluorescence lifetime of the coumarin-BF_3 complex as determined by single-photon counting is 0.8 ns. The fluorescence of coumarin-BCl_3 is weaker than that of coumarin-BF_3, while that of coumarin-$EtAlCl_2$ is very weak and has a lifetime too short for measurement by single-photon counting (<0.3 ns). Total emission spectra of coumarin and its Lewis acid complexes were also recorded at 77 K in methylcyclohexane glasses (Figure 2). A solution purged with BF_3 gas prior to cooling displays only broad emission similar to that obtained for the coumarin-BF_3 complex in solution, while a solution containing 5 equiv of $EtAlCl_2$ displays short-wavelength structure similar to that of noncomplexed coumarin as well as broad long-wavelength emission assigned to fluorescence of the Lewis acid complex. No phosphorescence was detected in the total emission spectra of free or complexed coumarin.[18]

The changes in absorption and fluorescence spectra of coumarin upon complexation with BF_3 are qualitatively similar to those previously reported for protonation of coumarin.[19] In both cases, the two long-wavelength absorption maxima at 274 and 313 nm are replaced by a single broad band located between 306 and 325 nm. Both the BF_3 complex and protonated coumarin are strongly fluorescent, the latter having a fluorescence quantum yield of 0.5 and singlet lifetime of 5 ns.[19]

The 274- and 313-nm absorption bands of coumarin have been assigned on the basis of semiempirical π-electron calculations to transitions from the SHOMO and HOMO, respectively, to the LUMO.[18,19] The absence of room-temperature fluorescence and the low efficiency of intersystem crossing have been attributed to the influence of a low-lying n,π^* state.[18] Increasing the gap between the lowest π,π^* and n,π^* singlet states by means of substitution on the aromatic ring has, in fact, been observed to result in an increase in fluorescence intensity.[20a] Protonation or Lewis acid complexation of the nonbonding electrons of coumarin should result in a lowest π,π^* singlet state unperturbed by a low-lying n,π^* state.[19]

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Table IV. Product Ratios and Quantum Yields for Photodimerization of Coumarin[a]

coumarin, M	yield, % 1	2	3	$\Phi_{total} \times 10^3$
0.10	5	90	4	1.7
0.15	14	80	6	2.1
0.25	20	71	10	3.1
0.35	20	73	7	3.6

[a] Data for 313-nm irradiation of deoxygenated CH_2Cl_2 solutions.

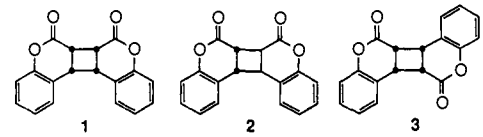
Table V. Quantum Yields and Product Ratios for BF_3-Catalyzed Dimerization of Coumarin[a]

coumarin, M	BF_3, M	Φ_{total}	yields, % 2	3
0.06	0.05	0.10	48	52
0.10	0.05	0.21	23	77
0.20	0.05	0.74	11	89
0.40	0.05	0.81	6	94
0.20	0.01	0.74	11	89
0.20	0.02	0.75	10	90
0.20	0.03	0.75	10	90
0.20	0.05	0.76	11	89
0.20	0.10	0.38	14	86
0.20	0.15	0.20	20	80

[a] Data for 313-nm irradiation of deoxygenated CH_2Cl_2 solutions.

Support for this interpretation of the coumarin optical spectra is provided by GAUSSIAN 82[20b] calculations (STO-3G basis set) for coumarin and protonated coumarin. The calculated orbital energies given in Table III do not provide accurate energies for the electronic transitions as they neglect configuration interaction. Thus, while n_0 is the third highest occupied orbital, the lowest singlet of coumarin is believed to be the n,π^* state.[18] The energies in Table III do provide an indication of the relative energies of the frontier orbitals. While protonation has little effect upon the HOMO-LUMO gap, it results in a decrease in the HOMO-SHOMO gap and an increase in the SHOMO-n_0 gap. The former change can account for the collapse of the two long-wavelength absorption bands in coumarin into a single broad band in its protonated form or BF_3 complex (Figure 1), while the latter change can account for the increase in singlet lifetime upon protonation or complexation.

Dimerization. Direct irradiation of coumarin in solution results in the formation of three dimers, syn head-to-head (**1**), anti



head-to-head (**2**), and syn head-to-tail (**3**), while triplet-sensitized irradiation yields predominantly dimer **2**.[2-5] The product ratios are highly dependent upon the choice of solvent and coumarin concentration, engendering a lively debate over the mechanism of photodimerization during the 1960s. A reasonable interpretation of these results is that at high concentrations the short-lived (<0.1 ns) coumarin singlet reacts with ground-state coumarin to yield dimer **1** and that at low concentrations inefficient intersystem crossing ($\Phi < 0.01$) generates triplet coumarin, which reacts with ground-state coumarin to yield dimer **2**.[4b]

In order to provide a basis for comparison of Lewis acid catalyzed vs uncatalyzed photodimerization, we have investigated both reactions in dichloromethane solution. Percent yields of the three dimers and total dimerization quantum yields obtained upon direct 313-nm irradiation using initial coumarin concentrations between 0.1 and 0.35 M are summarized in Table IV. Capillary GC analysis with on-column injection allows direct measurement of product ratios at low conversions, a capability not available to previous investigators. While **2** is the major product at all concentrations, its yield decreases, while that of **1** increases with increasing coumarin concentration, in accord with the proposal

Scheme I

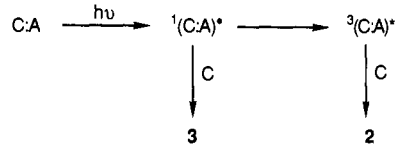


Table VI. Product Composition vs Irradiation Time for BF_3·OEt_2-Catalyzed Dimerization of Coumarin in the Absence and Presence of Oxygen[a]

	deoxygenated			oxygenated		
time, h	coumarin, % conv	2, %	3, %	coumarin, % conv	2, %	3, %
0.3	17	11	89	9	10	90
1.6	61	14	86	25	5	95
4.0	79	18	82	38	2	98
6.5	90	19	81	41	2	98
15	91	12	88			
24	99	11	89			
36	96	6	94			

[a] Data for 313-nm irradiation of 0.02 M coumarin with 1 equiv of BF_3·OEt_2 in CH_2Cl_2 solution.

of their formation via triplet- and singlet-state reactions, respectively.[4] The quantum yield for the 0.35 M solution is similar to the value previously reported for formation of **2** in CCl_4.[4b]

