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Lewis Acid Catalysis of Photochemical Reactions. 7. Photodimerization and Cross-Cycloaddition of Cinnamic Esters[1]

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Abstract: The effects of Lewis acid complexation upon the molecular structure, solid-state photodimerization, and solution dimerization and cross-cycloaddition of cinnamic esters have been investigated. Comparison of crystal structures for free and $SnCl_4$-complexed ethyl cinnamate indicates that the enone double bonds are lengthened, the single bonds are shortened, and the enone conformation changes from s-cis to s-trans upon complexation. These changes are consistent with calculated changes in π bonding and net charges. Solid-state photodimerization of free and complexed cinnamic esters and related molecules yield syn head-to-tail (α-truxillate) dimers. In most cases the Lewis acid complexes dimerize more efficiently and stereoselectively than the free esters. Photodimerization and cross-cycloaddition of methyl cinnamate in dilute solution is also catalyzed by Lewis acids. The mechanism of these reactions involves electronic excitation of a ground-state methyl cinnamate–Lewis acid complex followed by reaction of the excited complex with ground-state ester (dimerization) or simple olefin (cross-cycloaddition). The catalytic effect of Lewis acids is attributed to an increase in excited-state lifetime and reactivity.

The photochemical [2 + 2] cycloaddition of α,β-unsaturated carbonyl compounds with alkenes is one of the most extensively investigated and synthetically useful of photochemical reactions.[2] Its scope is limited by the failure of most acyclic α,β-unsaturated carbonyl compounds to undergo bimolecular reactions in competition with rapid unimolecular *E,Z* photoisomerization or deconjugation in fluid solution. Cinnamic esters are typical in this respect, undergoing only modestly efficient photodimerization, even when high local concentrations are achieved either by omission of solvent[3] or by linking two or more cinnamate residues together as a di- or polyester so that intramolecular photodimerization can occur.[4] Efficient photodimerization of (*E*)-cinnamic acid has been observed in the solid state (subject to topochemical control).[5] Similarly, cross-cycloaddition of cinnamic acid and its methyl esters with 2,3-dimethyl-2-butene is reported to occur slowly even when the alkene is used as the solvent.[6]

We have observed that Lewis acid complexation of α,β-unsaturated esters results in marked changes in their spectroscopic properties and unimolecular photochemistry.[1,7,8] The possibility that Lewis acids might also serve as catalysts for bimolecular photochemical reactions is suggested by early reports concerning the photodimerization of dibenzylideneacetone in the presence of $SnCl_4$ and ClO_2^+,[9] by preliminary reports from this laboratory concerning the effect of Lewis acids on the photodimerization of coumarin[10a] and cinnamic esters,[10b] and by a recent report of selective head-to-head dimerization of cyclopentenone in the presence of $SnCl_4$.[11] We describe here our detailed investigation of the molecular structure of the Lewis acid complexes of cinnamic esters, their photodimerization in the solid state and solution, and their cross-cycloaddition reactions with simple alkenes.

Table I. Bond Lengths (Angstroms) and Mulliken Populations

	free ester		complex	
bond	obsd[a]	calcd[b]	obsd[a]	calcd[b]
C2=C3	1.28	0.184	1.327 (5)	0.0975
C1—C2	1.51	0.020	1.450 (5)	0.0356
C1=O1	1.19	0.155	1.259 (4)	0.0335
C1—O2	1.41	0.031	1.312 (4)	0.0738
O1-SN			2.165 (2)	

[a] Crystallographic bond lengths from ref 10b and 12. [b] Calculated Mulliken populations.

Results and Discussion

Molecular Structure. Crystal structures have been reported for a large number of cinnamic acid and amide derivatives. The structures of the *m*- and *p*-bromo derivatives of methyl cinnamate were reported in 1965 by Leiserowitz and Schmidt.[12] While the bond lengths (Table I) and angles (Figure 1a) are imprecise by modern standards, they are similar to more recent values for cinnamic acids and amides and will suffice for the purposes of this discussion. Two important features of these structures are the preference for the *s-cis-* vs *s-trans*-enone conformation and the virtual planarity of the conjugated π system. While the s-cis conformation is observed for most cinnamate derivatives, α-methylcinnamic acid adopts the s-trans conformation in the solid state.[13] Planarity of the π system is achieved at the expense of bond angle distortions. The C2–C3–C4 bond angles in cinnamic acid derivatives range from 126 to 128° while that for α-methylcinnamic acid is 131°. These deviations from the normal 120° sp^2 bond angle reflect the nonbonded interactions between the ortho hydrogens of the benzene ring and the hydrogen or methyl group at C2.

