Table VII. Association Constants and Free Energies of Complexation at 25 °C in $CDCl_3$ Saturated with $D_2O$ Determined by Equilibration Experiments between Two Host-Guest Picrate Complexes Whose Cationic Partners Disproportionate

| picrate complexes | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | reference | | | | | | | |
| studied AD | AB | CD | $[CD]_i/[AB]_i$ | $[AD]_e/[AB]_i$ | $K_e$ | $K_a^{CD}/K_a^{CB}$ [b] | $K_a^{AD}$ [a] ($M^{-1}$) | $-\Delta G°$ (kcal $mol^{-1}$) |
| **2**·$Rb^+$ | **2**·$Li^+$ | **12**·$Rb^+$ | 2.703 | 0.810 | 1.82 | $8.20 \times 10^4$ | $9.18 \times 10^{14}$ | 20.4 |
| **2**·$Cs^+$ | **2**·$Li^+$ | **12**·$Cs^+$ | 3.969 | 0.200 | 0.013 | $1.28 \times 10^4$ | $1.02 \times 10^{12}$ | 16.4 |
| **2**·$NH_4^+$ | **2**·$Li^+$ | **12**·$NH_4^+$ | 1.829 | 0.679 | 1.25 | $5.50 \times 10^3$ | $4.22 \times 10^{13}$ | 18.6 |
| **3**·$Cs^+$ | **3**·$NH_4^+$ | **12**·$Cs^+$ | 0.695 | 0.530 | 3.62 | 2.32 | $5.50 \times 10^{15}$ | 21.5 |
| | | | 0.668 | 0.562 | 6.80 | 2.32 | $1.03 \times 10^{16}$ | 21.8 |

[a] The $K_a^{AB}$ values used to calculate these values are taken from Table VI and are as follows: for LiPic binding **2**, $K_a^{AB} = 6.14 \times 10^9$ $M^{-1}$; for $NH_4$Pic binding **3**, $K_a^{AB} = 6.53 \times 10^{14}$ $M^{-1}$. [b] The $K_a$ values for 18-crown-6 binding the various picrate salts at 25 °C in $CDCl_3$ saturated with $D_2O$ are as follows: $Li^+$, $4.44 \times 10^5$ $M^{-1}$; $Rb^+$, $3.64 \times 10^{10}$ $M^{-1}$; $NH_4^+$, $2.44 \times 10^9$ (ref 15). That for $Cs^+$ was estimated to be $5.67 \times 10^9$ $M^{-1}$ by interpolating a linear plot (similar to Figure 1) of $-\Delta G°$ values for KPic, RbPic, and $NH_4$Pic binding 18-crown-6 in $CDCl_3$–$D_2O$ at 25 °C, and $-\Delta G°$ values for 18-crown-6 binding the same ions in $CH_3OH$ (De Jong, F.; Reinhoudt, D. N. *Adv. Phys. Org. Chem.* **1980**, *17*, 279-433). These authors reported the $K_a$ values for 18-crown-6 binding $Cs^+$ in $CH_3OH$ but did not report the $K_a$ for 18-crown-6 binding CsPic in $CDCl_3$–$D_2O$ (ref 15).

Experimentally, stock solutions of the various complexes were prepared and mixed as in method A. The $^1H$ NMR spectral signals of complexes AB and AD were distinguished and integrated, as were the signals of total picrate ion. These signals were integrated immediately to give $[CD]_i/[AB]_i$ ratios, AB directly, and CD from total pic − AB. The complexes were allowed to equilibrate at 25 °C in the dark. After many hours, the integrals stopped changing, at which time AB, AD, and total pic integrals were taken. These, coupled with the initial integrals, gave $[AB]_e/[AB]_i$ directly, $[AD]_e/[AB]_i$ from eq 10, $[CB]_e/[AB]_i$ from eq 11, and $[CD]_e/[AB]_i$ from eq 12. These values and eq 8 provided $K_e$ values, which coupled with the known values of $K_a^{AB}$, $K_a^{CB}$, and $K_a^{CD}$ and eq 8 provided the desired $K_a^{AD}$ values. Table VII identifies the complex AD whose $K_a^{AD}$ is being determined, the reference complexes AB and CD, and lists the values of $[CD]_i/[AB]_i$, $[AD]_e/[AB]_i$, $K_e$, and $K_a^{CD}/K_a^{CB}$.

**Molecularity in the Equilibria.** The equations developed for converting the data of methods A and B into $K_a$ and $-\Delta G°$ values are valid only if the hosts and their complexes are monomeric at 25 °C in $CDCl_3$ saturated with $D_2O$ at concentrations $\approx 10^{-3}$ M. In extensive work in which we applied the picrate salt extraction method to a variety of chorands and hemispherands, we demonstrated the $-\Delta G°$ values obtained at 25 °C in $CDCl_3$ saturated with water were independent (within error) of initial concentrations of host and guest ranging from 0.015 to 0.001 M.[5,13] Many different experimentalists obtained $-\Delta G°$ values within 0.2 kcal $mol^{-1}$ or less of one another working with a large number of host-guest combinations. In equilibration experiments in the same medium at 25 °C with **9**·LiPic as the starting complex and **6** or **7** as the acceptor host, $[AG]_i/[B]_i$ values were varied between 0.69 and 5.0 to give $K_a$ values that lay between $0.93 \times 10^{12}$ and $2.9 \times 10^{12}$ $M^{-1}$ ($(K_a)_{av} = 1.7 \pm 0.5 \times 10^{12}$ $M^{-1}$ and $-\Delta G° = 16.7$ kcal $mol^{-1}$) for **9** binding LiPic.[5] Two different experimentalists were involved in obtaining these values. In the same medium at 25 °C with **10**·NaPic as the initial complex and **6** as the acceptor host, $[AG]_i/[B]_i$ values were varied in three runs between 1.1 and 5.9 (absolute concentrations $\approx 10^{-3}$ M) with only a $-\Delta G°$ change of 0.2 kcal $mol^{-1}$ for **10** binding NaPic.[21] The $-\Delta G°$ values for **6** binding NaPic in the same medium at 25 °C determined by the picrate salt-extraction method was 13.6 kcal $mol^{-1}$ and by a kinetic method was 13.3 kcal $mol^{-1}$.[5] Two different experimentalists were involved in these completely different types of measurements. The $^1H$ NMR chemical shifts in $CDCl_3$ of a wide variety of spherands, hemispherands, cryptahemispherands, and chorands, and of their alkali metal and ammonium complexes have been shown not to change as their concentrations were varied from 0.05 to 0.001 M concentration (former papers in this series). These facts, taken in sum, indicate that at the concentrations used, the hosts and their complexes are essentially monomeric at 25 °C in $CDCl_3$ saturated with $D_2O$. The outside error limits for $-\Delta G°$ values determined by method A we estimate to be ±1 kcal $mol^{-1}$ and for those by method B to be ±1.5 kcal $mol^{-1}$. In those cases where the results of a single run are reported, less exact runs were made to probe the concentrations required to maximize the sensitivities of the measurements. At least one inexact determination, and in most cases several more, were made which provided $-\Delta G°$ values closer to those reported than the above quoted error limits.

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[21] Cram, D. J.; Lein, G. M., unpublished results.

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# Lewis Acid Catalysis of Photochemical Reactions. 4. Selective Isomerization of Cinnamic Esters[1]

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*Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201.* *Received July 8, 1985*

**Abstract:** The spectroscopic properties and photoisomerization reactions of several (*E*)- and (*Z*)-cinnamic esters, bis cinnamic esters, and model esters and lactones in the presence and absence of Lewis acids have been investigated. The use of Lewis acids such as $BF_3$ or $EtAlCl_2$ results in enhanced photoisomerization efficiency and a shift in the photoequilibrium toward the thermodynamically less stable *Z* isomer. Enhanced *E* → *Z* photoisomerization results from selective excitation of ground-state ester-Lewis acid complexes. These complexes have been characterized by $^1H$ NMR, ultraviolet, and fluorescence spectroscopies. The equilibrium constants for complexation are dependent upon both the electron donor strength of the ester and its conformational mobility. These factors also determine the magnitude of the red shifts in the electronic absorption spectra observed upon complexation. Enhanced *E* → *Z* photoisomerization upon complex formation is a consequence of selective excitation of the *E* vs. *Z* complex, more efficient isomerization of the excited *E* vs. *Z* complex, and larger equilibrium constants for complexation of *E* vs. *Z* esters. The photoequilibria obtained for bis cinnamic esters are highly enriched in the *Z,Z* and *Z,E* isomers in accord with independent isomerization of the two cinnamate groups; however, in the case of 1,3-trimethylenebis(cinnamate), two-bond isomerization of the *E,E* to *Z,Z* isomer is observed at low conversions.

Photoisomerization presents the only direct method for contrathermodynamic *E* → *Z* isomerization of olefins.[2,3] Synthetic applications[4] of this method have been limited by its reversible nature, which, in the absence of other reactions, leads to a

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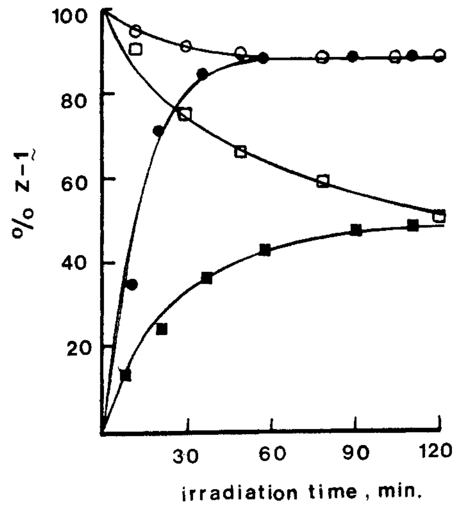

**Figure 1.** Formation of (*Z*)-**1** upon irradiation of (*E*)-**1** in the absence (■) and presence (●) of $BF_3\cdot OEt_2$ and the disappearance of (*Z*)-**1** upon irradiation in the absence (□) and presence (○) of $BF_3\cdot OEt_2$.

photostationary-state mixture of isomers. The composition of these mixtures is governed by isomerization quantum yields and extinction coefficients (direct irradiation) or rate constants for triplet energy transfer (triplet sensitization). Photostationary states enriched in the thermodynamically less stable *Z* isomer are observed only in cases where the *E* isomer is more strongly absorbing than the *Z* isomer (e.g., long-wavelength irradiation of the stilbenes[2]) or the triplet energy of the *E* isomer is lower than that of the *Z* isomer (e.g., triplet-sensitized isomerization of β-ionol[5]). Unfortunately, neither direct irradiation nor triplet sensitization provides a general method of selective $E \rightarrow Z$ isomerization. In addition to triplet sensitization, various additives (radical initiators,[6] electron acceptors,[7] protic acids,[8] metal ions,[9] metal carbonyls,[9] lanthanide shift reagents,[10] etc.) and restricted environments[11] (high pressure, organized assemblies, solid state, etc.) have been used to alter photoisomerization pathways; however, none of these methods effect high-yield $E \rightarrow Z$ conversion.

The effects of strong Brønsted acids on the photoisomerization reactions of α,β-unsaturated carbonyl compounds and imines have been investigated by Childs and co-workers.[8] While protonation of the carbonyl oxygen or imine nitrogen leads to changes in absorption spectra and enhanced isomerization of the conjugated double bond, acid-catalyzed thermal isomerization may preclude high $E \rightarrow Z$ conversions. It occurred to us that complexation of α,β-unsaturated carbonyl compounds by conventional strong Lewis acids such as $BF_3$ or $AlCl_3$ might alter the spectroscopic properties and photochemical behavior of α,β-unsaturated carbonyl compounds without the occurrence of competing thermal isomerization. Reports of photodimerization of enones[12] and valence isomerization of dienones[13] in the presence of Lewis acids encouraged us to believe that this might be the case. Our preliminary investigations have established that Lewis acids are effective catalysts not only for selective $E \rightarrow Z$ photoisomerization of α,β-unsaturated carbonyl compounds[14] but also for their photodimerization and cross-cycloaddition reactions.[1] We describe here our detailed investigation of the effects of Lewis acids on the photoisomerization of several cinnamic esters and related molecules.