In previous investigations of the BF_3-catalyzed photodimerization of coumarin, the syn head-to-tail dimer (**3**) was the only product isolated at high conversions.[10,11] This is, evidently, the method of choice for the preparation of **3**.[21] Reinvestigation of this reaction at low conversions (<15%) establishes that both **2** and **3** are formed and that their ratio is dependent upon the concentration of noncomplexed coumarin. Percent yields and quantum yields for 313-nm irradiation of 0.05 M coumarin–BF_3 with 0.01–0.035 M noncomplexed coumarin and for 0.2 M coumarin with 0.05–0.75 equiv of BF_3 are summarized in Table V. Quantum yields are corrected for incomplete absorption of light by coumarin–BF_3. While both free and complexed coumarin absorb 313-nm light, quantum yields for reaction of free coumarin (Table IV) are much smaller than those reported in Table V. Irradiation at 366 nm, where only coumarin–BF_3 complex absorbs, results in similar dimer ratios to those obtained with 313-nm light. This data supports the previously proposed mechanism for dimerization upon reaction of an excited coumarin–BF_3 complex with ground-state coumarin.[10,11]

The observed increase in the quantum yield for formation of **3** and in the **3**/**2** ratio with increasing free coumarin concentration (Table V) suggests that the BF_3-catalyzed photodimerization occurs via both singlet- and triplet-state reactions (Scheme I, C = coumarin, A = Lewis acid) as is the case for noncomplexed coumarin. The formation of dimer **3** via the reaction of the fluorescent singlet coumarin–BF_3 complex is supported by the calculations of values of $k_q\tau$ = 3.0 M^{-1} from a plot of Φ^{-1} vs [coumarin]$^{-1}$ and 5.7 M^{-1} from a Stern–Volmer plot for quenching of coumarin–BF_3 fluorescence by noncomplexed coumarin. In view of the scatter in both data sets, these values are in reasonable agreement. From the average of these $k_q\tau$ values and the measured singlet lifetime of coumarin–BF_3, a rate constant of 5 × 10^9 M^{-1} s^{-1} can be calculated for the singlet dimerization reaction. The quantum yield for formation of **3** in the limit of high free coumarin concentration is near unity, thus establishing that the reaction of the singlet-state complex is even more efficient than previously suggested.[10] The formation of dimer **2** via a triplet-state reaction (Scheme I) is analogous to its formation in the benzophenone-sensitized dimerization of free coumarin.[2a] The low quantum yield for formation of **2** at low coumarin concentrations (Table V) indicates that either intersystem crossing of singlet coumarin–BF_3 (like that of singlet coumarin) or the reaction of the triplet complex is inefficient.

Since the dimer ratio **2**/**3** increases with decreasing free coumarin concentration (Table V), it is not surprising that the dimer ratio changes during the course of long-term irradiation. Typical results obtained for irradiation of 0.02 M coumarin and 1.0 equiv of BF_3·OEt_2 with Pyrex-filtered light in degassed and oxygenated dichloromethane solution are summarized in Table VI. Similar results are obtained using 0.25 equiv of BF_3, in accord with the larger ^1H NMR chemical shifts observed for BF_3 vs BF_3·OEt_2 (Table II). In degassed solutions, the **2**/**3** ratio is seen to increase as expected with irradiation time, due to the decreased concentration of free coumarin. However, at conversions above 90% the **2**/**3** ratio decreases. The presence of oxygen selectively inhibits the formation of dimer **2**, resulting in highly selective formation of **3**. Slightly lower selectivity is observed for air- vs oxygen-saturated solutions.

While the ability of added oxygen to selectively inhibit the formation of dimer **2** might be attributed to oxygen quenching of the triplet coumarin–BF_3 complex (Scheme I), scrutiny of the data in Table VI does not support such a conclusion. At low conversions the **2**/**3** ratios obtained in the presence and absence of oxygen are similar. The decrease in the **2**/**3** ratio at moderate conversions in the presence of oxygen and at high conversions in the absence of oxygen suggests that dimer formation may occur reversibly. Irradiation of 0.02 M **2** and **3** in the presence of 1.0 equiv of BF_3·OEt_2 does in fact result in the formation of both coumarin and the other dimer (Table VII). In the absence of oxygen, reaction of dimers **2** and **3** proceeds slowly, yielding mainly isomerized dimer. Thus cycloreversion is expected to compete with dimerization only at very high conversions of coumarin to dimer. In the presence of oxygen, cycloreversion to yield coumarin occurs rapidly for dimer **2** and more slowly for dimer **3**. Thus efficient and selective cycloreversion of dimer **2** can account for the highly selective formation of dimer **3** upon irradiation of coumarin with BF_3 in the presence of oxygen (Table VI). While we can only speculate as to the origin of the unusual effect of oxygen upon the cycloreversion of dimer **2** in the presence of BF_3, its occurrence does provide an explanation for the selective formation of dimer **3** in previous studies of BF_3-catalyzed dimeri-

Table VII. Retrodimerization of Degassed and Oxygenated Solutions[a]

	degassed, % conv			oxygenated, % conv		
time	coumarin	other dimer[b]	total	coumarin	other dimer[b]	total
			Dimer **2**			
0.3	0	1	1	7	0	7
1.6	0	4	4	35	4	39
3.9	6	6	12	81	8	89
6.6	6	9	15	82	14	96
16.6	12	16	28	72	26	98
			Dimer **3**			
0.3	0	0	0	0	0	0
1.6	0	4	4	0	0	0
3.9	0	7	7	5	0	5
6.6	0	12	12	6	0	6
16.6	0	21	21	9	0	9

[a] Data for 313-nm irradiation of 0.02 M dimer with 1 equiv of BF_3·OEt_2 in dichloromethane solution. [b] Formation of **3** from **2** or **2** from **3**.

Table VIII. Quantum Yields for $EtAlCl_2$-Catalyzed Dimerization of Coumarin[a]

coumarin, M	Φ_3	yield, % 2	yield, % 3
0.05	0.024	29	71
0.15	0.029	19	81
0.20	0.049	19	81
0.25	0.050	15	85
0.35	0.052	12	88

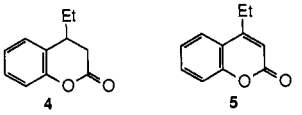
[a] Data for 313-nm irradiation of coumarin with 0.01 M $EtAlCl_2$.

(21) Hallberg, A.; Isaksson, R.; Martin, A. R.; Sandström, J. *J. Am. Chem. Soc.* **1989**, *111*, 4387.

zation in which oxygen may not have been rigorously excluded during the entire period of irradiation.[10,11]

The photodimerization of coumarin can also be catalyzed by $EtAlCl_2$. Percent yields of dimers **2** and **3** and quantum yields for the formation of dimer **3** upon 313-nm irradiation of dichloromethane solutions of 0.01 M coumarin–$EtAlCl_2$ containing 0.05–0.35 M uncomplexed coumarin are reported in Table VIII. The increase in quantum yield and decrease in the ratio of dimers **2**/**3** with increasing coumarin concentration parallel the results obtained for BF_3-catalyzed dimerization (Table V). The quantum yields for formation of dimer **3**, the product of singlet-state dimerization, are substantially lower for the $EtAlCl_2$ vs BF_3-catalyzed reaction, necessitating correction of the data in Table VIII for dimer formation via direct excitation of coumarin. Both the shorter singlet lifetime of the $EtAlCl_2$ vs BF_3 complex and more rapid cycloreversion of the dimers in the presence of $EtAlCl_2$ may contribute to the lower quantum yields obtained using $EtAlCl_2$.