We recently reported the molecular structure of the 2:1 complex of ethyl cinnamate with $SnCl_4$.[10b,14] Bond lengths and angles for

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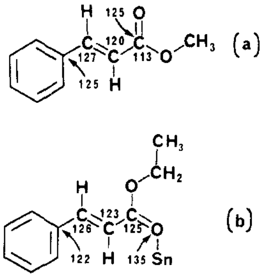


Figure 1. Selected bond angles for (a) methyl *m*-bromocinnamate[12] and (b) the 2:1 complex of ethyl cinnamate with $SnCl_4$.[11] Halogen atoms omitted for clarity.

the complex are given in Table 1 and Figure 1b, respectively. The ethyl cinnamate molecule is essentially planar, while Sn is ca. 24° out-of-plane. Comparison of Figure 1 parts a and b indicates that several significant structural changes occur upon complexation; viz., the enone conformation changes from s-cis to s-trans, the O1–C1–C2 and C1–C2–C3 bond angles increase, and the enone double bonds are lengthened and single bonds shortened. The *s-trans*-enone conformation, the location of Sn syn to the styryl group, and the out-of-plane location of Sn all reflect the steric demands of the $SnCl_4$. The 135° Sn–O–C bond angle is consistent with previous suggestions that the carbonyl oxygen has hybridization approximating to sp^2 in its Lewis acid complexes with σ-type acceptors.[15] Analysis of solution-phase ^1H NMR data supports a similar conformation for the BF_3 complexes of cinnamic esters.[7] In order to further understand the bonding of cinnamic esters and their Lewis acid complexes, GAUSSIAN 77 calculations for methyl cinnamate and its protonated form were carried out. The use of a proton as a model for the Lewis acid and the assumption of molecular planarity helped simplify the computational problem. The location of the proton syn to the styryl group with a H–O1–C1 bond angle of 122° is similar to the location of Sn; however, the lowest energy conformation remains *s*-cis, plausibly reflecting the smaller size of H^+ vs Sn. The calculated net charge on the carbonyl carbon increases from +0.307 to +0.470 upon protonation while the net charge on the ester oxygen decreases from –0.251 to –0.159. Changes on other atoms including the carbonyl oxygen are minor in comparison with these changes. The calculated changes in π bonding (Mulliken populations) upon protonation parallel the observed changes in bond length upon complexation (Table I). These changes are consistent with the model of a protonated ester based on classical resonance structures.

The calculated π and π^* orbital energies and atomic coefficients of free and protonated methyl cinnamate are shown in Figure 2. Both the HOMO and LUMO energies are lowered by protonation as a consequence of removing electron density from the π-bonding orbitals.[16] The LUMO energy is lowered by more than the HOMO energy, resulting in a lower HOMO–LUMO gap, in accord with the red-shift in the π,π^* absorption band observed upon complexation of methyl cinnamate with BF_3 or $EtAlCl_2$.[7] The atomic coefficients for the free ester HOMO resemble those of styrene, with small coefficients on the carbonyl group, while the LUMO is delocalized over the entire π system. The lowest energy electronic transition in methyl cinnamate is described by a PPP calculation as a relatively pure (93%) $\pi_{HO} \rightarrow \pi_{LU}$.[17] Protonation of methyl cinnamate results in drastic changes in the frontier orbital coefficients. The HOMO resembles the allyl bonding orbital and the LUMO resembles the allyl nonbonding orbital, localized on C1–C2–C3.

Solid-State Photodimerization. The photodimerization of cinnamic acids is one of the classical examples of a topologically controlled reaction.[5] In contrast, photodimerization of cinnamic esters in the solid state has not been extensively investigated. Early investigations of the photochemistry of the low-melting (33 °C) methyl cinnamate resulted in the isolation of small amounts in the centrosymmetric syn head-to-tail dimer, dimethyl α-truxillate (**1**, R = CH_3).[18] We find that irradiaton of microcrystalline

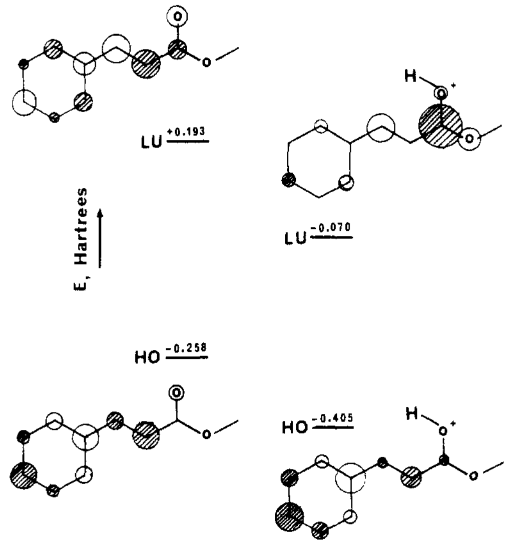
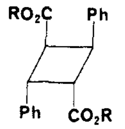


Figure 2. Frontier orbital energies and atomic coefficients of free and protonated methyl cinnamate.



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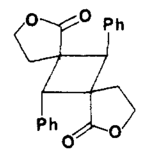

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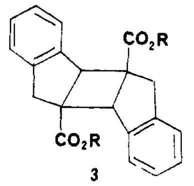

3

(*E*)-methyl cinnamate for 24 h at 20 °C yields a complex mixture of dimeric species, (*Z*)-methyl cinnamate, and loss of the crystalline integrity. Irradiation of an identical sample for 10 h at 0 °C results in a substantial increase in the efficiency of dimerization (62%) and stereoselective formation of the α-truxillate. The crystalline nature of the sample was maintained throughout the irradiation.