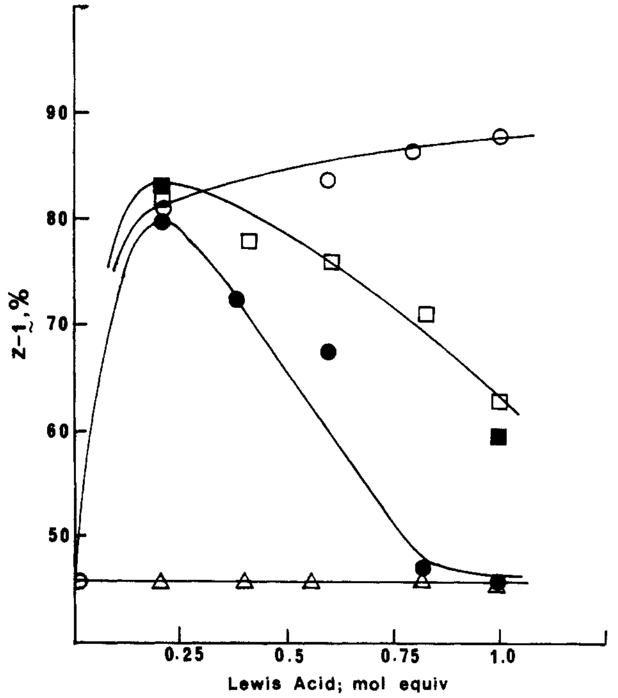

**Figure 2.** Effect of Lewis acid concentration on the optimum conversion of (*E*)-**1** to (*Z*)-**1** in the presence of $BF_3\cdot OEt_2$ (○), $SnCl_4$ (●), $AlCl_3$ (□), $EtAlCl_2$ (■), and $ZnCl_2$ (△) in dichloromethane solution.

## Results

**Photoisomerization of Methyl Cinnamate (1).** Irradiation of 0.01 M (*E*)-**1** or (*Z*)-**1** in benzene solution with a Pyrex-filtered high-pressure mercury lamp ($\lambda > 300$ nm) or monochromatic 313-nm light results in the formation of a photostationary state consisting of 54% (*E*)-**1** and 46% (*Z*)-**1** (Figure 1). Photodimerization[15] does not compete with *E*,*Z* isomerization under these conditions. Similar values of the photostationary state are obtained for dichloromethane, benzene, methanol, and acetonitrile solutions (46 ± 2% (*Z*)-**1**), while lower conversion to (*Z*)-**1** (25%) is observed in hexane solution. Somewhat higher conversions of *E* to *Z* isomers (57–69%) have been reported for 254-nm irradiation of cinnamic acids[16] and esters.[17]

Irradiation of 0.01 M (*E*)-**1** or (*Z*)-**1** with 0.8 equiv of $BF_3\cdot OEt_2$ in benzene or dichloromethane solution results in a photostationary state consisting of 12% (*E*)-**1** and 88% (*Z*)-**1** (Figure 1). Both

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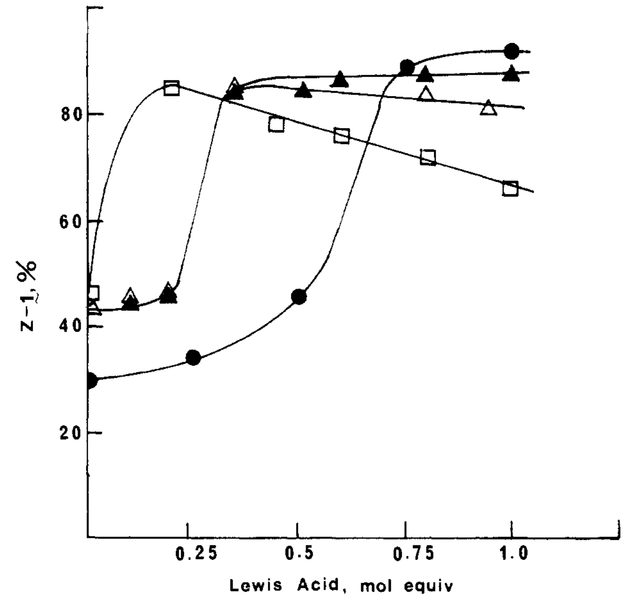


**Figure 3.** Solvent dependence of the optimum conversion of (*E*)-**1** to (*Z*)-**1** in the presence of $AlCl_3$ (empty symbols) and $EtAlCl_2$ (filled symbols) in hexane (○), benzene (△), and dichloromethane (□) solutions.

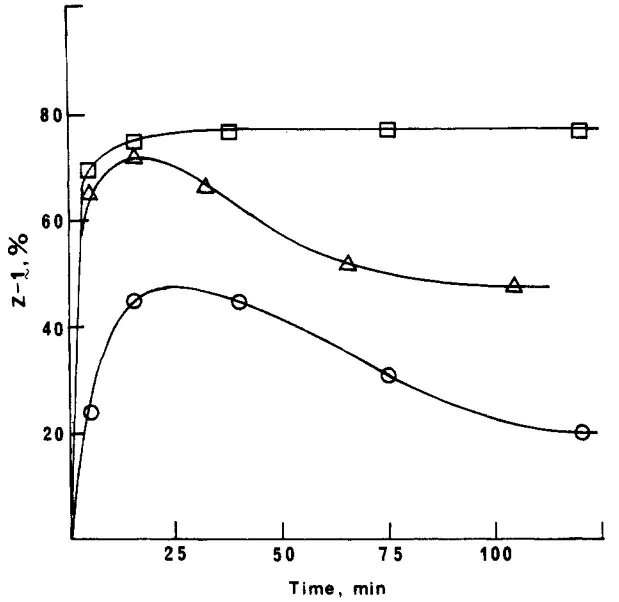


**Figure 4.** Time dependence of the conversion of (*E*)-**1** to (*Z*)-**1** in the presence of $EtAlCl_2$ (0.4 M) in dichloromethane solution (□), 0.4 M in benzene solution (△), and 0.5 M in hexane solution (○).

the initial rate of isomerization of (*E*)-**1** and the approach to equilibrium are more rapid in the presence of $BF_3$ than in its absence. The effect of varying Lewis acid concentration on the optimum conversion of (*E*)-**1** to (*Z*)-**1** in dichloromethane solution is shown in Figure 2. Conversions of ≥80% are observed with 0.2 equiv of $BF_3{\cdot}OEt_2$, $AlCl_3$, $EtAlCl_2$, and $SnCl_4$. At higher Lewis acid concentrations, the conversion increases slightly for $BF_3{\cdot}OEt_2$ but decreases using $AlCl_3$, $EtAlCl_2$, or $SnCl_4$. No change in the rate of isomerization or the photostationary state was observed in the presence of $ZnCl_2$. The Lewis acids $FeCl_3$, $TiCl_4$, Eu(fod)$_3$, and Ag(fod) retard the rate of photoisomerization of (*E*)-**1** and do not enhance the optimum conversion of (*E*)-**1** to (*Z*)-**1**. These results and the ease of handling $BF_3{\cdot}OEt_2$ and $EtAlCl_2$ solutions made them the Lewis acids of choice for our investigations. Solutions of (*E*)-**1** and (*Z*)-**1** with these Lewis acids are stable at room temperature in the absence of light.

The optimum conversion of (*E*)-**1** to (*Z*)-**1** in the presence of $AlCl_3$ or $EtAlCl_2$ in hexane, benzene, and dichloromethane solution is shown in Figure 3. Similar conversions (85–92%) were obtained in all three solvents; however, the amount of Lewis acid required to obtain the optimum conversion is solvent dependent. This dependence may reflect differences in photostability of $EtAlCl_2$ in these solvents. As shown in Figure 4, the conversion of (*E*)-**1** to (*Z*)-**1** obtained with 0.4 equiv of $EtAlCl_2$ in dichloromethane solution is independent of irradiation time (40–120 min), whereas the conversion obtained in benzene or hexane solution reaches an optimum value in 15–40 min and decreases with further irradiation. This decrease plausibly results from decomposition of the $EtAlCl_2$ under the conditions of irradiation, which would necessitate the use of higher concentrations to obtain optimum conversions of (*E*)-**1** to (*Z*)-**1** (Figure 3). The use of more strongly coordinating solvents such as ethers, alcohols, and nitriles would preclude effective complexation of the Lewis acid and cinnamic ester. Thus dichloromethane was the solvent of choice for our investigations.

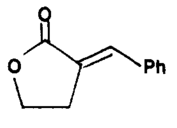
**Photoisomerization of Cinnamic Esters.** Optimum conversions of *E* to *Z* isomer for the cinnamic esters (**1–7**) are given in Table I. In the absence of Lewis acid, the optimum conversions range from 21% to 55%, while in the presence of Lewis acids optimum conversions of ≥85% are observed. The irradiation conditions are the same as those described in the preceding section for (*E*)-**1** and have not been optimized for the other esters. Variation in the alkoxy group in **1–3** has little effect on the conversions obtained in the absence or presence of Lewis acid. Conversions for the para-substituted esters **4** and **5** are higher than that for **1**, as previously reported for 254-nm irradiation,[17a] while that for **6** is lower than for **1**. The presence of an α-methyl group in **7** has little effect upon conversion of free or complexed ester, as previously reported for the free acid and ester.[16b]

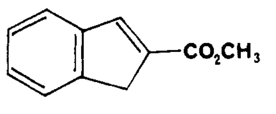
Table I. Optimum Conversions of *E* to *Z* Isomers for Cinnamic Esters and Related Molecules[a]

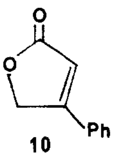
| | reactant | Lewis acid | | | |
|---|---|---|---|---|---|
| | | none | $BF_3{\cdot}OEt_2$ | $EtAlCl_2$ | $AlCl_3$ |
| **1** | methyl cinnamate | 46 | 88 | 86 (92)[b] | 83 |
| **2** | ethyl cinnamate | 42 | 81 | 85 | 87 |
| **3** | *tert*-butyl cinnamate | 42 | | 85 | 86 |
| **4** | methyl *p*-methylcinnamate | 57 | 87 | | |
| **5** | methyl *p*-chlorocinnamate | 55 | 87 | | |
| **6** | methyl *p*-(trifluoromethyl)-cinnamate | 21 | 85 | | |
| **7** | methyl α-methylcinnamate | 42 | 88 | 86 | |
| **8** | α-benzylidene-γ-butyrolactone | 24 | 26 | 17 | |

[a] Benzene solutions 0.01 M in ester and 0.01 M in $BF_3{\cdot}OEt_2$ or 0.004 M in $AlCl_3$ or dichloromethane solution. 0.004 M in $EtAlCl_2$ or $AlCl_3$ irradiated with Pyrex-filtered light. [b] Value for hexane solution.

The photoisomerization of (*E*)-α-benzylidene-γ-butyrolactone ((*E*)-**8**) has previously been reported without quantitative details by Ullman and Baumann.[18] We find that irradiation of either (*E*)-**8** or (*Z*)-**8** (313 nm) yields a photostationary state consisting of 75% *E* and 25% *Z* isomers. Irradiation of (*E*)-**8** in the presence of either $EtAlCl_2$ (0.2–1.0 equiv) or $BF_3{\cdot}OEt_2$ results in a constant or decreased conversion to (*Z*)-**8**. Two additional cinnamate ester analogues which are unable to undergo *E*,*Z* isomerization, methyl indenoate, **9**, and β-phenyl-γ-crotonolactone, **10**, were also prepared for purposes of spectral comparisons with acyclic cinnamic esters.


**E-8**


**9**


**10**

**Photoisomerization of *E*,*E* Bis Cinnamic Esters.** Irradiation of the *E*,*E* bis esters **11–13** (0.01 M) in benzene or dichloromethane solution results in the formation of the *E*,*Z* and *Z*,*Z* isomers and intramolecular 2 + 2 photodimers.[19] Isomerization

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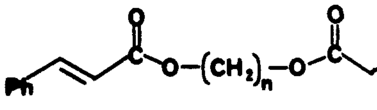

**11**, n = 2
**12**, n = 3
**13**, n = 4

is more efficient than dimerization and leads to the formation of quasi-stationary-state mixtures of *E*,*Z* isomers (Table II) prior to extensive conversion to dimers (<10%).[19a] Similar isomer mixtures are obtained for **11**–**13**. A plot of the isomer composition vs. irradiation time for **12** is shown in Figure 5a. The upward curvature observed for the formation of the *Z*,*Z* isomer at short irradiation times is indicative of its formation via the *E*,*Z* isomer.