An additional complication encountered in the $EtAlCl_2$-catalyzed photodimerization reaction is the formation of the alkylated coumarins, **4** and **5**. While dimerization is the major reaction



when <0.25 equiv of $EtAlCl_2$ is utilized, **4** and **5** are the only products obtained using >1 equiv of $EtAlCl_2$. The ratio of alkylation products **4**/**5** is also dependent upon the concentration of $EtAlCl_2$, decreasing from >10 for 1 equiv to 2.3 for 2 equiv and 1.1 for 10 equiv. This concentration dependence is suggestive of the formation of **4** via irradiation of the 1:1 coumarin–$EtAlCl_2$ complex and of **5** either via reaction of the 1:1 complex with excess $EtAlCl_2$ or irradiation of a 1:2 complex.[14]

Coumarin has been reported to undergo nonphotochemical 1,2-addition reactions with trialkylaluminum compounds, including Et_3Al.[22] While 1,2-addition reactions of enones with organoaluminum compounds are far more common than 1,4-addition reactions,[22] 1,4-addition has been observed in several cases, including the photoinduced reaction of $EtAlCl_2$ with benzalacetophenone.[23] A free-radical chain mechanism has been proposed for the thermal and photochemical addition of trialkylboranes with enones,[24] but we observe only modest increases in the low quantum yields for the formation of **4** ($\Phi < 0.02$) with increasing coumarin concentration. Since photoalkylation of coumarin was not the focus of this investigation, its mechanism was not further explored.

In summary, irradiation of coumarin in the presence of <1 equiv of BF_3 or $EtAlCl_2$ is found to significantly increase the quantum yield for dimer formation upon direct irradiation. This increase reflects the increased singlet lifetime for complexed vs uncomplexed coumarin and, quite likely, an increased rate constant for photodimerization. The calculated rate constant for reaction of singlet coumarin–BF_3 with ground-state coumarin is 5×10^9 M^{-1} s^{-1}, near the rate of diffusion in fluid solution. While the rate constant for the singlet coumarin reaction is unknown, formation of the presumed singlet excimer intermediate should be energetically less favorable than formation of a charge-transfer stabilized exciplex from singlet coumarin–BF_3 with ground-state coumarin. Similarly, the failure of the singlet complex to react with ground-state complex may reflect the relative instability of the excimer intermediate that would be formed. No dimer formation is observed for fully complexed coumarin or methyl cinnamate.[7]

Dimerization via singlet coumarin–BF_3, like that of uncomplexed coumarin, yields predominantly a syn adduct; however, the regiochemistry of dimerization is inverted. Stereoselective syn dimerization has previously been observed for singlet arenes including 9-substituted phenanthrenes[25] and acenaphthylene[26] and is attributed to the formation of a sandwich-type excimer with maximum π-orbital overlap prior to covalent bond formation. The syn head-to-head dimer **1** is indeed the product expected from the coumarin excimer.[4b] Inspection of the HOMO coefficients (Figure 3) for protonated coumarin (our model for coumarin–BF_3) and coumarin provides a plausible explanation for the formation of the head-to-tail dimer **3** in the Lewis acid catalyzed reaction. While both head-to-head and head-to-tail dimerization is symmetry allowed, the syn head-to-head interaction results in unfavorable secondary orbital interactions between the benzene rings, which are largely avoided in the anti head-to-tail geometry. Secondary orbital overlap does not control the stereochemistry of the stepwise triplet-state dimerization, and both the complexed and uncomplexed coumarin triplet yield the anti head-to-head dimer.

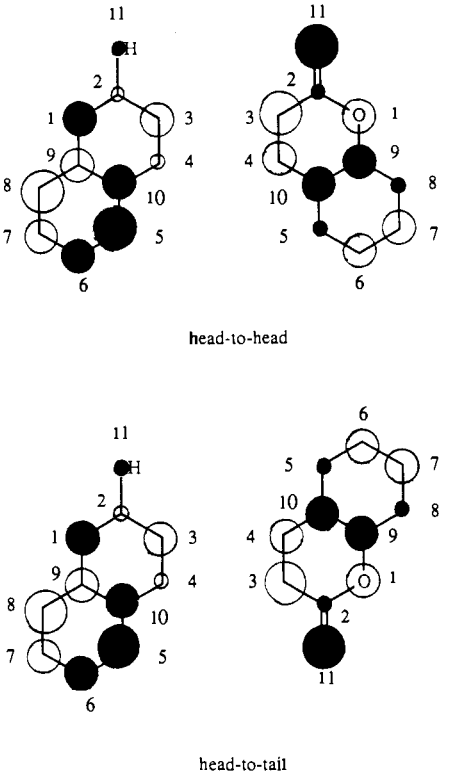


Figure 3. HOMO coefficients for the head-to-head and head-to-tail interaction of protonated coumarin (left) and coumarin (right).

Cross-Cycloaddition. Direct irradiation of coumarins in the presence of simple alkenes results in highly inefficient [2 + 2] cross-cycloaddition.[6-9] Wells and Morrison[8] report that irradiation of 0.3 M coumarin with 3.0 M tetramethylethylene in ethyl acetate solution results in cross-cycloaddition with a quantum yield of 3×10^{-3} and an isolated yield of 4%. We have observed comparable results with other simple alkenes. In contrast, moderately efficient benzophenone-sensitized addition has been reported for coumarin with indene[6] and several nonisomerizable alkenes.[7,8] These results parallel those previously described for coumarin photodimerization and reflect the short lifetime and low intersystem crossing efficiency of singlet coumarin. It should be noted, however, that various substituted coumarins undergo efficient cross-cycloaddition reactions with alkenes upon direct irradiation.[27]

The benzophenone-sensitized [2 + 2] cycloaddition reaction of coumarin with tetramethylethylene has previously been reported

(22) (a) Alberola, A.; Alonso Cermeño, F.; Gonzalez Ortega, A. *Anales de Quimica* **1982**, *78*, 9. (b) Baba, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 928. (c) Lyons, A.; Catterall, E. *J. Organomet. Chem.* **1970**, *25*, 351. (d) Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1979**, *44*, 4792.

(23) Furukawa, J.; Omura, K.; Ishikawa, K. *Tetrahedron Lett.* **1973**, 3119.

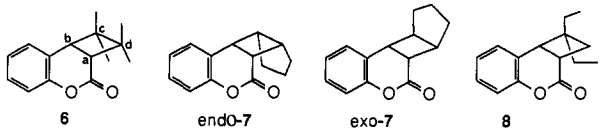
(24) (a) Kabalka, G. W.; Daley, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 4428. (b) Arase, A.; Masuda, Y.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2275.