The ethyl, *n*-propyl, and isopropyl esters of cinnamic acid are oils at room temperature and photodimerize inefficiently and nonstereospecifically. Several crystalline cinnamic esters and related compounds undergo stereospecific photodimerization to yield α-truxillate dimers. The stereospecific dimerizations of *n*-octadecyl cinnamate to the α-truxillate (**1**, R = *n*-$C_{18}H_{37}$)[19a] and α-benzylidene-γ-butyrolactone to yield dimer **2**[19b] have been previously reported. We observe the dimerization of methyl *p*-(trifluoromethyl)cinnamate to yield an α-truxillate. Several other crystalline cinnamates, including the *p*-Cl and *p*-CH_3 methyl esters, (*E*)-methyl α-methylcinnamate, and methyl indenoate (which yields predominantly dimer **3**) dimerize with fair to good efficiency and stereoselectivity. These results are summarized in Table II.

The occurrence of stereospecific photodimerization of cinnamic esters to yield α-truxillates is presumed to require a centrosymmetric arrangement of neighboring molecules within the unit cell and a C=C center-to-center distance of ≤4.2 Å, as found in the α-cinnamic acid series.[5] While crystals of methyl cinnamate are reported to be unsuitable for structure determination, crystals of methyl *p*-bromocinnamate[12] and α-benzylidene-γ-butyrolactone[20] are known to adopt centrosymmetric geometries with shortest C=C distances of 4.11 and 3.67 Å, respectively. In the case of the latter molecule, solid-state photodimerization is known to begin

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Table II. Solid-State Photodimerization of Cinnamic Esters and Their Lewis Acid Complexes

ester	Lewis acid	time, h	dimer, %
methyl cinnamate		10	62
	BF_3	10	94
	$SnCl_4$	10	70
ethyl cinnamate	*a*	5	3[b]
	BF_3	5	12[b]
	$SnCl_4$	5	34 (85)
n-propyl cinnamate	*a*	4	1[b]
	$SnCl_4$	4	45
isopropyl cinnamate	*a*	4	1[b]
	$SnCl_4$	4	6[b]
methyl *p*-(trifluoromethyl)cinnamate		8	65
	$SnCl_4$	8	22
methyl *p*-chlorocinnamate		8	18[b]
	$SnCl_4$	8	25
methyl *p*-methylcinnamate		8	35[b]
	$SnCl_4$	8	85
methyl α-methylcinnamate		5	9[b]
	$SnCl_4$	5	23
methyl indenoate		24	68[b]
	$SnCl_4$	24	61

[a] Results for irradiation of thin films. [b] Nonstereospecific dimerization.

at a specific nucleation site and progress by frontal motion, resulting in the buildup of strain, which is relieved by crystal fracture.[20] The absence of crystal fracture upon irradiation of methyl cinnamate at 0 °C suggests the possibility of a topotactic behavior, i.e., a single-crystal to single-crystal transformation without phase separation. The failure of some cinnamic esters and analogues to photodimerize efficiently and stereospecifically may reflect crystal-packing modes in which the C=C bonds of neighboring molecules are either separated by >4.2 Å or are not properly aligned for cyclodimerization.

Methyl cinnamate forms a crystalline 1:1 complex with BF_3 and a 2:1 complex with $SnCl_4$.[21] Irradiation of these microcrystalline complexes (λ >300 nm) for 10 h under a nitrogen atmosphere results in exclusive α-truxillate formation with yields of 94% and 70%, respectively. Irradiation of the 1:1 complex of ethyl cinnamate with BF_3 for 5 h results in 12% conversion to a mixture of dimers, accompanied by liquefaction and *E* → *Z* isomerization. Irradiation of the 2:1 $SnCl_4$ complex for 5 h results in 34% conversion to the α-truxillate, while prolonged irradition affords 85% conversion to the α-truxillate. No *E* → *Z* isomerization occurred for the irradiated complex. While fissures are formed upon irradiation of larger single crystals, no liquification or discoloration is observed upon extended irradiation of the microcrystalline complex. Efficient solid-state photodimerization was also observed for several other 2:1 complexes of cinnamic esters with $SnCl_4$. The results summarized in Table II are for fixed duration irradiation periods, and hence, most of the yields have not been fully optimized. In all cases, except methyl *p*-(trifluoromethyl)cinnamate, the yields of photodimerization for the $SnCl_4$ complexes are comparable or superior to those of the noncomplexed ester.

The exclusive formation of the α-truxillate dimer upon irradiation of the crystalline 2:1 ethyl cinnamate–$SnCl_4$ complex is in accord with the postulate of topochemical control of solid–state photodimerization.[5] A computer drawn space-filling model of two neighboring 2:1 complexes (Figure 3) shows the head-to-tail stacking of a symmetry-related pair of ester molecules. The distance between the reactive double bonds in the infinite stacks of esters is 4.023 (8) Å for one symmetry-related pair and 4.125 (8) Å for a second symmetry-related pair, well within the range of values previously reported for photodimerizable cinnamic acids.[5] Efficient solid-state photodimerization to yield α-truxillate dimers is also observed for the 2:1 $SnCl_4$ complexes of the trans isomers of methyl cinnamate, *n*-propyl cinnamate, methyl α-methylcinnamate, and methyl 2-indenoate, but not for isopropyl cinnamate. While the crystal structure of these complexes is not known, space-filling models of these esters indicate that the necessary close-packed head-to-tail stacking of essentially planar cinnamate ligands can be achieved for the reactive esters. The isopropyl ester cannot pack in this fashion, and hence, the C=C center-to-center distance must be >4.2 Å, regardless of the mode of crystal packing.