Irradiation of **11**–**13** in the presence of $\mathrm{BF_3{\cdot}OEt_2}$ results in more rapid isomerization (and dimerization) and substantially higher conversions to the *Z*,*Z* isomer than obtained in its absence (Table II). A plot of the isomer composition vs. irradiation time for **12** in the presence of 0.5 mol equiv of $\mathrm{BF_3{\cdot}OEt_2}$ is shown in Figure 5b. No induction period is observed for the formation of (*Z*,*Z*)-**12**; the ratio of *E*,*Z*/*Z*,*Z* isomers is 3.2 ± 0.4 for 0.5–15% conversion of (*E*,*E*)-**11** (0.25–5.0-min irradiation, data not included in Figure 5b) and decreases only at longer irradiation times. Induction periods are observed for the formation of (*Z*,*Z*)-**11** and (*Z*,*Z*)-**13** in the presence or absence of $\mathrm{BF_3{\cdot}OEt_2}$.

**Absorption and Emission Spectra.** Ultraviolet absorption spectral data for the esters **1**–**10** and their Lewis acid complexes with $BF_3$ or $EtAlCl_2$ in dichloromethane solution are summarized in Table III. The free esters all display a single long-wavelength absorption band between 261 and 285 nm. With the exception of ester **8**, the *E* isomer absorbs at a longer wavelength and with a higher extinction coefficient than the *Z* isomer. The bulk of the alkoxy group has little effect on the spectra of **1**–**3**, while the $\alpha$-methyl group causes a blue shift in the absorption band of **7**. The *p*-$CH_3$ and *p*-Cl esters **4** and **5** and the cyclic molecules **8** and **9** display longer wavelength maxima than **1**–**3**, while the *p*-$CF_3$ ester **6** and the lactone **10** display shorter wavelength maxima.

The absorption spectra of ester (*Z*)-**4** in dichloromethane solution in the presence of 1, 2, and 3 equiv of $\mathrm{BF_3{\cdot}OEt_2}$ and saturated with $BF_3$ gas are shown in Figure 6. The complete disappearance of the 280-nm band of the free ester and the appearance of a new band at 322 nm is consistent with complete conversion with (*Z*)-**4** to its $BF_3$ complex upon saturation with $BF_3$. The observation of an isosbestic point at 300 nm for the solutions containing $\mathrm{BF_3{\cdot}OEt_2}$ is indicative of incomplete complexation with light absorption by both free and complexed esters. The spectra of (*E*)-**4** and (*Z*)-**4** in the presence and absence of $BF_3$ shown in Figure 7 are typical of esters **1**–**6**. The spectra of both *E* and *Z* isomers (except for (*Z*)-**6**) are red shifted by 9–13.3 kcal and increase in intensity upon complexation with $BF_3$ (Table III). Much smaller shifts in absorption maxima are observed for the $BF_3$ complexes of esters (*Z*)-**6** and **7**–**10**. In the case of (*E*)-**8**, a distinct shoulder appears at 325 nm upon complexation with $BF_3$. In the case of ester **9**, the entire absorption band gains in intensity upon complexation, especially in the long-wavelength region ($\lambda > 320$ nm).

Addition of excess $EtAlCl_2$ to dichloromethane solutions of esters **1**–**10** causes changes in absorption spectra similar to those observed for $BF_3$. Childs and co-workers[20] have reported somewhat larger spectral shifts for (*E*)- and (*Z*)-**2** with $EtAlCl_2$ than those we observe with $BF_3$ (Table III). We have used $BF_3$ rather than $EtAlCl_2$ in most of our spectroscopic studies since $BF_3$ forms 1:1 complexes with esters while $EtAlCl_2$ can form higher order (e.g., 2:1, 2:2) complexes.[21] Addition of 1 equiv of $TiCl_4$ or $FeCl_3$ to dichloromethane or benzene solutions of (*E*)-**1** results in the formation of yellow and yellow–orange solutions, respectively. The intense 290-nm absorption of Eu(fod)$_3$[10] obscures the absorption of (*E*)-**1**, and no longer wavelength absorption band is observed upon mixing of Eu(fod)$_3$ or Ag(fod) with (*E*)-**1**.

Table II. Optimum Conversions of *E*,*E* Bis Cinnamic Esters to Their *E*,*Z* and *Z*,*Z* Isomers[a]

| diester (*n*) | Lewis acid[b] mol equiv | *E*,*E* | *E*,*Z* | *Z*,*Z* |
|---|---|---|---|---|
| **11** (2) | 0 | 35 | 47 | 18 |
| | 0.25 | 18 | 49 | 33 |
| | 1.0 | 10 | 48 | 42 |
| **12** (3) | 0 | 36 | 45 | 19 |
| | 0[c] | 43 | 42 | 16 |
| | 0.50 | 8 | 38 | 54 |
| | 0.50[c] | 8 | 33 | 59 |
| **13** (4) | 0 | 35 | 46 | 19 |
| | 0.25 | 21 | 45 | 34 |
| | 0.50 | 6 | 35 | 59 |
| | 1.0 | 8 | 36 | 56 |

[a] Dichloromethane solutions (except as noted) 0.01 M in bis cinnamic ester irradiated with Pyrex-filtered light. [b] Based on two cinnamate groups per mole of bis cinnamic ester. [c] Benzene solutions.

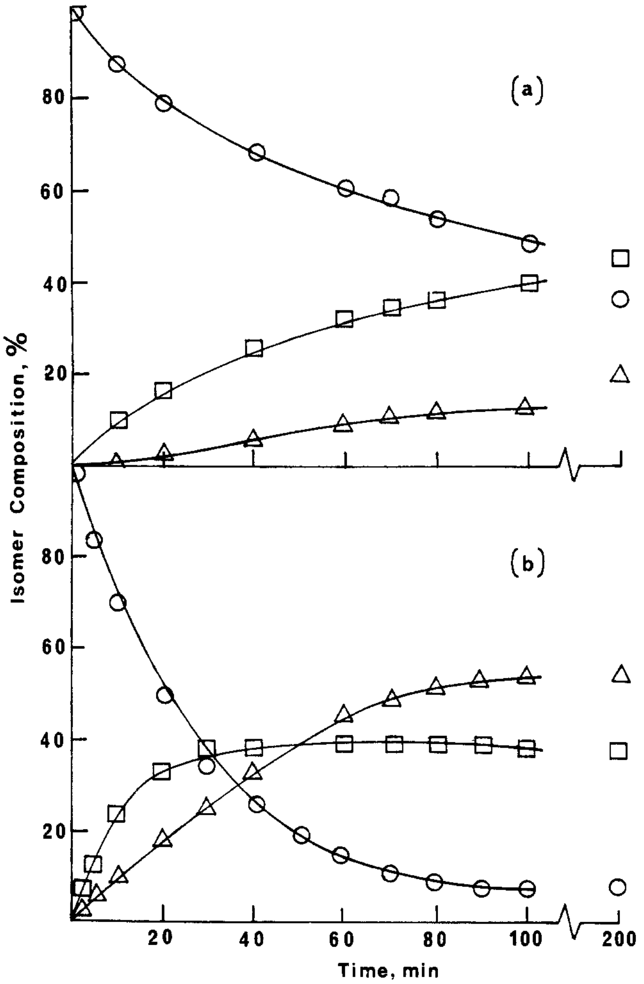

Figure 5. Composition of the isomer mixture vs. irradiation time for isomerization of 0.01 M (*E*,*E*)-**12** (○) to (*E*,*Z*)-**12** (□) and (*Z*,*Z*)-**12** (△) in the absence (a) and presence (b) of 0.01 M $\mathrm{BF_3{\cdot}OEt_2}$.

Equilibrium constants ($K_{eq}$) for ground-state complex formation between the esters (*E*)-**1**, (*E*)-**4**, (*Z*)-**4**, (*E*)-**5**, and (*E*)-**6** and

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[20] Childs, R. F.; Duffey, B.; Mika-Gibala, A. *J. Org. Chem.* **1984**, *49*, 4352.

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**Table III.** Absorption Spectral Data for Cinnamic Esters and Their Lewis Acid Complexes[a]

| ester (R)[b] | Lewis acid | $\lambda_{max}$, nm | log $\epsilon_{max}$ | log $\epsilon_{313}$ | $\Delta E$, kcal/mol |
|---|---|---|---|---|---|
| (*E*)-**1** | | 277 | 4.38 | 2.60 | |
| | $BF_3$ | 313 | 4.52 | 4.52 | 11.9 |
| (*Z*)-**1** | | 269 | 4.03 | 2.70 | |
| | $BF_3$ | 303 | 4.08 | 4.06 | 11.9 |
| (*E*)-**2** | | 276 | 4.24 | | |
| | $BF_3$ | 311 | 4.33 | 4.33 | 11.6 |
| | $EtAlCl_2$[c] | 328 | 4.46 | | 16.0 |
| (*Z*)-**2** | | 269 | 4.03 | | |
| | $EtAlCl_2$[c] | 328 | 4.05 | | 19.1 |
| (*E*)-**3** | | 275 | 4.43 | 2.51 | |
| | $BF_3$ | 310 | 4.63 | 4.62 | 11.7 |
| (*E*)-**4** (*p*-$CH_3$) | | 285 | 4.29 | 3.70 | |
| | $BF_3$ | 327 | 4.46 | 4.39 | 12.9 |
| (*Z*)-**4** | | 280 | 4.09 | 3.60 | |
| | $BF_3$ | 322 | 4.18 | 4.16 | 13.3 |
| (*E*)-**5** (*p*-Cl) | | 285 | 4.39 | 3.45 | |
| | $BF_3$ | 317 | 4.45 | 4.44 | 10.1 |
| (*Z*)-**5** | | 276 | 4.10 | 3.48 | |
| | $BF_3$ | 305 | 4.23 | 4.20 | 9.9 |
| (*E*)-**6** (*p*-$CF_3$) | | 270 | 4.35 | 2.00 | |
| | $BF_3$ | 295 | 4.46 | 4.34 | 9.0 |
| (*Z*)-**6** | | 261 | 4.03 | 2.48 | |
| | $BF_3$ | 268 | 4.15 | 3.70 | 2.9 |
| (*E*)-**7** ($\alpha$-$CH_3$) | | 268 | 4.15 | 3.70 | |
| | $BF_3$ | 270 | 4.33 | | 0.8 |
| (*Z*)-**7**[d] | | 258 | 4.21 | | |
| (*E*)-**8** | | 284 | 4.41 | | |
| | $BF_3$ | 284 (325) | 4.52 (3.68) | | 0 (13) |
| | $EtAlCl_2$ | 282 | 4.43 | | 0 |
| (*Z*)-**8** | | 285 | 4.18 | | |
| | $EtAlCl_2$ | 285 | 4.23 | | 0 |
| **9** | | 285 | 4.25 | | |
| | $BF_3$ | 287 | 4.77 | | 0.7 |
| | $EtAlCl_2$ | 289 | 4.35 | | 1.4 |
| **10** | | 270 | 4.25 | | |
| | $BF_3$ | 273 | 4.42 | | 1.2 |
| | $EtAlCl_2$ | 278 | 4.33 | | 3.0 |

[a] Data for dichloromethane solutions of esters in the absence of Lewis acid, saturated with $BF_3$ or with excess $EtAlCl_2$. [b] Methyl cinnamate substituents. [c] Data from ref 19. [d] Data from ref 16a.

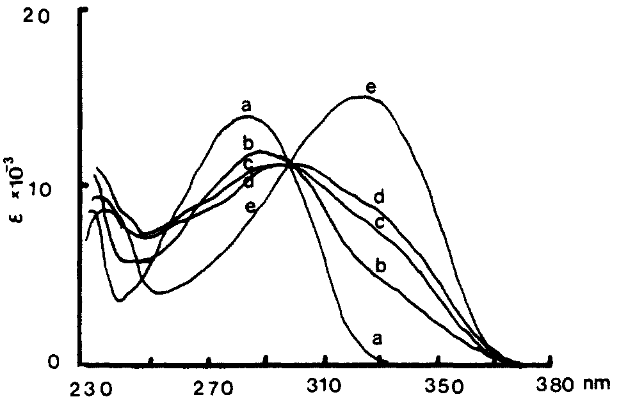

Figure 6. Absorption spectra of $5 \times 10^{-5}$ M (*Z*)-**4** in the absence of $BF_3$ (a), in the presence of 1 equiv (b), 2 equiv (c), and 3 equiv (d) of $BF_3 \cdot OEt_2$, and saturated with $BF_3$ (e).