(25) Sargent, M. V.; Timmons, C. J. *J. Chem. Soc.* **1964**, 5544.

(26) Cowan, D. O.; Drisko, R. L. E. *J. Am. Chem. Soc.* **1970**, *92*, 6286.

(27) (a) Haywood, D. J.; Hunt, R. G.; Potter, C. J.; Reid, S. T. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2458. (b) Shim, S. C.; Kim, Y. Z.; Kang, H. K. *Photochem. Photobiol.* **1984**, *40*, 171. (c) Suginome, H.; Liu, C. F.; Furusaki, A. *Chem. Lett.* **1984**, 911.

by Hanifin and Cohen[7] to yield a single adduct **6**. We find that



6 endo-**7** exo-**7** **8**

irradiation of 0.02 M coumarin with 1 equiv of BF_3·OEt_2 and 10 equiv of this alkene results in the formation of the same adduct as obtained upon benzophenone sensitization. The cis ring fusion in **6** is supported by the large value of J_{ab} = 10.0 Hz. The *endo*-methyl protons are also shielded by the aromatic ring (δ 0.75 and 1.02 vs δ 1.22 and 1.27 for the *exo*-methyl protons). Essentially quantitative conversion of coumarin to cycloadduct is obtained with BF_3, while conversions of ca. 50% are obtained using benzophenone sensitization. Benzophenone sensitization also results in the formation of oxetanes via the reaction of triplet benzophenone with the alkene.

Hanifin and Cohen[7] also reported the formation of a single adduct in the benzophenone-sensitized reaction of coumarin with cyclopentene. A recent reinvestigation of this reaction by Suginome and Kobayashi[28] established that both syn and anti adducts **7** are formed in a ratio of 0.7/1 and corrected Hanifin and Cohen's stereochemical assignment. We find that irradiation of 0.02 M coumarin with 1 equiv of BF_3·OEt_2 and 10 equiv of cyclopentene results in the formation of *syn*- and *anti*-**7** in a ca. 2:1 ratio. Our assignment of syn stereochemistry to the major product is based upon comparison of ^{1}H NMR data with that reported by Suginome and Kobayashi[28] and with data for the cyclopentene adducts of 4-hydroxycoumarin, for which syn stereochemistry has been established by means of X-ray crystallography,[27c] and of quinolone, the nitrogen analogue of coumarin.[29] Salient features of the ^{1}H NMR data for *syn*- and *anti*-**7** include large cis coupling constants (J = 10–11 Hz) for all of the cyclobutane ring protons in *syn*-**7** and larger cis vs trans couplings for *anti*-**7** (J_{ab} = 9.3 Hz, J_{ad} = 4.9 Hz, J_{bc} = 3.9 Hz).[28] In addition, shielding of endo protons or alkyl groups at C_c and to a lesser extent at C_d by the aromatic system can be used to aid stereochemical assignments.

Benzophenone-sensitized irradiation of coumarin with 2-ethyl-1-butene results in the selective formation of the [2 + 2] adduct **8**. The assignment of regiochemistry is based upon comparison of ^{1}H NMR data with that of the quinolone-2-ethyl-1-butene and 2-methylpropene adducts.[29a] The cyclobutane protons constitute a four-spin ABDD′ system with large cis and geminal coupling constants (J_{ab} = 8.4 Hz, J_{ad} = 12 Hz, $J_{d,d'}$ = 11.6 Hz) and a small trans coupling constant ($J_{ad'}$ = 4.8 Hz). The *endo*-ethyl group is shielded and its diastereotopic methylene protons resolved due to hindered rotation. Addition of 2-ethyl-1-butene to a solution of 0.02 M coumarin and 1 equiv of BF_3·OEt_2 resulted in isomerization of this alkene to a mixture of (*E*)- and (*Z*)-3-methyl-2-pentene prior to irradiation. The use of $EtAlCl_2$ in place of BF_3 allowed investigation of photochemical cross-cycloaddition without competing nonphotochemical alkene isomerization. The extensive investigations of Snider and co-workers[30] on the Lewis acid catalyzed ene reactions have established the suitability of $EtAlCl_2$ as a catalyst for alkenes that are susceptible to acid-catalyzed isomerization. Thus irradiation of a dichloromethane solution of 0.02 M coumarin and $EtAlCl_2$ with 0.4 M 2-ethyl-1-butene resulted in quantitative conversion of coumarin to two products formed in a ratio of 7:1. The major product proved to be identical with the product of benzophenone sensitization, **8**. The minor product was not isolated or characterized but may be the other regioisomer. The ratio of major to minor products is independent of alkene concentration (0.1–1.0 M). Formation of the alkylation products **4** and **5** was not observed to compete with cycloadduct formation.

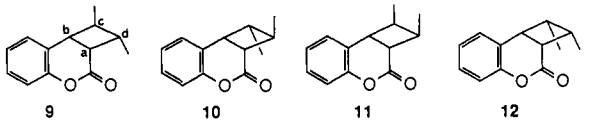
(28) Suginome, H.; Kobayashi, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3782.
(29) (a) Evanega, G. R.; Fabiny, D. L. *J. Org. Chem.* **1970**, *35*, 1757. (b) Whipple, E. B.; Evanega, G. R. *Org. Magn. Reson.* **1970**, *2*, 1.
(30) (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (b) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.

Table IX. Product Ratios for the Benzophenone-Sensitized and $EtAlCl_2$-Catalyzed Photocycloaddition of Coumarin to (*E*)- and (*Z*)-2-Butene[a]

time, min	[alkene], M	additive[b]	coumarin adducts, % 9	10	11	12
		(*E*)-2-Butene				
70	0.50	Ph_2C=O	6	27	64	3
60	0.10	$EtAlCl_2$	13	31	54	2
60	0.40	$EtAlCl_2$	15	42	42	2
85	1.00	$EtAlCl_2$	19	50	30	1
150[b]	1.96	$EtAlCl_2$	19	73	8	0
		(*Z*)-2-Butene				
100	0.50	Ph_2C=O	25	19	35	21
50	0.10	$EtAlCl_2$	9	20	45	27
50	0.40	$EtAlCl_2$	6	13	34	47
60	1.00	$EtAlCl_2$	2	4	20	74
95[b]	1.06	$EtAlCl_2$	1	2	12	84

[a] Data for 313-nm irradiation of coumarin (0.02 M) with 1 equiv of $EtAlCl_2$ in dichloromethane solution to high conversions (>80%). [b] Data for preparative scale reactions.

Irradiation of coumarin with (*E*)- or (*Z*)-2-butene in the presence of either benzophenone or $EtAlCl_2$ results in the formation of all four possible stereoisomeric [2 + 2] adducts (**9–12**).