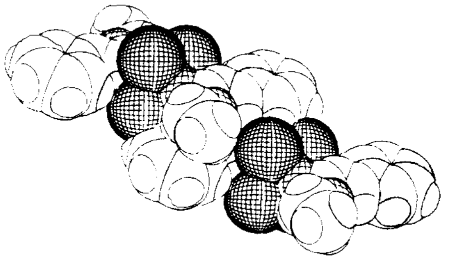

Figure 3. Space-filling model drawing of two neighboring 2:1 ethyl cinnamate–$SnCl_4$ complexes. Oxygen atoms are loosely cross-hatched and chlorine atoms tightly cross-hatched.

The only other reported examples of solid-state photodimerization reactions of Lewis acid complexes are those of 2:1 complexes of dibenzylideneacetone with UO_2^+ or $SnCl_4$, which proceed in poor yield to the syn head-to-tail dimer,[9] and of the 1:1 complex of coumarin with $HgCl_2$, which proceeds in an unspecified yield to the syn head-to-head dimer.[5c] In these cases the Lewis acid occupies the apices of the unit cell, whereas the 2:1 complex of ethyl cinnamate with $SnCl_4$ (Figure 3) occurs in infinite edge-to-edge stacks (one complex per unit cell), which may serve to maintain an intact crystal lattice even at high conversions to dimer. While many approaches toward controlling photochemical dimerization in the solid state have been reported, the results presented here represent a significant improvement in yield and stereoselectivity for dimerization by crystal engineering.

Solution Photodimerization. Photochemical cyclodimerization of cinamic acid derivatives is highly inefficient in dilute solution due to very rapid competing *E*,*Z* photoisomerization. Even for linked bis(cinnamates), photostationary-state mixtures of *E* and *Z* isomers are obtained prior to extensive photodimerization.[4,7] Egerton, et al.[3a] studied the photodimerization of neat liquid ethyl cinnamate at 25 °C and of its glasses at low temperature. Mixtures of head-to-head (truxinate) and head-to-tail (truxillate) dimers are obtained, the former predominating in the liquid phase. The α-truxillate **1** increases in importance with decreasing temperature, plausibly indicating local packing in the glass similar to that in crystalline cinnamate esters. α-Truxillates are also the major products obtained from irradiation of long-chain *n*-alkyl cinnamates in ordered liquid–crystalline solvents,[22a] while β-truxinates were formed in ordered monolayer assemblies.[22b] Selective dimerization has also been observed in "memory-containing" polymers.[22c]

We previously reported that irradiation of dilute solutions (0.01 M) of cinnamic esters in the presence of several Lewis acids results in selective *E* → *Z* photoisomerization to yield photostationary states enriched in the *Z* isomers.[7] Photodimerization does not occur to an observable extent within the time necessary to obtain photostationary states. Similar results are obtained for more concentrated solutions; however, prolonged (36 h) irradiation of 0.2 M methyl cinnamate with 0.1 M $BF_3{\cdot}OEt_2$ in dichloromethane solution results in consumption of 86% of the initial methyl cinnamate and the formation of a mixture of truxinate and truxillate dimers. Analysis of the product mixture by capillary GC/MS indicated the presence of 8 of the 11 possible [2 + 2] dimers of methyl cinnamate. All eight of the dimers were isolated by column chromatography and were characterized by their mass spectra and ^1H NMR spectra and by comparison with authentic samples of five of the isomers that were available from our previous in-

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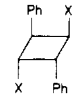
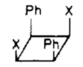
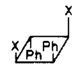
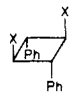
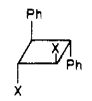
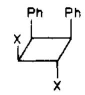
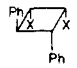
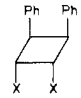
Table III. Dimer Distribution Obtained upon Irradiation of Cinnamate Esters in the Absence and Presence of Lewis Acids

dimer		BF$_3$·OEt$_2$[a]	SnCl$_4$[b]	neat[c]
α		10.4	13.7	6.3
peri		3.5		
ν		12.6	2.8	
ε		14.0	1.1	
δ		11.7	32.8	55.2
neo		18.1		7.1
ξ		8.6		
β		16.3	23.6	24.0

[a] 0.2 M methyl cinnamate and 0.1 M BF$_3$·OEt$_2$ in dichloromethane solution irradiated with λ >300. [b] 0.2 M methyl cinnamate and 0.1 M SnCl$_4$ in dichloromethane irradiated with λ 300. [c] Data for ethyl cinnamate from ref 3a.

vestigation of stilbene cycloaddition reactions (see the Experimental Section).[23] Irradiation of methyl cinnamate (0.20 M) in the presence of AlCl$_3$ or EtAlCl$_2$ (0.1 M) also results in efficient photodimerization (>80%) with a similar product distribution, while use of SnCl$_4$ in place of BF$_3$·OEt$_2$ results in 20% conversion to a substantially different mixture of dimers. The difference in product mixtures may reflect the reaction of 1:1 (BF$_3$, EtAlCl$_2$) vs 2:1 (SnCl$_4$) complexes. Isomer distributions obtained by using BF$_3$·OEt$_2$ and SnCl$_4$ are reported in Table III along with the results of Egerton et al.[3a] for the neat liquid. No dimerization is observed upon irradiation of 0.2 M methyl cinnamate under our conditions in the absence of Lewis acid.