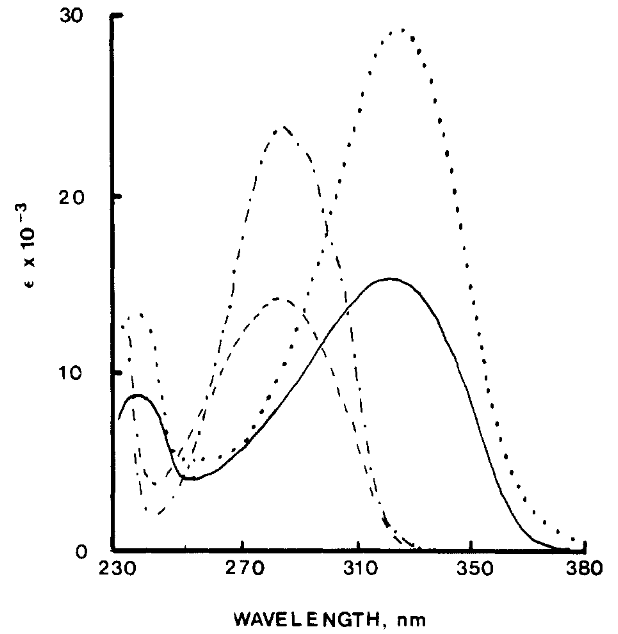

Figure 7. Absorption spectra of $5 \times 10^{-5}$ M (*E*)-**4** in the absence (·–·) and presence (···) of $BF_3$ and of (*Z*)-**4** in the absence (- - -) and presence (—) of $BF_3$ in dichloromethane solution.

**Table IV.** Equilibrium Constants for Ester/Lewis Acid Complex Formation

| | | | $K_{EA}/K_{ZA}$[b] | |
|---|---|---|---|---|
| ester (R) | $K(BF_3 \cdot OEt_2)$[a] | $K(BF_3)$[b] | $BF_3$ | $EtAlCl_2$ |
| (*E*)-**1** (H) | 104 | 860 | | |
| (*Z*)-**1** | | 360 | 2.4 | 3.2 |
| (*E*)-**4** ($CH_3$) | 140 | 870 | | |
| (*Z*)-**4** | 55 | 350 | 2.5 | |
| (*E*)-**5** (Cl) | 40 | 240 | | |
| (*Z*)-**5** | | 110 | 2.2 | |
| (*E*)-**6** ($CF_3$) | | 160 | | |
| (*Z*)-**6** | 12 | 80 | 2.0 | |
| (*E*)-**8**, (*Z*)-**8** | | | | 0.4 |

[a] Data from linear Benesi–Hildebrand plots. [b] Data from $^1H$ NMR measurements.

$BF_3 \cdot OEt_2$ in dichloromethane solution were obtained by the method of Benesi and Hildebrand[22] using eq 1, $\epsilon_c$ is the extinction

$$\frac{[\text{ester}]_0}{A} = \frac{1}{\epsilon_c} + \frac{1}{K_{eq}\epsilon_c[BF_3 \cdot OEt_2]} \tag{1}$$

coefficient of the complex. For a series of solutions in which $[BF_3 \cdot OEt_2] \gg [\text{ester}]_0$, a linear plot of $[\text{ester}]_0/A$ vs. $[BF_3 \cdot OEt_2]$ has an intercept of $\epsilon_c - 1$ and a slope of $K_{eq}\epsilon_c$. Values of $\epsilon_c$ thus obtained are in agreement with the values obtained by bubbling with $BF_3$ gas (Table III). Values of $K_{eq}$ for $BF_3 \cdot OEt_2$ obtained by this method are summarized in Table IV.

Esters (*E*)-**1**[23] and (*E*)-**8** ($5 \times 10^{-5}$ M) are very weakly fluorescent at room temperature in dichloromethane solution ($\Phi_f < 10^{-3}$) with emission maxima at 325 and 332 nm, respectively, while their *Z* isomers are nonfluorescent. The cyclic esters **9** and **10** fluoresce more strongly with emission maxima at 346 and 325 nm, respectively. The fluorescence quantum yield for ester **9** is $0.015 \pm 0.005$. Neither fluorescence nor isomerization efficiency is quenched by oxygen (1 atm). Addition of $EtAlCl_2$ results in enhanced fluorescence intensity from esters (*E*)-**1**, (*E*)-**8**, and **10** and shifts in the emission maxima to 352, 345, and 425 nm, respectively. No change in the intensity or wavelength of emission from ester **9** is observed upon addition of 1 equiv of $EtAlCl_2$ or $BF_3 \cdot OEt_2$.

**Proton NMR Spectra.** $^1H$ NMR data for the esters **1**–**10** and their Lewis acid complexes with $BF_3$ or $EtAlCl_2$ in $CDCl_3$ solution are summarized in Table V. For the free esters, the $OCH_3$ chemical shifts increase in the order (*Z*)-(**1**, **4**, **5**, **6**) < (*E*)-(**1**, **4**, **5**, **6**) < (*E*)-**7** < **9**. The $H_\alpha$ chemical shifts increase for electron-withdrawing aryl substituents[24] ((*E*)- or (*Z*)-**6** > **5** > **1** >

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(22) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

(23) Frings, R. B.; Schnabel, W. *Polym. Photochem.* **1983**, *3*, 325.

(24) (a) de la Mare, P. B. D.; Wilson, M. A.; Rosser, M. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1480. (b) Shim, S. C.; Park, J. W. *Bull. Korean Chem. Soc.* **1981**, *2*, 29.

**Table V.** $^1$H NMR Data for Cinnamate Esters and Their Lewis Acid Complexes[a]

| | | chemical shift, ppm | | | | |
|---|---|---|---|---|---|---|
| ester (R) | Lewis acid | $OCH_3$ | $H_\alpha$ | $H_\beta$ | other | $J_{\alpha,\beta}$, Hz |
| (*E*)-**1** (H) | | 3.78 | 6.41 | 7.70 | | 15.7 |
| (*E*)-**1** | $BF_3 \cdot OEt_2$ | 3.83 | 6.47 | 7.74 | | 15.7 |
| (*E*)-**1** | $BF_3$ | 4.18 | 6.95 | 8.05 | | 15.7 |
| (*E*)-**1** | $EtAlCl_2$ | 4.13 | 6.78 | 8.08 | | 15.7 |
| (*Z*)-**1** | | 3.67 | 5.87 | 6.87 | | 12.4 |
| (*Z*)-**1** | $EtAlCl_2$ | 3.97 | 6.33 | 7.52 | | 12.3 |
| (*E*)-**2** | | 4.27[b] | 6.45 | 7.63 | 1.35[c] | 16.1 |
| (*E*)-**3** | | | 6.30 | 7.60 | 1.60[c] | 15.0 |
| (*E*)-**4** (*p*-$CH_3$) | | 3.73 | 6.30 | 7.62 | 2.30[d] | 15.8 |
| (*E*)-**4** | $BF_3 \cdot OEt_2$ | 3.80 | 6.40 | 7.70 | 2.31[d] | 15.8 |
| (*E*)-**4** | $BF_3$ | 4.19 | 6.87 | 8.07 | 2.38[d] | 16.0 |
| (*Z*)-**4** | | 3.68 | 5.83 | 6.86 | 2.33[d] | 12.4 |
| (*Z*)-**4** | $BF_3 \cdot OEt_2$ | 3.70 | 5.87 | 6.90 | 2.34[d] | 12.6 |
| (*Z*)-**4** | $BF_3$ | 3.98 | 6.37 | 7.48 | 2.37[d] | 12.6 |
| (*E*)-**5** (*p*-Cl) | | 3.80 | 6.37 | 7.70 | | 16.0 |
| (*E*)-**5** | $BF_3 \cdot OEt_2$ | 3.86 | 6.45 | 7.76 | | 16.0 |
| (*E*)-**5** | $BF_3$ | 4.18 | 6.83 | 7.93 | | 16.0 |
| (*Z*)-**5** | | 3.67 | 5.90 | 6.83 | | 12.2 |
| (*Z*)-**5** | $BF_3 \cdot OEt_2$ | 3.70 | 5.93 | 6.88 | | 12.4 |
| (*Z*)-**5** | $BF_3$ | 3.97 | 6.46 | 7.43 | | 12.2 |
| (*E*)-**6** (*p*-$CF_3$) | | 3.77 | 6.43 | 7.65 | | 16.2 |
| (*E*)-**6** | $BF_3 \cdot OEt_2$ | 3.81 | 6.47 | 7.68 | | 16.0 |
| (*E*)-**6** | $BF_3$ | 4.22 | 7.00 | 8.05 | | 16.0 |
| (*Z*)-**6** | | 3.68 | 6.00 | 6.93 | | 12.4 |
| (*Z*)-**6** | $BF_3 \cdot OEt_2$ | 3.70 | 6.02 | 6.95 | | 12.4 |
| (*Z*)-**6** | $BF_3$ | 3.93 | 6.51 | 7.57 | | 12.3 |
| (*E*)-**7** ($\alpha$-$CH_3$) | | 3.85 | | 7.75 | 2.10[e] | |
| (*E*)-**7** | $EtAlCl_2$ | 4.10 | | 8.15 | 2.20[e] | |
| (*E*)-**8** | | 4.46[b] | | 7.60 | 3.25[f] | |
| (*E*)-**8** | $EtAlCl_2$ | 5.00[b] | | 8.10 | 3.40[f] | |
| (*Z*)-**8** | | 4.38[b] | | 6.99 | 3.12[f] | |
| (*Z*)-**8** | $EtAlCl_2$ | 4.80[b] | | *g* | 3.30[f] | |
| **9** | | 3.90[b] | | 7.80 | 3.75[f] | |
| **9** | $EtAlCl_2$ | 4.20[b] | | 8.60 | 3.85[f] | |
| **10** | | 5.20[b] | 6.30 | | | |
| **10** | $EtAlCl_2$ | 5.50[b] | 6.82 | | | |

[a] Chemical shifts for 0.1 M ester in $CDCl_3$ vs. TMS in the absence or presence of 1.0 equiv of Lewis acid. [b] Signal for O–$CH_2$ protons. [c] Signal for O–C–$CH_3$ protons. [d] Signal for *p*-methyl protons. [e] Signal for $\alpha$-methyl protons. [f] Signal for $\alpha$-$CH_2$ protons. [g] Obscured by phenyl group.

4). Addition of Lewis acid results in downfield shifts for all the $^1$H signals but only minor changes in the $J_{\alpha,\beta}$ coupling constants. The shifts observed when using 1.0 mol equiv of $BF_3$ or $EtAlCl_2$ are similar and substantially larger than those observed when using 1.0 mol equiv of $BF_3 \cdot OEt_2$. Further increases in the concentration of $BF_3$ or $EtAlCl_2$ had no effect on the chemical shifts, indicative of the formation of a 1:1 complex with a large equilibrium constant.[25] Use of <1.0 mol equiv of $BF_3$ or $EtAlCl_2$ results in time-average chemical shifts for the free and complexed ester. Increasing the $BF_3 \cdot OEt_2$ concentration results in larger downfield shifts, indicative of equilibrium complexation of $BF_3$ with the esters and diethyl ether. The $BF_3$-induced $\Delta\delta$ values for the $OCH_3$ chemical shifts are larger for the *E* vs. *Z* esters (**1**, **4**–**7**, **8**). Values of $\Delta\delta$ for $H_\alpha$ are similar for the *E* and *Z* isomers (**1**, **4**–**6**, **8**), while values for $H_\beta$ are larger for *Z* vs. *E* isomers. An unusually large value for the $H_\beta$ ($\Delta\delta$ = 0.80 ppm) is observed for ester **9**. Similar $\Delta\delta$ values are observed for the $\alpha$-$CH_3$ signal of ester **7** and the $\alpha$-$CH_2$ signals of **8** and **9**.