9 **10** **11** **12**

Percent yields obtained in high-conversion experiments are summarized in Table IX. Product ratios for the $EtAlCl_2$-catalyzed reaction vary only slightly over the course of the reaction but are dependent upon the alkene concentration, high concentration favoring the products in which alkene stereochemistry is retained (**9** and **10** from (*E*)-2-butene and **11** and **12** from (*Z*)-2-butene). Similar results were obtained using BF_3 as the catalyst; however, somewhat greater retention of alkene stereochemistry was observed using BF_3 vs $EtAlCl_2$ at the same alkene concentration.

Samples of the four cycloadducts were obtained by chromatography of reaction mixtures enriched in a specific adduct and structures assigned on the basis of ^{1}H NMR data. Salient data for the cis endo adduct **12** include two large couplings for both H_a (br t, J = 9.0 Hz) and H_b (br t, J = 9.4 Hz), shielding of both Me_c and Me_d (δ 0.75 and 1.01), and the absence of shielding for H_c and H_d (δ 3.63 and 3.83). In contrast, the cis exo adduct **11** displays the effects of shielding for H_c and H_d (δ 3.12 and 3.22) but not for Me_c and Me_d (δ 1.18 and 1.21). Proton H_b displays one large and one small coupling constant (dd, J = 8.8, 4.0 Hz), as expected for cis coupling to H_a and trans coupling to H_c; however, H_a displays two large couplings (t, $J \sim 8$ Hz) indicative to a puckered cyclobutane ring with H_a and H_d trans diaxial and H_b and H_c trans diequatorial. The cyclobutane protons H_a and H_b of the trans adducts **9** and **10** also appear as triplets with J = 8.4–9.1 Hz, indicative of puckered rings in which $J_{cis} \sim J_{trans}$ (diaxial). Thus while vicinal coupling constants can be used to assign stereochemistry for planar cyclobutane rings such as those in **7**,[28,29a] they are unreliable in puckered cyclobutanes, as has previously been noted inter alia for the adducts of quinolone with monosubstituted olefins.[29b,31] Another indication of significant puckering in adducts **9–12** is the appearance of H_c and H_d as broadened hextets ($J \sim 8$ Hz) except in the case of H_c in adduct **11**. Evidently, $J_{cd} \sim 8$ Hz for both cis and trans isomers. We have relied upon chemical shift differences to distinguish between **9** and **10**, the upfield methyl in adduct **10** (δ 0.87) being assigned to endo Me_c.

The observation of increased stereospecificity with increasing alkene concentration (Table IX) suggests the possibility that Lewis acid catalyzed cross-cycloaddition, like coumarin dimerization, can occur via both singlet- and triplet-state mechanisms (Scheme

(31) Lewis, F. D.; Hirsch, R. H. *Tetrahedron Lett.* **1973**, 4947.

Table X. Rate Constants for Quenching of Coumarin–BF_3 Fluorescence by Coumarin and Alkenes

quencher	$k_q\tau$,[a] M^{-1}	k_q,[b] M^{-2} $s^{-1} \times 10^9$
coumarin	5.7	7.1
1-hexene	9.6	11
(*E*)-2-pentene	7.0	8.8
(*Z*)-2-pentene	14.8	19
cyclohexene	14.4	18
tetramethylethylene	24.5	31

[a] Slope of linear Stern–Volmer plot for quenching of the fluorescence of 10^{-4} M coumarin–BF_3 by 0.01–0.15 M quencher in deoxygenated CH_2Cl_2 solution. [b] Calculated using a lifetime of 0.8 ns (see text).

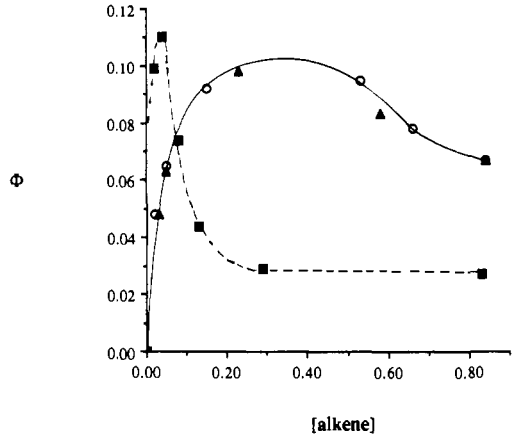


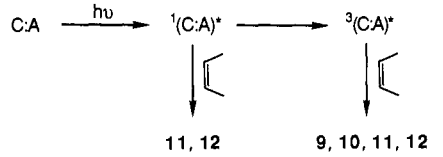
Figure 4. Cross-cycloaddition quantum yields vs alkene concentration for addition of tetramethylethylene (■), (*E*)-2-butene (○), and (*Z*)-2-butene (▲) to coumarin–$EtAlCl_2$.

II, C = coumarin, A = Lewis acid). Evidence for the reaction of the singlet coumarin–BF_3 complex with alkenes is provided by the fluorescence quenching data summarized in Table X. Rate constants for singlet quenching by alkenes, like that for quenching by ground-state coumarin, are near the rate of diffusion. The modest increase in rate constant with decreasing alkene ionization potential is indicative of exciplex formation in which the singlet complex serves as the electron acceptor and the alkene as the electron donor. The fluorescence quenching data suggests that 0.1 M alkene should suffice to quench ca. 40–70% of the coumarin–BF_3 singlet. Less extensive singlet quenching would be expected for the shorter lived coumarin–$EtAlCl_2$ complex.

Further evidence for the addition of alkenes to both singlet and triplet coumarin–$EtAlCl_2$ is provided by the concentration dependence of the cycloaddition quantum yields (Figure 4). Unlike the addition of alkenes to singlet and triplet alkanones for which quantum yields increase asymptotically with alkene concentration,[32] quantum yields for addition to coumarin–$EtAlCl_2$ are observed to increase to a maximum value and then decrease. This behavior can be attributed to a higher inherent quantum yield for the triplet-state reaction, which occurs at low alkene concentration, than for the singlet-state reaction, which occurs at high concentration. The change from mainly triplet-state to singlet-state addition over the 2-butene concentration range in Figure 4 parallels the change in cycloaddition stereospecificity observed over the same concentration range (Table IX). The occurrence of the quantum yield maximum for reaction of tetramethylethylene at lower concentrations than for the butenes is consistent with its higher rate constant for quenching of singlet coumarin–BF_3 (Table X).