Analysis of dimer stereochemistry (Table III) indicates that head-to-head dimers (truxinates) account for 76% and 55% of the SnCl$_4$ and BF$_3$·OEt$_2$ catalyzed reactions and 65% of neat liquid reaction. Similar results are obtained for methyl 2-indenoate, which in the solid state yields 90% and 100% syn head-to-tail dimer **3** in the absence and presence of SnCl$_4$, respectively, and in solution yields 64% and 66% syn head-to-tail dimer in the absence and presence of EtAlCl$_2$. Kaupp et al.[19b] reported that photodimerization of α-benzylidene-γ-butyrolactone yields 75% head-to-head dimer in benzene solution but exclusively head-to-tail dimer **2** in the solid state. The preference for α-truxillate formation in the solid-state dimerization of both free and complexed cinnamic esters apparently is a consequence of topological control rather than any inherent regioselectivity in the photodimerization reactions of either free or complexed esters.

Approximately half of the dimers formed in the BF$_3$-catalyzed reaction of methyl cinnamate incorporate a single *Z* monomer and ca. 4% incorporate two *Z* monomers. Dimerization of the neat liquid results in 12% incorporation of a single *Z* monomer and no incorporation of two *Z* monomers. The higher incorporation of *Z* monomer in the BF$_3$-catalyzed reaction reflects the higher *Z* content of the photostationary state in the presence of Lewis acid (88% vs 46%).[7]

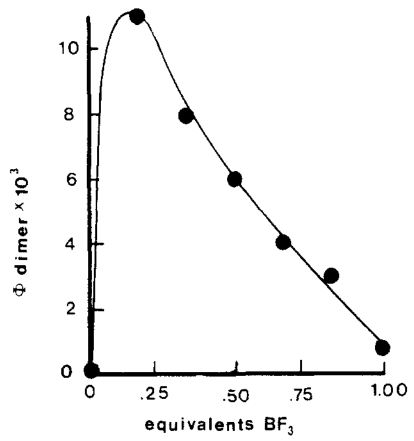


Figure 4. Effect of BF$_3$ concentration on the quantum yield for dimerization of methyl cinnamate (0.2 M) in dichloromethane solution.

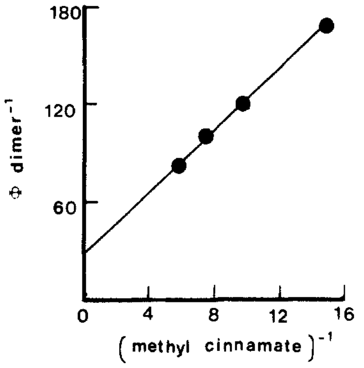


Figure 5. Effect of excess methyl cinnamate on the quantum yield for photodimerization of 0.033 M methyl cinnamate–BF$_3$ in dichloromethane solution.

The effect of BF$_3$ concentration on the quantum yield for photodimerization of 0.2 M methyl cinnamate using monochromatic 313-nm light is shown in Figure 4. The dimerization quantum yield increases from $<10^{-4}$ in the absence of BF$_3$ to 0.011 with 0.125 equiv of BF$_3$ and decreases at higher Bf$_3$ concentrations. Similar results were obtained with AlCl$_3$ in place of BF$_3$. Under these conditions, all of the Lewis acid is complexed and the complex absorbs >90% of the incident light. Higher concentrations of BF$_3$·OEt$_2$ (ca. 1.0 equiv) were necessary to obtain optimum quantum yields due to the lower equilibrium complexation of BF$_3$ with methyl cinnamate in the presence of ether.[7] The optimum quantum yields for photodimerization are substantially lower than those for $E \rightarrow Z$ photoisomerization in the Lewis acid complexes (Φ ~0.70),[7] in accord with the observation of photoisomerization to a stationary-state mixture of ca. 12% (*E*) and 88% (*Z*)-methyl cinnamate prior to detectable photodimerization.

The observation of optimum dimerization quantum yields with ca. 0.1 equiv of Lewis acid under conditions where the Lewis acid complex absorbs most of the incident irradiation is suggestive of a mechanism in which an electronically excited complex (either singlet or triplet) reacts with ground-state methyl cinnamate to yield dimer (Scheme I). Further support for this mechanism is provided by the increase in dimerization quantum yield with increasing methyl cinnamate concentration and a constant (0.033 M) BF$_3$ concentration. The linear double-reciprocal plot shown in Figure 5 has an intercept (Φ^{-1}) of 29, corresponding to a limiting dimerization quantum yield of 0.035. The intercept/slope ratio provides a value of $k_q\tau$ = 3.1 M^{-1}, indicative of reaction of a short-lived intermediate (singlet or triplet) or a low bimolecular reaction rate constant.