Relative equilibrium constants for ester Lewis acid complex formation can be obtained from $^1$H NMR shift data as previously described by Fratiello and Schuster.[26] Comparison of the $\Delta\delta$ values obtained when using 1.0 equiv of $BF_3 \cdot OEt_2$ and $BF_3$ when using eq 2 provides the values of $K_{eq}(BF_3)$ given in Table III.

**Table VI.** Quantum Yields for Isomerization of (*E*)-**1** and (*Z*)-**1**[a]

| ester (R)[b] | *T*, °C | Lewis acid | $\Phi_E$ | $\Phi_Z$ |
|---|---|---|---|---|
| **1** (H) | 25 | | 0.30 (0.30) | 0.29 (0.28) |
| **1** | 0 | | 0.30 | 0.30 |
| **1** | −41 | | 0.29 | 0.29 |
| **1** | −63 | | 0.24 | 0.33 |
| **1** | −84 | | 0.20 | 0.32 |
| **1** | 25 | $BF_3 \cdot OEt_2$ | 0.70 | 0.28 |
| **1** | 25 | $AlCl_3$ | (0.70) | (0.30) |
| **4** (*p*-$CH_3$) | 25 | | 0.45 | 0.28 |
| **4** | 25 | $BF_3 \cdot OEt_2$ | 0.53 | 0.25 |
| **5** (*p*-Cl) | 25 | | 0.38 | 0.25 |
| **5** | 25 | $BF_3 \cdot OEt_2$ | 0.55 | 0.20 |
| **6** (*p*-$CF_3$) | 25 | | 0.20 | 0.19 |
| **6** | 25 | $BF_3 \cdot OEt_2$ | 0.59 | 0.20 |
| **8** | 25 | | 0.36 | 0.52 |
| **8** | 25 | $EtAlCl_2$ | 0.58 | 0.75 |

[a] Quantum yields for 313-nm irradiation in dichloromethane solution or benzene solution (values in parentheses). [b] Methyl cinnamate substituent.

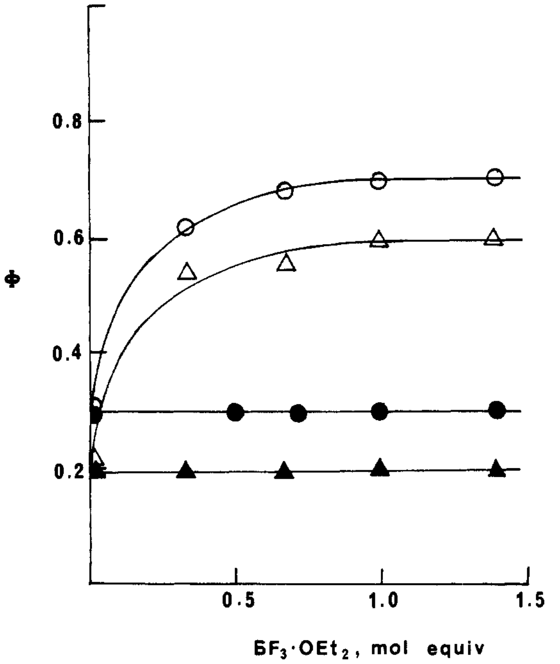

**Figure 8.** Effect of added $BF_3 \cdot OEt_2$ on the quantum yields for isomerization of (*E*)-**1** (○), (*Z*)-**1** (●), (*E*)-**6** (△), and (*Z*)-**6** (▲).

$$K(BF_3) = \frac{\Delta\delta BF_3}{\Delta\delta BF_3 \cdot OEt_2} K(BF_3 \cdot OEt_2) \tag{2}$$

$$K_E/K_Z = \frac{\Delta\delta_E^{obsd}/\Delta\delta_E}{\Delta\delta_Z^{obsd}/\Delta\delta_Z} \tag{3}$$

Comparison of the $\Delta\delta^{obsd}$ values obtained from equimolar mixtures of *E* and *Z* esters with 0.5 equiv of $BF_3$ or $EtAlCl_2$ with the values from Table V when using eq 3 provides values of $K_E/K_Z$. For all the esters investigated except **8**, $K_E > K_Z$, as previously observed by Childs and co-workers[20] for the $EtAlCl_2$, $SnCl_4$, and $SbCl_5$ complexes of (*E*)- and (*Z*)-**2**. Values of *K* for both *E* and *Z* esters follow the same inductive order for aryl substitution (**4** > **1** > **5** > **6**).

**Quantum Yield Measurements.** Quantum yield data for isomerization of 0.02 M *E* ($\Phi_E$) and *Z* ($\Phi_Z$) esters using 313-nm irradiation are summarized in Table VI. Irradiated solutions were analyzed for product isomer formation by analytic GC at low

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(25) (a) Gillespie, R. J.; Hartman, J. S. *Can. J. Chem.* **1968**, *46*, 2147. (b) Brunn, J.; Beck, C. *Z. Chem.* **1977**, *17*, 296. (c) Brunn, J.; Radeglia, R.; Lewanscheck, B.; Peust, S. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 681. (d) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801.

(26) Fratiello, A.; Schuster, R. E. *Inorg. Chem.* **1972**, *11*, 11.

conversions (<5%) of the reactant isomer. This method is considered to be more accurate than the use of changes in absorption spectra employed in previous investigations of cinnamic acid and ester isomerization due to the small differences in the spectra of the *E* and *Z* isomers (Figure 5).[16,17] Values obtained for (*E*)-**1** and (*Z*)-**1** (Table VI) are the same in dichloromethane and benzene solution. Decreasing temperature results in a decrease in $\Phi_E$, while the variation in $\Phi_Z$ with temperature is within the experimental error of measurement (±10%). The sum of the measured quantum yields $\Phi_E + \Phi_Z < 1.0$ for esters **1**, **4–6**, and **8** and $\Phi_E > \Phi_Z$ for all these esters except **8**.

The effect of added $BF_3{\cdot}OEt_2$ (0.33–1.4 equiv) on the isomerization quantum yields for (*E*)- and (*Z*)-**1** and **6** is shown in Figure 8. The values of $\Phi_E$ are seen to increase with $BF_3{\cdot}OEt_2$ concentration, reaching a maximum value when the ester/$BF_3$ complex becomes the predominant light-absorbing species at 313 nm (Figure 6). The value of $\Phi_Z$ remains constant or decreases slightly upon addition of $BF_3{\cdot}OEt_2$. Similar results were obtained for esters **4** and **5** with $BF_3{\cdot}OEt_2$ and **1** with $AlCl_3$ in benzene solution. Values of $\Phi_E$ and $\Phi_Z$ obtained when using 1.0 equiv of $BF_3{\cdot}OEt_2$ or $AlCl_3$ with esters **1** and **4–6** and 0.2 equiv of $EtAlCl_2$ with ester **8** are summarized in Table VI.

## Discussion

**Photoisomerization of Cinnamic Esters.** Both direct and triplet-sensitized irradiation of cinnamic acid[16] and cinnamic esters[17] in dilute solution result in *E,Z* isomerization. Photodimerization does not compete efficiently with isomerization in dilute solutions but is observed in the solid state (subject to topological control[27]) and in solution when high local concentrations are achieved either by omission of solvent[15] or by linking two or more cinnamate residues together as a di- or polyester.[19,28] The mechanism of *E,Z* photoisomerization upon direct irradiation remains the subject of some controversy, both singlet- and triplet-state isomerization having been proposed.[16,17] The absence of $O_2$ quenching of photoisomerization or the weak fluorescence of (*E*)-**1** and the absence of an azulene effect on the photostationary state[17a] would appear to support a singlet-state mechanism.

The lowest energy absorption band of cinnamic acid was assigned to an intramolecular charge-transfer transition by Tanaka[29] on the basis of absorption polarization measurements. Calculations of the electronic structure of cinnamic acid by both SCF-MO[30] and INDO/S-CI[31] methods indicate that this band is due to a relatively pure HOMO → LUMO ($\pi,\pi^*$) transition in which the HOMO is localized on the styryl portion of the molecule and the LUMO on the enone portion of the molecule. (A similar description of the HOMO and LUMO of (*E*)-**1** is provided by a GAUSSIAN 77 calculation.[32]) This type of charge-transfer transition is consistent with the absence of a pronounced solvent effect on the absorption maxima[16d] and our observations that electron-donating substituents lower the energy of the absorption band of para-substituted cinnamic esters (Table III).

**Table VII.** Observed and Calculated Photostationary States[a]

| ester (R) | %Z obsd | %Z calcd | %Z (BF$_3$) obsd | %Z (BF$_3$) calcd |
|---|---|---|---|---|
| **1** (H) | 46 | 46 | 88 | 93 |
| **4** (*p*-CH$_3$) | 57 | 63 | 87 | 90 |
| **5** (*p*-Cl) | 55 | 60 | 87 | 92 |
| **6** (*p*-CF$_3$) | 21 | 26 | 85 | 98 |
| **8** | 24 | 23 | 17[b] | 33[b] |

[a] Observed values from Table I. Calculated values from eq 4 using data in Table VI for $\Phi_E$ and $\phi_Z$, Table III for $\epsilon_{313}$, and Table IV for $K_{EA}/K_{ZA}$. [b] Values for $EtAlCl_2$.

The energy of the long-wavelength absorption band is dependent upon the planarity of the extended $\pi$ system as well as electronic effects. Crystallographic data indicate that (*E*)-cinnamic acid,[33a] methyl *m*- and *p*-bromocinnamate,[33b] and (*E*)-**8**[33c] are essentially planar in the solid state and that the esters exist in the s-cis conformation. (*E*)-$\alpha$-Methylcinnamic acid is nonplanar due to the nonbonded interactions between the $\alpha$-methyl and phenyl groups.[33d] While crystallographic data are unavailable for *Z* isomers lacking substituents on the C=C bond, the phenyl group is estimated to be rotated 45° out of the enone plane.[16b,34] The higher energy and smaller extinction coefficient of (*Z*)- vs. (*E*)-cinnamic acid and its esters (Table III) are attributed to the nonplanarity of the *Z* isomer. $\alpha$-Alkylation results in a blue shift for **7** vs. **1**, presumably due to its diminished planarity. In contrast, the absorption maxima of the planar s-cis lactone **8** is red shifted, as is that of ester **9**, which is presumed to adopt a planar s-cis conformation. The absorption maximum of the s-trans lactone **10** is blue shifted, reflecting either a difference in absorption maxima for s-trans vs. s-cis cinnamates or nonplanarity of the extended chromophore.

The lowest singlet state of (*E*)-cinnamic acid is nonfluorescent,[35] and ester (*E*)-**1** is very weakly fluorescent at room temperature in solution. The fluorescence lifetime of (*E*)-**1** in fluorocarbon or dichloromethane solution is estimated to be 2 ns.[23] In view of the absence of oxygen quenching of the fluorescence or isomerization of (*E*)-**1**, this estimate is probably an upper bound. An increase in fluorescence intensity is observed for the cyclic analogues of (*E*)-**1**, **9** ($\Phi_f = 0.015$) and **10**. Incorporation of the C=C bond into a five-membered ring may inhibit nonradiative decay via twisting about the C=C bond and thus increase the singlet lifetime, as is the case for the lowest singlet state of (*E*)-stilbene.[2a]

Quantum yields for photoisomerization of (*E*)- and (*Z*)-cinnamic acids have been reported by Clampett and Callis[16a] and by Bolte et al.[16d] In cyclohexane and acidic (pH 2) aqueous solution, $\Phi_E = 0.70$ and $\Phi_Z = 0.30$. The sum of the quantum yields is unity, in accord with isomerization of both isomers via a common twisted intermediate without competing nonradiative decay.[2a] Smaller quantum yields were observed for the isomeric acids in diethyl ether and dimethyl sulfoxide solvents and for ethyl cinnamate in nonaqueous solvents.[17c,22] Our value for 313-nm irradiation of (*E*)-**1** ($\Phi = 0.30$) in benzene and dichloromethane solution is in good agreement with the values reported by Frings and Schnabel[23] for 265-nm irradiation of (*E*)-**2** ($\Phi_E = 0.26 \pm 0.03$) in dichloromethane solution and by Shindo et al.[17c] for 254-nm irradiation of (*E*)-**2** ($\Phi_E = 0.27$) in ethanol solution.