Analysis of the product ratios in Table IX reveals several interesting features of the singlet- and triplet-state reactions.[33] If the products formed with inversion of butene stereochemistry are formed only via a triplet mechanism, their ratio should not change with increasing alkene concentration. This is clearly illustrated by the constant ratio for the formation of adducts **9** and **10** from (*Z*)-2-butene. Moreover, this ratio is different from the ratio for the formation of these products in the benzophenone-sensitized reaction. This difference indicates that the triplet complex does not dissociate to yield triplet coumarin prior to cycloaddition. Other interesting stereochemical features include the selective formation of the *exo-cis*-dimethyl adduct **11** in the triplet reactions of (*E*)-2-butene and of the *endo-cis*-dimethyl adduct **12** in the singlet-state reaction of (*Z*)-2-butene. The reaction of coumarin–BF_3 with cyclopentene is also more endoselective than is the benzophenone-sensitized reaction. The enhanced endoselectivity of complexed vs noncomplexed coumarin indicates that complexation does not introduce significant steric effects in the photocyclization process, thus discouraging efforts to induce chirality using chiral Lewis acids.

Scheme II



In summary, the [2 + 2] cross-cycloaddition reactions of coumarin with tetramethylethylene, cyclopentene, and 2-ethyl-1-butene can be effected using either benzophenone sensitization[7] or Lewis acid catalysis. Both procedures yield the same adducts; however, Lewis acid catalysis offers the advantage of somewhat higher optimum conversions and avoids the completing formation of sensitizer–olefin adducts. Similarly, both the benzophenone-sensitized and Lewis acid catalyzed reactions of coumarin with (*E*)- or (*Z*)-2-butene yield mixtures of all four possible [2 + 2] adducts. However, stereospecific cycloaddition can be achieved using Lewis acid catalysis and high olefin concentrations. Thus $EtAlCl_2$ catalysis was the method of choice for the preparation of adducts **9**, **10**, and **12**, while benzophenone sensitization was employed for the preparation of **11** (see the Experimental Section).

Concluding Remarks. Comparison of the results of this investigation with those of our previous study of the dimerization and cross-cycloaddition reactions of cinnamic esters[1] reveals several important characteristics of Lewis acid catalyzed photochemical [2 + 2] cycloaddition reactions. Both coumarin and the cinnamic esters form 1:1 ground-state complexes with the strong Lewis acids BF_3 and $EtAlCl_2$. These complexes have moderately large association constants (>100 M^{-1}) and absorb more strongly at long wavelengths than do the noncomplexed molecules. This permits selective excitation of the ground-state complexes using standard photochemical light sources and catalytic concentrations of Lewis acid (ca. 0.1 equiv). The excited complex can then react with noncomplexed coumarin or cinnamic ester to yield dimers or with alkenes to yield cross adducts.

A different mechanism has recently been reported by Ogawa et al.[34] for the dimerization of cyclopentenone in the presence of $SnCl_4$. Irradiation of the 2:1 complex results in regioselective formation of the anti head-to-head dimer rather than the anti head-to-tail dimer, which is the major product of direct irradiation. The yield of dimer is significantly lower in the presence of $SnCl_4$, and $BF_3{\cdot}OEt_2$ has little effect on the absorption spectrum or photochemical behavior of cyclopentenone.[34,35]

The observation of fluorescence from the coumarin–BF_3 singlet state facilitated investigation of the mechanism of cycloaddition. Singlet dimerization was found to yield the syn head-to-tail dimer (**3**), whereas triplet dimerization yields the anti head-to-head dimer (**2**; Scheme I). Similarly, the singlet cross-cycloaddition with (*E*)- and (*Z*)-2-butene occurs with retention of stereochemistry while the triplet reaction occurs with loss of butene stereochemistry (Scheme II). Unlike the stereoselective dimerization of singlet coumarin–BF_3, the dimerization of methyl cinnamate–BF_3 in

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solution yields a complex mixture of stereo- and regioisomers.[1] The absence of fluorescence from the cinnamic ester–BF_3 complex and competing *E,Z* isomerization[13] make it difficult to distinguish between singlet- and triplet-state mechanisms. An important difference in the cross-cycloaddition processes is the addition of tetramethylethylene to coumarin–BF_3 but not to methyl cinnamate–BF_3.

The enhanced photochemical reactivity of complexed vs noncomplexed coumarin and cinnamic esters can be attributed to increases in singlet-state lifetimes and electrophilicity. Both coumarin[18] and cinnamic esters[36] have low-lying n,π^* states, which are involved in the rapid decay of the spectroscopically observed lowest π,π^* states. Complexation of the carbonyl nonbonding electrons effectively removes this decay pathway. The quantum yield for dimerization of 5,7-dimethoxycoumarin, in which the π,π^* state lies well below the n,π^* state, is actually decreased upon BF_3 complexation; however, it is not known whether this results from a decrease in the excited-state lifetime or rate constant for dimerization.[11] While it is now clear that Lewis acid complexation can dramatically alter the photophysical and photochemical behavior of organic molecules, it is not yet possible to make generalized predictions from the limited data available.

Experimental Section

General Methods. Melting points were determined by using a Fisher-Johns melting point apparatus and are uncorrected. Ultraviolet absorption spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 283 infrared spectrophotometer. NMR spectra were obtained on a Varian EM390 or XLA 400 spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer MFP-44A spectrometer. Air-sensitive manipulations were performed under a N_2 atmosphere in a Kewaunee Scientific Products or Vacuum Atmospheres drybox.

The light source was a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex glass well. A potassium chromate solution filter was used to isolate the 313-nm line, and Corning glass filters 7-54 and 0-52 were used to isolate the 365-nm line. Analytical scale and quantum yield measurements were conducted under dry N_2 in 13-mm-o.d. Pyrex tubes fitted with rubber septa (cross-cycloaddition reactions) or 15-mm-o.d. Pyrex tubes equipped with Ace threads and O-ring seals (dimerization reactions) on a merry-go-round apparatus in a water bath. Light intensities were measured by using (*E*)-stilbene chemical actinometers run in triplicate.[37] Fluorescence lifetimes were measured on a PRA photon-counting apparatus.

Irradiated solutions were analyzed on a Varian 3700 or Hewlett-Packard 5890 gas chromatograph equipped with a flame-ionization detector. Cross-cycloaddition reactions were monitored by use of either a 6 ft × $^1/_8$ in. column containing 4% SF96 on Chromosorb G or a 10 m × 0.53 mm fused silica column coated with poly(dimethylsiloxane). Dimerization reactions were followed on a 10 m × 0.53 mm fused silica column coated with poly(dimethylsiloxane).

Materials. Coumarin (Aldrich) was recrystallized from diethyl ether prior to use. Coumarin syn head-to-tail (**3**) and anti head-to-head (**2**) dimers were prepared according to literature procedures.[2a,10] Tetramethylethylene (Wiley Organics) and cyclopentene (Aldrich) were distilled from P_2O_5 before use. 2-Ethyl-1-butene (Wiley Organics) and (*E*)- and (*Z*)-2-butene (Phillips) were used as received. Boron trifluoride (Matheson), ethyl aluminum dichloride (Aldrich), and boron trifluoride etherate (Aldrich, redistilled) were all used without any further purification. The coumarin–BF_3 complex was prepared by purging a concentrated (~0.6 M) solution of coumarin in dichloromethane with BF_3 and evaporating the solvent with a stream of N_2. The coumarin–$EtAlCl_2$ complex was prepared by adding 1 mol equiv of $EtAlCl_2$ to a solution of coumarin in dichloromethane and evaporating the solvent with a stream of N_2. Dichloromethane (Mallinckrodt, spectroscopic grade) was refluxed over calcium hydride and distilled immediately prior to use. For the dimerization experiments, dichloromethane was deoxygenated under vacuum (0.01–0.02 mmHg) by four freeze–pump–thaw cycles and stored and manipulated under an N_2 atmosphere in a Vacuum Atmospheres drybox.