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(23) (a) Green, B. S.; Rejtö, M.; Johnson, D. E.; Hoyle, C. E.; Ho, T.-I.; McCoy, F.; Simpson, J. T.; Lewis, F. D. *J. Am. Chem. Soc.* **1979**, *101*, 3325. (b) Hung, J. D.; Lahav, M.; Luwisch, M.; Schmidt, G. M. J. *Isr. J. Chem.* **1972**, *10*, 585. (c) Ben-Efriam, D. A.; Green, B. S. *Tetrahedron* **1974**, 2357.

Scheme I

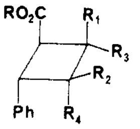
$$\mathrm{PhHC{=}CHCO_2Me + BF_3 \rightleftarrows PhHC{=}CHCO_2Me{-}BF_3}$$

$$\mathrm{PhHC{=}CHCO_2Me{-}BF_3 \xrightarrow{h\nu} PhHC{=}CHCO_2Me{-}BF_3{}^*}$$

$$\mathrm{PhHC{=}CHCO_2Me{-}BF_3{}^* + PhHC{=}CHCO_2Me \rightarrow dimer + BF_3}$$

Cross-Cycloaddition Reactions. Previous examples of cross-cycloaddition reactions of excited-state cinnamic esters with ground-state olefins are limited to communications by Chapman et al.,[6a] reporting the reaction of methyl cinnamate with neat 2,3-dimethyl-2-butene to yield both [2 + 2] and ene adducts, and by Ishigami et al.,[6b] reporting the competition between photodimerization and cross-addition of methyl *p*-nitrocinnamate with several 1,3-dienes and styrene derivatives. The failure of cross-addition to occur with various monoolefins was attributed to their high ionization potentials, which render them unreactive with the electrophilic excited state of methyl *p*-nitrocinnamate. In agreement with these reports, we find that irradition of (*E*)-methyl cinnamate (0.02 M) with several simple alkenes (0.40 M) in dichloromethane solution results in inefficient cross-cycloaddition and no detectable quenching of *E* → *Z* photoisomerization. Typical results obtained upon reaction with (*Z*)-2-butene are shown in Figure 6a. After 52-h irradiation, an 18% yield of an ca. 1:1 mixture of two cycloadducts is observed (GC and MS).

Since the proposed mechanism for dimerization of methyl cinnamate in the presence of BF_3 involves absorption of light by a ground-state BF_3 complex followed by reaction of the excited complex with a ground-state noncomplexed cinnamate molecule (Scheme I), it seemed likely that simple alkenes might also fulfill the role of ground-state reactant. The results obtained for irradiation of methyl cinnamate (0.02 M) and (*Z*)-2-butene (0.40 M) in the presence of $BF_3{\cdot}OEt_2$ (0.03 M) are shown in Figure 6b. Comparison of Figure 6 parts a and b clearly demonstrates the enhanced rates of both dimerization and isomerization obtained in the presence of BF_3. After 52-h irradiation, a 93% yield of an ca. 1:1 mixture of two cycloadducts is observed. Similarly, irradiation of methyl cinnamate with (*E*)-2-butene for 48 h in the absence and presence of $BF_3{\cdot}OEt_2$ results in 10% and 65% conversion to a mixture of two cycloadducts (0.5:1 and 0.7:1 mixtures, respectively), which differ in GC retention time from the adducts obtained with (*Z*)-2-butene. The two adducts obtained with (*E*)-2-butene were isolated by preparative GC and characterized as the isomeric cyclobutanes **4** and **5** on the basis of their ^1H NMR, IR, and mass spectra. The two adducts with (*Z*)-2-butene resisted all attempts at chromatographic separation and are tentatively assigned structures **6** and **7** on the basis of their mass spectra and the ^1H NMR spectrum of their 1:1 mixture.



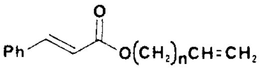
4: $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$
5: $R_2 = R_3 = CH_3$; $R_1 = R_4 = H$
6: $R_1 = R_2 = CH_3$; $R_3 = R_4 = H$
7: $R_3 = R_4 = CH_3$; $R_1 = R_2 = H$

The structures assigned to adducts **4**–**7** display retention of 2-butene stereochemistry. The phenyl and carbomethoxy groups are trans in all four adducts, as previously reported by Chapman et al.[6a] for the adduct of methyl cinnamate with 2,3-dimethyl-2-butene. Since both (*E*)- and (*Z*)-methyl cinnamate absorb comparable amounts of light once the stationary state is reached, the apparent absence of *Z* adducts indicates that either excited (*Z*)-methyl cinnamate is much less reactive than its *E* isomer or cycloaddition of the *Z* isomer occurs via a 1,4-biradical intermediate in which stereomutation occurs in the cinnamate but not the butene portion of the biradical. We favor the former explanation. A singlet mechanism for both the cross-addition and dimerization of free and complexed (*E*)-cinnamic esters is consistent with the observed stereochemistry of these processes. The failure of excited-state (*Z*)-cinnamic esters (free or complexed) to react efficiently with ground-state ester of simple alkenes is suggestive of a shorter singlet-state lifetime, as in the case of (*Z*)-stilbene.