The sum of $\Phi_E + \Phi_Z$ for esters **1** and **4–6** is 0.39–0.76 (Table VI), indicating that varying degrees of nonradiative decay compete with isomerization. The value of $\Phi_E$ for ester (*E*)-**1** decreases with decreasing temperature, indicating the existence of a small barrier for isomerization of singlet (*E*)-**1**. Values of $\Phi_Z$ for ester (*Z*)-**1** increase slightly with decreasing temperature, indicating that no such barrier exists for singlet (*Z*)-**1**. This difference in the excited-state behavior between (*E*)- and (*Z*)-**1** is analogous to the behavior of (*E*)- and (*Z*)-stilbene[2a] and suggests that the observed inefficiency in the isomerization process is largely due to nonradiative decay of (*E*)-**1**. Somewhat larger quantum yields are observed for the lactones (*E*)- and (*Z*)-**8**. This increase plausibly reflects decreased competition of nonradiative decay with twisting about the more highly substituted double bond, as in the case of the $\alpha$-methylstilbenes.[36]

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Photostationary states for *E*,*Z* photoisomerization of olefins are governed by isomerization quantum yields and extinction coefficients (eq 4).[2a] Values calculated using the available quantum yield data (Table VI) and $\epsilon_{313}$ values (Table III) are

$$\frac{[Z]}{[E]} = \frac{\Phi_E}{\Phi_Z}\frac{\epsilon_E}{\epsilon_Z} \qquad (4)$$

given in Table VII along with the observed values from Table I. The agreement between observed and calculated values is good, considering the errors in determining $\epsilon_{313}$ values from a steeply rising portion of the absorption spectra (Figures 6–8). Neither the size of the alkoxy group (**1**–**3**) nor the presence of an $\alpha$-methyl substituent (**7**) has a substantial effect on the observed photostationary state. Aromatic substitution does result in changes in the photostationary state, as previously observed by Ishigami et al.[17a] The higher conversions of (*E*)-**4** and (*E*)-**5** to their *Z* isomers reflect larger $\Phi_E$ values and $\Phi_E/\Phi_Z$ ratios than those for **1**, while the low conversion of (*E*)-**6** to (*Z*)-**6** reflects a lower $\epsilon_E/\epsilon_Z$ ratio than that for **1**. The low conversion of (*E*)-**8** to (*Z*)-**8** reflects low ratios for both $\Phi_E/\Phi_Z$ and $\epsilon_E/\epsilon_Z$.

The *E*,*E* bis cinnamic esters **11**–**13** form mixtures of *E*,*E*, *E*,*Z*, and *Z*,*Z* isomers upon irradiation. The observation of an induction period for the formation of the *Z*,*Z* isomers (Figure 5a) indicates that isomerization of the two cinnamate groups occurs independently. Independent isomerization of two *E* cinnamate groups to 42% *Z* isomer (Table I) should yield a steady-state mixture of 34% *E*,*E*, 48% *E*,*Z*, and 18% *Z*,*Z* isomers. The observed isomer ratios (Table II) are in excellent agreement with this prediction.

**Photoisomerization of Lewis Acid Complexes.** Irradiation of the cinnamic esters **1**–**7** in the presence of Lewis acids such as $BF_3$, $AlCl_3$, $EtAlCl_2$, or $SnCl_4$ results in the formation of photostationary-state mixtures enriched in the *Z* isomer (Table I). Optimum conversions obtained by using standard a photochemical apparatus (Pyrex-filtered high-pressure mercury lamp) range from 85% to 92%. The most dramatic change in the photostationary state was observed with methyl *p*-(trifluoromethyl)cinnamate (**6**) for which the optimum conversion to the *Z* isomer increases from 21% to 85% upon addition of $BF_3{\cdot}OEt_2$. As seen in Figure 1, the rate of $E \rightarrow Z$ photoisomerization as well as the yield of *Z* isomer increases in the presence of Lewis acid.

The optimum conversion of (*E*)-**1** to (*Z*)-**1** is dependent upon the choice of Lewis acid, solvent, and irradiation time. The relatively weak Lewis acid $ZnCl_2$ has little effect on the photoisomerization or spectral properties of (*E*)-**1**, presumably due to its failure to form a stable ground-state complex with (*E*)-**1**. Lewis acids such as $Eu(fod)_3$ or Ag(fod) which have strong metal-centered long-wavelength absorption bands act as quenchers for the *E*,*Z* photoisomerization of (*E*)-**1**, as do Lewis acids such as $FeCl_3$ and $TiCl_4$ which form colored complexes with (*E*)-**1**. The failure of these complexes to undergo efficient photoisomerization plausibly reflects the absence of a cinnamate-localized $\pi,\pi^*$ lowest singlet or triplet state. The Lewis acids which are effective catalysts of *E*,*Z* photoisomerization all form relatively strong complexes with cinnamic esters (Table IV) and cause moderate shifts in the absorption (Table III) and $^1H$ NMR spectra (Table V) of the esters but do not possess low-energy metal-centered excited states.

Optimum conversions of (*E*)-**1** to (*Z*)-**1** are obtained with ca 0.2 mol equiv of $AlCl_3$, $EtAlCl_2$, or $SnCl_4$ and 1.0 mol equiv of $BF_3{\cdot}OEt_2$ (Figure 2). Since $BF_3$ forms a stronger complex with ether than with (*E*)-**1** (Tables IV and V), the use of 1.0 mol equiv of $BF_3{\cdot}OEt_2$ is necessary for complexation of 10–20% (*E*)-**1**. In the case of $BF_3{\cdot}OEt_2$ or $AlCl_3$ in dichloromethane solution, neither the isomer ratio (Figure 4) nor the absorption of $^1H$ NMR spectrum of the irradiated solution changes once the photostationary state is reached. Thus the Lewis acid must be stable under the irradiation conditions. In contrast, conversions of (*E*)-**1** to (*Z*)-**1** obtained with $EtAlCl_2$ in benzene or hexane solution reach a maximum value and then decrease with continued irradiation to the value obtained without Lewis acid (Figure 4). This behavior is attributed to photochemical instability of the Lewis acid, which can also account for the requirement of higher Lewis acid concentrations for optimum conversions of (*E*)-**1** to (*Z*)-**1** in benzene or hexane vs. dichloromethane solution (Figure 3). The Lewis acids $SnCl_4$ and $TiCl_4$ also appear to be unstable to the conditions of irradiation. Thus, of the Lewis acids and solvents we have investigated, $BF_3$ or $EtAlCl_2$ in dichloromethane solution have proven to be the most effective for solution-phase photoisomerization of $\alpha,\beta$-unsaturated esters.

Our investigations of the mechanistic basis for Lewis acid enhanced *E*,*Z* photoisomerization of cinnamic esters have revealed that three factors are important: (a) enhanced quantum yield ratios ($\Phi_E/\Phi_Z$) upon complexation, (b) more selective absorption of light by *E* vs. *Z* isomers in their complexed vs. noncomplexed forms, and (c) larger equilibrium constants for complexation of the *E* vs. *Z* isomers. Quantum yields for *E*,*Z* isomerization ($\Phi_E$) but not *Z*,*E* isomerization ($\Phi_Z$) increase upon addition of Lewis acid (Table VI). As shown in Figure 8, values of $\Phi_E$ increase with increasing $BF_3{\cdot}OEt_2$ concentration, reaching an optimum value at ca. 0.7 mol equiv, conditions under which the complexed ester becomes the predominant light absorbing species. Based upon changes in quantum yield ratios alone, the conversion of (*E*)-**1** to (*Z*)-**1** should increase from 51% to 69% upon addition of 1 mol equiv of $BF_3{\cdot}OEt_2$ or $AlCl_3$.

The changes in absorption spectra observed upon complex formation (Figures 6 and 7) allow selective excitation of complexed vs. free ester with Pyrex-filtered or monochromatic 313-nm irradiation even when only ca. 20% of the ester is complexed. For example, 313-nm irradiation of (*E*)-**1** or (*Z*)-**1** with 0.2 equiv of $BF_3$ results in 94% and 86% absorption by complex. The $BF_3$ complexes of *E* cinnamic esters absorb more strongly than their *Z* isomers, as in the case for the free esters (Table III). The absorption spectra of free and complexed (*E*)- and (*Z*)-**4** shown in Figure 6 are typical of the cinnamic esters **1**–**6** and their $BF_3$ complexes. Based on the changes in $\epsilon_{313}$ alone, the conversion of (*E*)-**1** to (*Z*)-**1** should increase from 44% for the free ester to 71% for the fully complexed ester. The photostationary state calculated by using eq 4 and the quantum yield and absorption data for the $BF_3$ complexes of (*E*)- and (*Z*)-**1** is 85% *Z*, slightly lower than the observed value (Table I).

Optimum conversion of (*E*)-**1** to (*Z*)-**1** is obtained when using ca. 0.2 mol equiv rather than 1.0 mol equiv of Lewis acid (Figure 2). Under these conditions a photoequilibrium is established between free and complexed (*E*)- and (*Z*)-**1**. Since complexed esters are the major light-absorbing species, the photoequilibrium can be described by Scheme I. Making the further simplifying assumption that most of the Lewis acid is complexed, the photostationary state can be described by eq 5 (see Appendix section) as the product of the ratios of quantum yields, extinction coefficients, and equilibrium constants. The importance of the

$$\frac{[Z] + [Z{:}A]}{[E] + [E{:}A]} = \frac{\Phi_{EA}}{\Phi_{ZA}}\frac{\epsilon_{EA}}{\epsilon_{ZA}}\frac{K_{EA}}{K_{ZA}} \qquad (5)$$

ratio $K_{EA}/K_{ZA}$ in cases where [*Z*] + [*E*] > [A] has been emphasized by Childs et al.[20] The photostationary state for ester **1** with $BF_3$ calculated by using eq 5 and the value of $K_{EA}/K_{ZA}$ from Table I is 93% *Z*, slightly higher than the observed value (Table I). In practice, it is difficult to attain the optimum conversion predicted by eq 5, as selective excitation of the complexed vs. free esters requires the use of Lewis acid concentrations higher than the equilibrium concentration of *E* isomers.

**Scheme I**

$$E{:} + A \underset{}{\overset{K_{EA}}{\rightleftharpoons}} E{:}A \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} Z{:}A \overset{K_{ZA}}{\rightleftharpoons} Z{:} + A$$

Observed and calculated photostationary states for photoisomerization of esters **1**–**8** in the presence of Lewis acids are summarized in Tables I and VII. In all cases, the observed conversion is less than the calculated photostationary state. $\alpha$-Benzylidene-$\gamma$-butyrolactone (**8**) is the only isomerizable $\alpha,\beta$-unsaturated ester in Table I that fails to yield a photostationary state enriched in the *Z* isomer upon irradiation in the presence of Lewis acids. In the case of **8**, both $\Phi_E/\Phi_Z$ and $K_{EA}/K_{ZA}$ are less than unity.

Possible explanations for the abnormal behavior of **8** are considered in the following sections.

*E,E* bis cinnamic esters **11–13** are converted to mixtures consisting largely of *Z,Z* and *E,Z* isomers upon irradiation in the presence of $BF_3{\cdot}OEt_2$ (Table II). The isomer mixture obtained from **12** and **13** in dichloromethane solution is nearly that predicted for independent isomerization of each cinnamate group to 77% *Z* isomer (5% *E,E*, 36% *E,Z*, 59% *Z,Z*), a value only slightly lower than that observed for the monoesters **1** or **2**. Lower conversions are observed for (*E,E*)-**11** vs. **12** or **13**, possibly reflecting a lower equilibrium constant for complexation when only two methylenes separate the cinnamate groups.

The most remarkable aspect of the photoisomerization of the bis cinnamic esters in the presence of $BF_3$ is the direct conversion of (*E,E*)-**12** to (*Z,Z*)-**12** (Figure 5b). The ratio of *E,Z*/*Z,Z* products at low conversions (0.5–15%) is 3.2 ± 0.4, indicative of two-bond isomerization occurring with ca. 24% of the efficiency of one-bond isomerization. Two-bond isomerization might reflect competition between intramolecular energy transfer and nonradiative decay from the initially formed twisted excited state. The occurrence of two-bond isomerization from (*E,E*)-**12** but not **11** or **13** is suggestive of the intervention of a sandwich-type intramolecular excimer in the two-bond isomerization process.[37] As originally observed by Hirayama,[38] intramolecular excimer formation occurs most readily when the interacting chromophores are separated by three carbon atoms ($n = 3$ rule).