Irradiation of Coumarin in the Presence of $EtAlCl_2$. Coumarin (1.46 g, 0.01 mol) was dissolved in dichloromethane in a 0.05-L volumetric flask and transferred to a dried Pyrex annulus, which was sealed with a rubber septum. The sample was purged with N_2 for 10 min and $EtAlCl_2$ (0.075 mL, 7.1 × 10^{-4} mol) added to the sample by syringe. The sample was then irradiated with a 450-W lamp for 32.5 h. Examination of the solution by GC after irradiation was terminated showed that >95% of the coumarin had been consumed and that two major photoproducts had been formed. The solution was extracted with water, the organic and aqueous layers were separated, and the aqueous layer was extracted with dichloromethane. The aqueous layer was discarded. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation to give 1.27 g (87%) of a solid brown material. Comparison of the ^1H NMR spectrum of the solid with the ^1H NMR spectra of authentic samples of the coumarin anti head-to-head (**2**)[2a] and syn head-to-tail (**3**)[10] dimers indicated that it consisted of **3** and **2** in a 3.5:1 ratio. Addition of dichloromethane to the solid yielded 0.44 g (30%) of white crystals. ^1H NMR analysis of the crystals indicated that they were composed of **3** and **2** in a 1:1 ratio. ^1H NMR analysis of the remaining material showed that it was composed solely of **3**.

Irradiation of Coumarin in the Presence of Excess $EtAlCl_2$. Preparation of 4 and 5. Coumarin (0.292 g, 0.002 mol) was dissolved in 0.1 L of dichloromethane and the solution purged with N_2 for 5 min. $EtAlCl_2$ (2.1 mL, 0.02 mol) was then added to the solution by syringe. The solution was transferred to a dry, sealed, N_2-purged Pyrex annulus and purged with N_2 for an additional 5 min. Irradiation with a 450-W lamp for 35 min followed by analysis by GC indicated quantitative consumption of coumarin and the formation of two major products in a 1.1:1 ratio. After workup as described above, 0.35 g of a brown oil was obtained. Most of this oil (0.30 g) was subjected to chromatographic separation on 30 g of silica gel with a 25% ethyl acetate/75% hexane solvent mixture. Early fractions were found to be enriched in product **4**.[38] These fractions were combined, and the solvent was removed by rotary evaporation to yield 0.070 g (20%) of a yellow oil: ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7 Hz, 3 H), 1.63 (q, J = 7 Hz, 2 H), 2.67–3.10 (m, 3 H), 6.90–7.10 (m, 4 H); IR (neat) λ_{max} 2980, 2940, 2890, 1775, 1615, 1590, 1490, 1460, 1360, 1220, 1150, 910, 870, 760 cm^{-1}. Later fractions were found to be enriched in product **5**.[39] Combining these fractions and removing the solvent by rotary evaporation afforded 0.063 g (18%) of a yellow oil: ^1H NMR ($CDCl_3$) δ 1.32 (t, J = 7.5 Hz, 3 H), 2.80 (q, J = 7.5 Hz, 2 H), 6.25 (s, 1 H), 6.77–7.70 (m, 4 H); IR (neat) λ_{max} 3075, 3030, 2990, 2330, 1770 (sh), 1720, 1600, 1440, 1375, 1180, 925, 865, 790 cm^{-1}.

Irradiation of Coumarin and Tetramethylethylene in the Presence of BF_3·OEt_2. Preparation of 6. Coumarin (0.29 g, 0.002 mol) and BF_3·OEt_2 (0.123 mL, 0.001 mol) were combined with dichloromethane in a 0.1-L volumetric flask and allowed to stand for approximately 15 min. Tetramethylethylene (2.4 mL, 0.020 mol) was then added to the flask and the solution made to volume with additional dichloromethane. The sample was transferred to a Pyrex annulus, sealed with a rubber septum, and purged with dry N_2 gas for approximately 5 min. The sample was then irradiated with a 450-W lamp equipped with a Pyrex lamp well for 4.75 h. The sample was cooled in an ice water bath throughout the irradiation period. Workup as described above afforded a dark brown oil. The oil was dissolved in benzene and filtered through a thin layer of silica gel, and the sample was reconcentrated to give a bright yellow oil. Addition of hexane to this material resulted in crystallization, yielding 0.26 g (57%) of small, flat white crystals: mp 82–83 °C (lit.[7] mp 81 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 0.75 (s, 3 H), 1.02 (s, 3 H), 1.22 (s, 3 H), 1.27 (s, 3 H), 3.16, 3.38 (AB quartet, 2 H, J_{AB} = 10 Hz), 6.87–7.33 (m, 4 H); IR ($CHCl_3$) λ_{max} 1745, 1500, 1460, 1245, 1210, 1180, 1155, 1120, 1020 cm^{-1}.

Irradiation of Coumarin and Cyclopentene in the Presence of BF_3·OEt_2. Preparation of *endo*-7. A solution of coumarin (0.292 g, 0.002 mol), BF_3·OEt_2 (0.256 mL, 0.002 mol), and cyclopentene (3.51 mL, 0.050 mol) in 0.1 L of dichloromethane was prepared as described in the previous procedure. Irradiation with a 450-W lamp for 1.25 h followed by analysis by GC indicated quantitative consumption of coumarin. After workup as described in the previous procedure, a dark brown oil was obtained. The oil was dissolved in benzene and filtered through a thin layer of silica gel, and the sample was reconcentrated to yield 0.30 g (70%) of a white solid. The ^1H NMR spectrum of this solid showed it to be a ca. 2:1 mixture of the endo and exo adducts reported by Suginome and Kobayashi.[28] Recrystallization of this solid from benzene/hexane afforded 0.16 g (37%) of white crystals: mp 136–138 °C (lit.[7] mp 139 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 1.03–2.23 (m, 6 H), 3.0–3.6 (m, 2 H), 3.60–4.17 (m, 2 H), 6.93–7.47 (m, 4 H); IR ($CHCl_3$) λ_{max} 1750, 1500, 1460, 1360, 1180, 1110 cm^{-1}.