We have also observed marked Lewis acid enhancement of the rate of reaction of methyl cinnamate with cyclohexene, 2-ethyl-1-butene, and 1-pentene. Mass spectra indicate that the products are mixtures of isomeric cyclobutanes. However, efforts to separate these isomers by standard chromatographic methods were unsuccessful. The available GC/MS data indicate that these reactions are not highly regio- or stereoselective. No Lewis acid enhancement of cross-cycloaddition was observed upon irradiation of methyl cinnamate with 2,3-dimethyl-2-butene, 2-methyl-2-butene, or with several α,β-unsaturated esters and carbonitriles. Dienes and styrenes react thermally with strong Lewis acids, precluding their use in cross-cycloaddition reactions.

The catalytic effect of Lewis acids on the cross-cycloaddition reactions of cinnamic esters with simple mono- and dialkyl olefins could result from either an increase in excited-state lifetime or reactivity of the complexed vs free ester. The very weak fluorescence of methyl cinnamate in dichloromethane solution is observed to increase in intensity upon addition of $EtAlCl_2$, possibly reflecting an increase in single lifetime.[7] The calculated decrease in HOMO energy that occurs upon protonation (Figure 2) should result in stabilization of an encounter complex or exciplex formed from excited-state state complexed vs noncomplexed ester with donor olefins. This would result in increased reactivity with weak donor olefins, but not acceptor olefins, as is observed. The failure to observe addition of either free or complexed methyl cinnamate with 0.4 M 2,3-dimethyl-2-butene might reflect a steric effect on the cycloaddition process.

In an effort to control the regiochemistry of cross-cycloaddition of cinnamate esters with terminal olefins, the unsaturated esters **8** and **9** were synthesized. Irradiation of (*E*)-**8** or -**9** in the absence of Lewis acid resulted in *E* → *Z* isomerization to photostationary states containing 37% and 39% *Z* isomer, respectively. Irradiation in the presence of $BF_3{\cdot}OEt_2$ resulted in more rapid isomerization of (*E*)-**8** or -**9** to photostationary states containing 63% and 68% *Z* isomer, respectively. Only minor amounts (<10%) of other products could be detected by GC following irradiation for several hours. Triplet sensitization of (*E*)-**8** using Michler's ketone also resulted exclusively in *E*,*Z* isomerization. The failure of **8** and **9** to undergo intramolecular cycloaddition stands in marked contrast to the behavior of the corresponding polymethylene dicinnamates.[4] The occurrence of intramolecular dimerization but not cross-addition may reflect either a higher ground-state population of photochemically reactive geometries or a faster reaction rate for the dimerization vs cross-addition process.



8 n = 3
9 n = 4

Concluding Remarks. In summary, we find that Lewis acids can serve as catalysts for the dimerization reactions of cinnamic esters both in the solid state and in solution. The solid-state photodimerization of the 2:1 complex of ethyl cinnamate with $SnCl_4$ is subject to topochemical control, addition of a planar cinnamate ligand to one located directly above or below it and bonded to a different Sn resulting in the formation of diethyl α-truxillate. Efficient solid-state photodimerization is observed for the $SnCl_4$ complexes of methyl, ethyl, and *n*-propyl, but not isopropyl cinnamate, presumably reflecting inability of the isopropyl ester to adopt the same crystal packing as the smaller esters.

The solution-phase photodimerization and cross-cycloaddition reaction of methyl cinnamate are catalyzed by Lewis acids. Reaction of the excited-state complexed ester with ground-state ester or simple alkenes competes inefficiently with *E*,*Z* photoisomerization. Thus, photostationary states enriched in (*Z*)-methyl cinamate are obtained prior to appreciable cycloaddition. The observed dependence of the photodimerization quantum yield upon the concentrations of BF_3 and methyl cinnamate are indicative

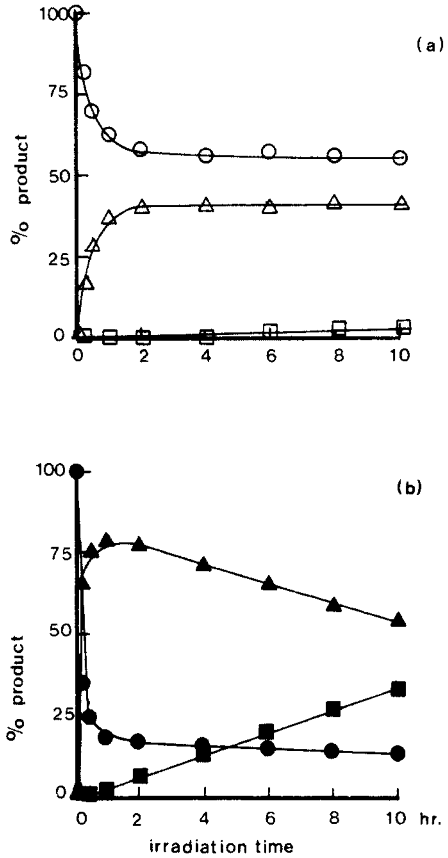


Figure 6. Progress of the photoisomerizaion of (*E*)-methyl cinnamate (○, ●) to (*Z*)-methyl cinnamate (△, ▲) and cycloaddition with (*Z*)-2-butene (□, ■): (a) in the absence of BF_3, (b) in the presence of BF_3.

of a reaction mechanism in which an excited complex reacts with noncomplexed ground-state ester to yield dimers. The cross-addition reactions with (*E*)- and (*Z*)-2-butene exclusively yield products with retention of alkene and (*E*)-methyl cinnamate stereochemistry. Thus, these reactions are presumed to occur via the singlet complex of (*E*)-methyl cinnamate, which evidently is more reactive than the singlet complex of (*Z*)-methyl cinnamate. The enhanced efficiency of both photodimerization and cross-addition of methyl cinnamate upon Lewis acid complexation may reflect an increase in excited-state lifetime or reactivity. Increased reactivity with weakly electron-donating olefins is consistent with the decrease in HOMO and LUMO energies that occurs upon complexation.