Changes in the efficiency of photoisomerization for complexed vs. free esters are one of the three factors responsible for altered photostationary states (eq 5). Since $\Phi_E$ for free (*E*)-**1** is temperature dependent (Table VI), the increase in $\Phi_E$ upon complexation can be attributed to increased efficiency of isomerization vs. nonradiative decay of the complexed ester. The sum of $\Phi_E = \Phi_Z$ for complexed **1** is near unity, in accord with the prediction for formation of a common intermediate from the *E* and *Z* isomers without competing nonradiative decay.[2a] In the absence of lifetime data for the nonfluorescent complexes, it is not possible to distinguish between an increased rate of twisting about the excited C=C bond and a decreased rate of nonradiative decay.

In the case of α,β-unsaturated esters with geometrically accessible γ-hydrogens (e.g., isocrotonic or β-methylcinnamic esters), photoinduced γ-hydrogen abstraction is known to compete with *E,Z* isomerization.[39] We have observed that Lewis acid complexation inhibits γ-hydrogen abstraction and enhances *E,Z* isomerization quantum yields for such esters.[14] It is possible that the Lewis acid inhibits a nonproductive photoprocess of singlet (*E*)-**1** such as electrocyclization to a thermally labile oxetene intermediate.[40] Crystallographic data indicate that free *E* cinnamic esters exist in the s-cis conformation necessary for oxetene formation,[34] whereas the $SnCl_4$ complex of (*E*)-**2** exists in the s-trans conformation.[1]

The effect of $EtAlCl_2$ on the efficiency of photoisomerization of **8** differs from that observed for Lewis acid complexes of **1–6** in that both $\Phi_E$ and $\Phi_Z$ are increased (ca. 50%) upon complexation and the sum $\Phi_E + \Phi_Z > 1.0$. Even in the absence of Lewis acid, $\Phi_E + \Phi_Z = 0.88$, indicating that nonradiative decay is less important for **8** vs. **1–6**, plausibly due to steric acceleration of twisting about the more substituted double bond of both *E* and *Z* isomers. The vast majority of reversible *E,Z* photoisomerization reactions have $\Phi_E + \Phi_Z \leq 1.0$,[2a] as expected for isomerization via a common equilibrated twisted intermediate which can decay to either reactant or product.[2a] While examples of photoisomerization reactions for which $\Phi_E + \Phi_Z > 1.0$ are uncommon, they are consistent with a dynamic model for *E,Z* photoisomerization proposed by Weiss and Warhsel.[41] The increased steric demands of the complexed vs. free esters may result in a higher probability of transition from the excited-state to ground-state surface prior to vibrational equilibratium of the twisted intermediate.

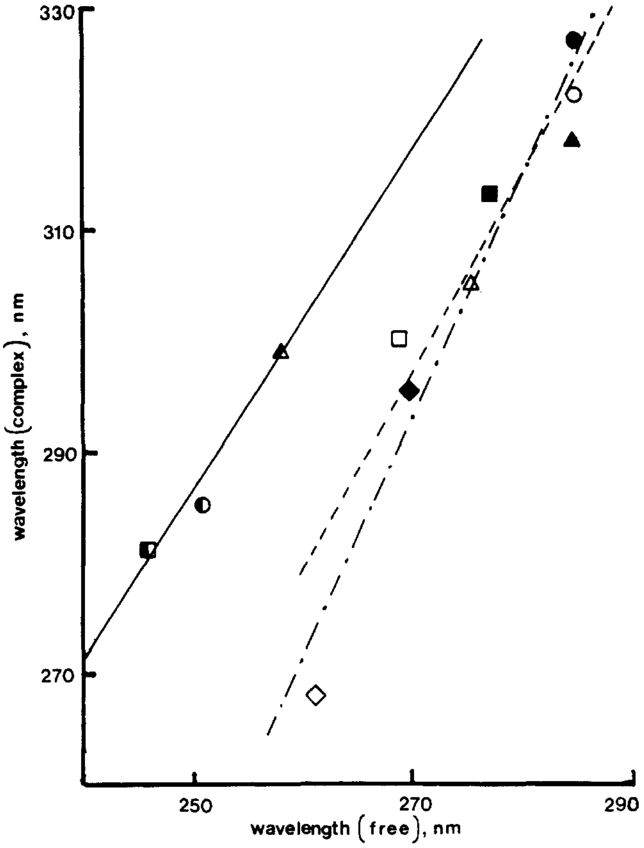
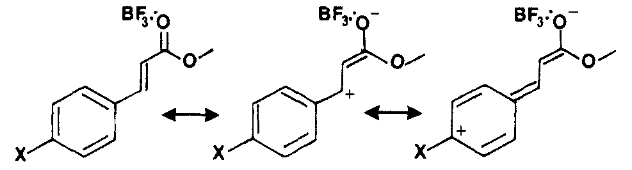


**Figure 9.** Effect of substituents on the absorption maxima of noncomplexed vs. $BF_3$-complexed benzaldehyde (half-filled symbols), *E* cinnamic esters (filled symbols), and *Z* cinnamic esters (empty symbols): H (□), $CH_3$ (○), Cl (△), $CF_3$ (◇).

**Scheme II**



**Spectroscopic Characterization of Lewis Acid Complexes.** Cinnamic acid[42] and esters[1] form crystalline 1:1 complexes with $BF_3$, $AlCl_3$, and $TiCl_4$ and 2:1 complexes with $SnCl_4$. A decrease in the C=O stretching frequency upon complexation in the solid state or solution provides evidence for complexation of the carbonyl oxygen which has been confirmed by X-ray crystallography in the case of the 2:1 complex of (*E*)-**2** with $SnCl_4$.[1]

A red shift in the absorption maxima of (*E*)- and (*Z*)-cinnamic acids in ethanol solution upon addition of $AlCl_3$ was reportedby Mēndez and Lojo.[43] We observe that complexation of the cinnamic esters **1–6** with $BF_3$ induces a red shift in the long-wavelength $\pi,\pi^*$ absorption band and an increase in the extinction coefficient of both *E* and *Z* isomers (Table III). Similar results have been reported for the $BF_3$ complexes of benzaldehyde by Rabinovitz and Grinvald,[44] who treat $CHO{:}BF_3$ as an extremely strong electron-withdrawing group in analyzing its perturbation of the benzene $^1B_{2u} \leftarrow {}^1A_{1g}$ transition. Plots of $\lambda_{max}$ of the complexes vs. $\lambda_{max}$ of the free para-substituted benzaldehydes and *E* and *Z* cinnamic esters are shown in Figure 9. The linearity of these plots is taken as evidence that the long-wavelength absorption

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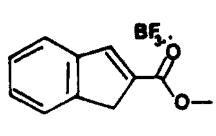
bands of the free and complexed molecules are derived from similar $\pi,\pi^*$ transitions.[44]

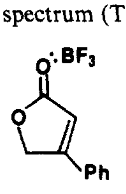
Electron-releasing para substituents cause a red shift in the absorption maxima of both free ($\Delta E°$) and complexed ($\Delta E$) esters. A plot of log $\Delta E/\Delta E°$ vs. $\sigma$-para for the *E* esters **1** and **4–6** has a slope of −0.18 ($r = 0.99$) indicating that the spectral shifts, like the equilibrium constants (Table IV), depend upon substituent $\pi$-donor ability. Viewed in terms of resonance structures (Scheme II), $\pi$-donor substituents should raise the energy of the cinnamate HOMO (styrene localized), and $BF_3$ complexation should lower the energy of the LUMO[45] (enone localized), leading to a red shift in the charge-transfer $\pi,\pi^*$ absorption band.

The resonance structures of Scheme II depict the (*E*)-**1**:$BF_3$ complex in the s-trans, C,O-*E* conformation adopted by the 2:1 complex of (*E*)-**2** with $SnCl_4$ in the solid state.[1] This conformation is also concluded to be more stable in solution than the s-trans, C,O-*Z* conformation, or either s-cis conformation on the basis of $^1H$ chemical shift changes upon complexation (Table V). Childs et al.[25] have investigated the NMR spectra of the Lewis acid complexes of several $\alpha,\beta$-unsaturated carbonyl compounds and conclude that charge resonance (cf. Scheme II) results in greater deshielding for $H_\beta$ vs. $H_\alpha$. However, $H_\alpha$ can also experience through-space deshielding when it is close to the Lewis acid. The observation of larger $\Delta\delta$ values for $H_\alpha$ vs. $H_\beta$ for the $BF_3$ complexes of (*E*)-**1–6** (Table V) and similar UV red shifts for (*E*)-**1–3** (Table III) supports the assignment of C,O-*E* stereochemistry for these complexes. The similar $\Delta\delta$ values for $H_\alpha$ of *E* and *Z* esters indicate that the latter also adopt C,O-*E* stereochemistry.

Further information about the conformational preference of cinnamate Lewis acid complexes was sought using lactones (*E*)-**8** and **10** as rigid models for the s-cis and s-trans conformations. Addition of $BF_3$ to the esters **7–10** induces an increase in their extinction coefficients and broadening of the $\pi,\pi^*$ absorption band (Figure 8) but little or no red shift of the absorption maxima. The absence of red-shifted absorption might be attributed to the effects of $\alpha$ or $\beta$ substitution and decreased conformational mobility for **7–10** vs. **1**. The s-trans C,O-*E* complexes of **7** and **9** should be destabilized by the interaction of the Lewis acid and $\alpha$-methylene groups. The similar $\Delta\delta$ values (0.10–0.15 ppm) of the $\alpha$-$CH_2$ groups of **7–9** suggest that the $BF_3$ complexes of **7** and **9**, like that of **8**, exist in s-cis conformations. The unusually large $\Delta\delta$ value of $H_\beta$ for **9** (0.80 ppm) vs. **1** (0.35 ppm) supports the assignment of the s-cis C,O-*E* conformation. On the basis of the similar $\Delta\delta$ values of $H_\alpha$ for the $BF_3$ complexes **1** and **10**, the latter is assigned a C,O-*E* conformation. The intermediate $\Delta\delta$ value of $H_\beta$ for (*E*)-**8** (0.50 ppm) suggests that its $BF_3$ complex may exist in both C,O-*E* and C,O-*Z* conformations, in accord with the observation of a long-wavelength shoulder in its absorption spectrum (Table III).



**9 s-cis, C,O-E**



**10 C,O-E**

In addition to restricted conformational mobility, esters **7–10** may be less able to undergo bond angle deformations upon complexation than the acyclic esters **1–6**. The 2:1 complex of (*E*)-**2** with $SnCl_4$ has abnormally large $sp^2$ bond angles ($C(O),C_\alpha,C_\beta = 123.4°$; $C_\alpha,C_\beta,Ph = 126.2°$).[1] The ability of the $BF_3$ complexes of acyclic esters **1–6** to adopt fully planar conformations with expanded bond angles may be responsible for the red-shifted absorption spectra observed for these complexes. The noncomplexed esters **7** and **8** have larger $sp^2$ bond angles due to nonbonded repulsion between the phenyl and $\alpha$-$CH_3$ or $CH_2$ groups[34c,d] and hence may not be able to undergo further deformation upon complexation. The severely distorted geometry of (*E*)-**8** may also account for the lower equilibrium constant for complexation of (*E*)-**8** vs. (*Z*)-**8** (Table IV). The endocyclic C=C bonds of **9** and **10** are incapable of significant bond angle deformation.

While absorption and NMR spectral data provide significant information about the ground state of Lewis acid complexes of cinnamic esters, the only currently available information about the excited states of these complexes is provided by the fluorescence of the $BF_3$ or $EtAlCl_2$ complexes. The observation of undiminished or enhanced fluorescence intensity upon complexation of **1** and **8–10** indicates that the excited singlet complexes are *not dissociative* and that neither nonradiative decay nor intersystem crossing occurs more rapidly than for the free esters. Since oxygen (1 atm) quenches neither the fluorescence nor isomerization of the excited complexes, we conclude that *E,Z* photoisomerization most likely occurs via a short-lived singlet excited state of the compexed ester.