Irradiation of Coumarin and 2-Ethyl-1-butene in the Presence of

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$EtAlCl_2$. Preparation of 8. A solution of coumarin (0.292 g, 0.002 mol), $EtAlCl_2$ (0.205 mL, 0.002 mol), and 2-ethyl-1-butene (4.88 mL, 0.040 mol) in 0.1 L of dichloromethane was prepared as described above except that the solution was cooled in an ice bath prior to addition of 2-ethyl-1-butene. The sample was transferred to a dry, sealed, N_2-purged Pyrex annulus through a cannula and irradiated for 3.75 h with a 450-W lamp. Examination of the irradiated solution by GC indicated quantitative consumption of coumarin and the formation of two products in a 6.7:1 ratio. Workup as described above afforded a dark brown oil (91%). The oil was dissolved in benzene and filtered through silica gel, and the solvent was removed by rotary evaporation to yield an oily residue, which upon crystallization from hexane yielded 0.16 g (35%) of small white crystals: mp 80–81 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.62 (t, J = 7.5 Hz, 3 H), 0.95 (t, J = 7.5 Hz, 3 H), 1.08 (q, J = 7.5 Hz, 1 H), 1.21 (q, J = 7.5 Hz, 1 H), 1.67 (q, J = 7.5 Hz, 2 H), 2.19 (dd, J = 11.6 and 4.8 Hz, H_d endo), 2.36 (br t, J = 12 Hz, H_d exo), 3.46 (m, H_a), 3.53 (d, J = 8.0 Hz, H_b), 6.92–7.38 (m, 4 H); IR ($CHCl_3$) λ_{max} 1755, 1495, 1460, 1225, 1175 cm^{-1}; MS m/e 230, 147, 146, 118. Exact mass calcd for $C_{15}H_{18}O_2$: 230.2307. Found: 230.1301.

Irradiation of Coumarin and (E)-Butene in the Presence of $EtAlCl_2$. Preparation and Isolation of 9 and 10. Coumarin (0.293 g, 0.002 mol), (E)-2-butene (11.0 g, 0.196 mol), and $EtAlCl_2$ (0.205 mL, 0.002 mol) were combined in 0.1 L of dichloromethane and irradiated (2.5 H) as described in the previous procedure. Examination of the solution by GC after irradiation was terminated indicated near quantitative consumption of coumarin and the formation of one major (81%) and one minor (19%) product. Workup as described above yielded 0.40 g (100%) of a brown oil. This material was dissolved in benzene and filtered through silica gel, and the solvent was removed by rotary evaporation, yielding 0.30 g (75%) of a bright yellow oil. This oil was subjected to chromatographic separation on 20 g of silica gel with a 75% CCl_4/25% benzene solvent mixture. Adduct **9** was found to be enriched (>90%) in early fractions. These fractions were combined, and the solvent was removed by rotary evaporation to afford 0.03 g (7.5%) of a semicrystalline solid: ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, J = 8.5 Hz, Me_d), 1.20 (d, J = 7.0 Hz, Me_c), 2.02 (br h, $J \sim 7$ Hz, H_c), 2.53 (br h, $J \sim 7$ Hz, H_d), 3.13 (t, $J_1 \approx J_2$ = 8.4 Hz, H_a), 3.50 (t, $J_1 \approx J_2$ = 8.9 Hz, H_b), 7.03–7.28 (m, 4 H). Adduct **10** was found to be enriched in later fractions. These fractions were combined, and the solvent was removed by rotary evaporation to afford 0.06 g (15%) of a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, J = 6.8 Hz, Me_c), 1.25 (d, J = 7.2 Hz, Me_d), 2.27 (br h, $J \sim$ 7 Hz, H_d), 2.50 (br h, $J \sim 7$ Hz, H_c), 3.04 (t, $J_1 \approx J_2$ = 8.6 Hz, H_a), 3.69 (t, $J_1 \approx J_2$ = 8.4 Hz, H_b), 6.96–7.31 (m, 4 H).

Irradiation of Coumarin and (Z)-2-Butene in the Presence of Benzophenone. Preparation of 11. Coumarin (0.293 g, 0.002 mol) and benzophenone (0.0728 g, 0.004 M) were combined in dichloromethane in a dry, N_2-purged 0.1-L volumetric flask. The flask was sealed with a rubber septum and the solution purged with N_2 for 5 min and immersed in an ice/NaCl bath. (Z)-2-Butene (2.63 g, 0.047 mol) was condensed into a graduated test tube cooled in dry ice/CCl_4 and transferred by cannula to the cooled volumetric flask. The sample was made to volume by addition of N_2-purged dichloromethane with a gas-tight syringe and transferred by cannula to a sealed, dry N_2-purged Pyrex annulus. The sample was then irradiated with a 450-W lamp for 0.75 h while cooled in ice water. Examination of the solution by GC after irradiation was terminated indicated near quantitative consumption of coumarin and the formation of five products. Removal of solvent by rotary evaporation afforded 0.59 g of a colorless oil. This oil was subjected to chromatographic separation on silica gel with a 4% ethyl acetate/hexane solvent mixture. The solvent was removed from fractions enriched in adduct **11** (>85%) by rotary evaporation to yield 0.04 g (10%) of a colorless oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J = 8.0 Hz, 3 H), 1.21 (d, J = 7.2 Hz, 3 H), 2.50 (m, H_c), 2.94 (br h, $J \sim 7.6$ Hz, H_d), 3.12 (t, J = 8.0 Hz, H_a), 3.22 (dd, J = 8.8 and 4.6 Hz, H_b), 7.00–7.26 (m, 4 H).

Irradiation of Coumarin and (Z)-2-Butene in the Presence of $EtAlCl_2$. Preparation of 12. A solution of coumarin (0.293 g, 0.002 mol), $EtAlCl_2$ (0.205 mL, 0.002 M), and (Z)-2-butene (5.91 g, 0.047 mol) was prepared and irradiated (1.6 h) as described above. Examination of the solution by GC after irradiation was terminated indicated near quantitative consumption of coumarin and the formation of one major (84%) and three minor products. Workup as described above yielded 0.38 g (94%) of a yellow oil, which formed impure crystals at room temperature. This material was dissolved in benzene and filtered through silica gel, the solvent was removed by rotary evaporation, and the residue was recrystallized from hexane, yielding 0.14 g (37%) of white crystals: mp 86–88 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75 (d, J = 7.4 Hz, Me_c), 1.01 (d, J = 7.8 Hz, Me_d), 2.99 (br h, $J \sim 7.5$, H_d), 3.11 (br h; $J \sim 7.5$ Hz, H_c), 3.63 (t, $J_1 \approx J_2$ = 9.0 Hz, H_a), 3.82 (t, $J_1 \approx J_2$ = 9.4 Hz, H_b), 6.95–7.25 (m, 4 H); IR ($CHCl_3$) 1760, 1500, 1460, 1240, 1190, 1170 cm^{-1}; MS m/e 202, 147, 146, 118. Exact mass calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.0996.

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