**Concluding Remarks.** Our investigations of the photochemical reactions of cinnamic acids have established that Lewis acids can significantly enhance the efficiency of *E* → *Z* photoisomerization. We have also observed Lewis acid enhanced *E* → *Z* photoisomerization of crotonic, tiglic, and sorbic esters and $\alpha,\beta$-unsaturated amides.[14,46] Childs et al.[20] have reported similar results for an $\alpha,\beta$-unsaturated ketone. Thus irradiation in the presence of Lewis acids may provide a general method for the conversion of *E* $\alpha,\beta$-unsaturated carbonyl compounds to their thermodynamically less stable *Z* isomers.

The mechanistic basis for Lewis acid enhanced *E* → *Z* photoisomerization is the irradiation of ground-state complexes, which have different spectroscopic properties and photochemical behavior than noncomplexed $\alpha,\beta$-unsaturated carbonyl compounds. We have referred to this process as Lewis acid catalyzed photoisomerization since the Lewis acid is not consumed and as little as 0.1 mol equiv is sufficient to promote essentially quantitative *E,Z* isomerization in certain cases.[46] It should of course be recognized that calysis of the photoisomerization of the noncomplexed ester does not occur and that the process is not truly a catalyzed photochemical reaction as defined by Wubbels.[47]

Since Lewis acid enhanced *E* → *Z* photoisomerization requires selective excitation of the Lewis acid complex, a significant fraction of the $\alpha,\beta$-unsaturated carbonyl compound must be in the complexed form and the complex must absorb strongly at the excitation frequency. This in turn requires the use of relatively strong Lewis acids and bases. In contrast, Lewis acid catalysis of thermal reactions may require only low equilibrium concentrations of complexed substrate. Further limitations on the choice of Lewis acid are imposed by the necessity of thermal stability of the reactants at the temperature of irradiation, photochemical stability of the Lewis acid, and the formation of a complex in which the lowest excited states are localized on the organic molecules rather than the Lewis acid. In view of these rather stringent limitations, it is perhaps not surprising that Lewis acid catalysis of photochemical reactions remains largely unexplored. Nonetheless, our investigations of the effects of Lewis acids on photoisomerization and dimerization reactions clearly indicate their potential utility in photochemistry, Childs et al.[20] have recently reported that heterogeneous acid catalysts such as Nafion can be used in place of homogeneous Lewis acids to effect selective *E* → *Z* photoisomerization. The use of solid catalysts may offer substantial advantages in preparative applications.

The three factors responsible for enhanced *E* → *Z* isomerization of complexed vs. noncomplexed cinnamic esters are enhanced quantum yield ratios ($\Phi_E/\Phi_Z$), enhanced extinction coefficient ratios ($\epsilon_E/\epsilon_Z$) for complexed vs. noncomplexed esters (eq 4 vs. 5), and preferential complexation of *E* vs. *Z* esters. Enhanced quantum yields for *E* → *Z* but not *Z* → *E* isomerization upon complexation reflects changes in the rates of singlet-state isomerization and nonradiative decay upon complexation. Further elucidation of these changes will require an extensive kinetic spectroscopic investigation. Enhanced long-wavelength absorption for *E* vs. *Z* complexes plausibly reflects differences in the planarity and/or conformations of the isomeric complexes. Investigation

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of the spectroscopic properties of the cyclic cinnamate analogues **8**–**10** establishes the dependence of complex absorption spectra on conformational mobility. Stronger complex formation of *E* vs. *Z* cinnamic esters, like the previously observed higher basicity of (*E*)- vs. (*Z*)-cinnamic acids,[48] probably also reflects the greater charge delocalization for the protonated or complexed planar *E* cinnamate (Scheme II). Thus it may be possible to further increase the selectivity of *E* → *Z* photoisomerization by the use of hindered Lewis acids such as alkyl- and dialkylaluminum chlorides which may be more selective for *E* vs. *Z* complexation.

## Experimental Section

**General Methods.** Melting points were determined by using a Fischer-Johns melting point apparatus and are uncorrected. Ultraviolet absorption spectra were obtained on a GCA/McPherson EU-700 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 283 infrared spectrophotometer. NMR spectra were obtained on Varian EM360A or CFT20 NMR spectrometer. Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-44A spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5985A gas chromatograph/mass spectrometer system using an ionizing voltage of 70 eV or chemical ionization. Air-sensitive manipulations were performed under a $N_2$ atmosphere in a Kewaunee Scientific Products drybox.

The light source for 365- and 313-nm irradiation was a 450-W Hanovia medium-pressure mercury lamp enclosed in a water-cooled Pyrex glass well. Corning glass filters 7-54 and 0-52 were used in combination to isolate the 365-nm line, and a potassium chromate solution filter was used to isolate the 313-nm line. A voltage regulator was employed to maintain a constant intensity during quantum yield measurements. Analytical scale irradiations and quantum yield measurements were conducted under dry $N_2$ in 13 mm o.d. Pyrex tubes on a merry-go-round apparatus in a temperature-controlled water bath. Irradiated solutions were analyzed on a Hewlett-Packard 5750 or Varian 3700 gas chromatograph with a flame ionization detector. Isomerization reactions were monitored by using a 6 ft × $^1/_8$ in. column containing 5% SF-96 on Chromosorb G. Light intensities were measured by using (*E*)-stilbene chemical actinometers[49] run in triplicate.

**Solvents.** Benzene (Aldrich Spectroquality) was refluxed successively from phosphorus pentoxide and sodium. Dichloromethane (Aldrich gold label) was distilled from phosphorus pentoxide, refluxed over calcium hydride, and distilled immediately prior to use. Hexane (Aldrich Spectroquality) was distilled from phosphorus pentoxide. Methanol (Burdick & Jackson) was used without further purification.

**Lewis Acids.** Boron trifluoride etherate (Aldrich, redistilled), boron trifluoride (Matheson), zinc dichloride (Alfa, anhydrous), ethyl aluminum dichloride (Texas Alkyls, 25% weight solution in heptane), and $Eu(fod)_3$ and Ag(fod) (Aldrich) were all used without further purification. Tin tetrachloride and titanium tetrachloride were purchased from Aldrich and distilled under vacuum. Aluminum trichloride (Aldrich, anhydrous) was vacuum sublimed from aluminum powder. Iron trichloride hexahydrate (Aldrich) was dehydrated with thionyl chloride.

***E* Cinnamic Esters.** (*E*)-Cinnamic acid and its para methyl, chloro, and trifluoromethyl α-methyl derivatives (Aldrich) were esterified via their acid chlorides to yield the *E* cinnamic esters (*E*)-**1**–(*E*)-**7** and the diesters (*E*,*E*)-**11**–**13**. Esters (*E*)-**1**, (*E*)-**4**–**7**, and (*E*,*E*)-**11**–**13** were recrystallized from hexane and had melting points in agreement with literature values. Esters (*E*)-**2** and (*E*)-**3** were fractionally distilled. All *E* esters were >99% pure by GC analysis. Spectral data for these esters are summarized in Tables III and V.

***Z* Cinnamic Esters.** The *E* isomers of esters **1**–**6** were converted to their *Z* isomers by photoisomerization in the presence of $BF_3{\cdot}OEt_2$, $AlCl_3$, or $EtAlCl_2$. The following procedure yielded *Z* esters as colorless oils or low melting solids in >99% purity by GC and NMR analysis. Spectral data are summarized in Tables III and V.

**(*Z*)-Methyl Cinnamate ((*Z*)-1).** (*E*)-Methyl cinnamate (1.0 g, $6.2 \times 10^{-3}$ mol) and $BF_3{\cdot}OEt_2$ (4.2 g, $3.1 \times 10^{-3}$ mol) were dissolved in 0.05 L of dichloromethane under a dry $N_2$ atmosphere. The solution was transferred to a preparative irradiation vessel and irradiated with a 450-W Hanovia medium-pressure mercury lamp in a Pyrex lamp well for 3 h. The solution was monitored by GC for cis isomer content until no further enhancement in the cis/trans ratio was observed (88%). The irradiated solution was quenched with water and the aqueous portion discarded. The organic layer was dried over $MgSO_4$, concentrated, and subjected to flash chromatography on silica gel (200 g) with 1% ethyl acetate/hexane. Pure (*Z*)-methyl cinnamate (0.85 g, 85%) was eluted cleanly in earlier fractions followed by the *E* isomer.

**(*E*)-α-Benzylidene-γ-butyrolactone ((*E*)-8).** To a solution of γ-butyrolactone (8.0 g, 50 mmol) and benzaldehyde (5.0 g, 47 mmol) in 20 mL of dry benzene was added NaOMe (3.50 g, 65 mmol). The thick orange solution was stirred for 2 h, at which time the mixture was acidified with dilute $H_2SO_4$, and the products were extracted with ether. The ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo to yield 4.4 g (54%) of crystalline product, mp 117 °C [lit.[50] mp 118.5 °C]. Spectroscopic properties (Tables III and V) are identical with those reported in the literature.[51]

**(*Z*)-α-Benzylidene-γ-butyrolactone ((*Z*)-8).** A solution of 800 mg (4.6 mmol) of (*E*)-α-butyrolactone in 200 mL of $CH_2Cl_2$ was irradiated with Pyrex-filtered light for 11 h. The reaction progress was monitored by GC to a final photostationary state of 26% *Z*, 74% *E*. The solid obtained after concentration in vacuo was subjected to preparative TLC on silica gel (4% ethyl acetate in benzene) to yield 184 mg of crystalline *Z* isomer. The material had spectroscopic and physical properties identical with those reported in the literature.[18]

**Methyl Indene-2-carboxylate (9).** Indene-2-carboxylic acid was prepared from the reaction of indene and oxalyl bromide by using the method of Treibs and Ortmann.[52] The acid (2.5 g, 0.016 mol) was esterified via the acid chloride to yield (2.4 g, 0.014 mol) of a light-brown solid which was recrystallized from ethanol–water, mp 78–79 °C.

**β-Phenyl-γ-crotonolactone (10).** The preparation of **10** by the method of Krauser and Watterson[53] via an intramolecular Wittig reaction of the phosphonium salt of α-(bromoacetoxy)acetobenzene afforded crystalline material with physical and spectroscopic properties identical with those reported.

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## Appendix

The equilibrium constants $K_{EA}$ and $K_{ZA}$ (Scheme I) are described by eq 6 and 7.

$$K_{EA} = \frac{[E{:}A]}{[E][A]} \qquad (6)$$

$$K_{ZA} = \frac{[Z{:}A]}{[Z][A]} \qquad (7)$$

Adding [*E*:A] to both sides of eq 6 and [*Z*:A] to both sides of eq 7 provides eq 8 and 9. Dividing eq 9 by eq 8 provides eq 10.

$$[E] + [E{:}A] = \frac{[E{:}A]}{K_{EA}[A]} + [E{:}A] \qquad (8)$$

$$[Z] + [Z{:}A] = \frac{[Z{:}A]}{K_{ZA}[A]} + [Z{:}A] \qquad (9)$$

$$\frac{[Z] + [Z{:}A]}{[E] + [E{:}A]} = \frac{[Z{:}A]}{[E{:}A]} \frac{(1 + K_{ZA}[A])}{(1 + K_{EA}[A])} \frac{K_{EA}}{K_{ZA}} \qquad (10)$$

The photostationary state for the fully complexed esters can be described by eq 11. Substitution of [*Z*:A]/[*E*:A] from eq 11 into eq 10 provides eq 12.

$$\frac{[Z{:}A]}{[E{:}A]} = \frac{\Phi_{EA}}{\Phi_{ZA}} \frac{\epsilon_{EZ}}{\Delta_{ZA}} \qquad (11)$$

$$\frac{[Z] + [Z{:}A]}{[E] + [E{:}A]} = \frac{\Phi_{EA}}{\Phi_{ZA}} \frac{\epsilon_{EA}}{\epsilon_{ZA}} \frac{(1 + K_{ZA}[A])}{(1 + K_{EA}[A])} \frac{K_{EA}}{K_{ZA}} \qquad (12)$$

If most of the Lewis acid is complexed, then $K_{ZA}[A]$ and $K_{EA}[A] \ll 1$ and eq 12 can be simplified to the form of eq 5.

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