The observation of Lewis acid catalyzed stereospecific cross-addition reactions of an acyclic α,β-unsaturated ester with simple olefins raises the exciting possibility of significantly extending the scope and synthetic utility of enone cycloaddition reactions. Preliminary investigations of the cross-cycloaddition reactions of coumarin and quinoline complexes with simple olefins have provided further encouragement in this respect. However, our efforts to improve upon the cycloaddition reactions of cycloalkenones have to date been unsuccessful.

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 in a Perkin-Elmer 283 infrared spectrophotometer. NMR spectra were obtained on a Varian EM301A or CFT20 NMR spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer MPF-44A spectrophotometer. Mass spectra were recorded on a Hewlett-Packard 5958A 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 313-nm irradiation 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. 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 merrry-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.

Table IV. Spectral Characterization of Truxillate and Truxinate Dimers Obtained upon Irradiation of Methyl Cinnamate and $BF_3 \cdot OEt_2$

dimer	RT,[a] min	MS,[b] *m/e*	^{1}H NMR, δ		
			OCH_3	cyclobutyl	Ph
α-truxillate	11.47	324, 162, 131 (s)	3.29 (s)	3.60–4.70 center (4.18)	7.25
peritruxillate	11.49	324, 162, 131 (s)	3.08 (s)	*c*	7.26
ν-truxillate	11.30	324, 162, 131 (s)	3.35 (s)	4.60–4.90 (t)	7.25
				4.10–4.35 (m) 3.50–3.75 (m)	7.32
ϵ-truxillate	10.90	324, 162, 131 (s)	3.70 (s)	*c*	7.26
δ-truxinate	11.10	324, 162, 131, 113 (A)	3.67 (s)	3.32–3.85	7.19
neotruxinate	10.50	324, 162, 131, 113 (A)	3.28 (s) 3.72 (s)	4.00–4.50	6.70–7.30
ξ-truxinate	11.80	324, 162, 131, 113 (A)	3.28 (s) 3.73 (s)	*d*	7.20–7.30
β-truxinate	11.28	3.24, 162, 131, 113 (A)	3.70 (s)	4.00–4.50	6.80–7.30

[a] Retention time, 10-m WCOT glass capillary coated with OV-1, 50 °C for 1 min, 20 °C/min to 200 °C. [b] s and A refer to symmetric and asymmetric cleavage, respectively, based on retro [2 + 2] fragmentation. [c] Cyclobutyl proton resonances not resolved due to inseparable mixture of peri and ϵ. [d] Cyclobutyl resonances were too weak for assignment.

Ionization and cycloaddition reactions were monitored by use of either a 6 ft or 11 ft × $^1/_8$ in. column containing 5% SF-96 on Chromosorb G. Methyl cinnamate dimer analysis was performed on a 10-m fused silica open tubular capillary column coated with OV-1. Preparative gas chromatography was carried out on a Hewlett-Packard 700 gas chromatograph with thermal conductivity detectors. Light intensities were measured by using (E)-stilbene chemical actinometers run in triplicate.[24]

Chemicals. Boron trifluoride (Matheson) and ethyl aluminum dichloride (Texas Alkyls, 25% weight solution in heptane) were used as received. Boron trifluoride etherate (Aldrich) and tin tetrachloride were distilled prior to use. Dichloromethane (Aldrich Gold Label) was refluxed over calcium hydride and distilled immediately prior to use. Cinnamic esters were prepared and purified as previously described.[7] Boron trifluoride–ester complexes were prepared by either purging a solution of ester in dichloromethane with BF_3 gas or addition of boron trifluoride etherate to the ester solution and removal of the solvent under reduced pressure.

4-Pentenyl Cinnamate (8). To a solution of cinnamoyl chloride (6.8 g, 0.04 mol) in 25 mL of dichloromethane cooled to −78 °C was added 1.1 equiv of triethylamine followed by 1.1 equiv of 4-penten-1-ol (Aldrich). After being stirred for 1 h, the mixture was warmed to room temperature, stirred for 0.5 h, and extracted four times with 20% aqueous NaOH. The organic layer was dried over $MgSO_4$, filtered, and concentrated to yield 4.2 g (49%) of low-melting yellow crystals: ^{1}H NMR ($CDCl_3$) δ 2.0 (m, 2 H), 2.2 (m, 2 H) 4.3 (t, 2 H), 5.2 (m, 2 H), 5.7–6.1 (m, 1 H) 6.5 (d, 1 H), 7.4–7.7 (m, 5 H), 7.8 (d, 1 H).

5-Hexenyl Cinnamate (9). Repetition of the above procedure using 5-hexene-1-ol (Aldrich) resulted in the formation of a yellow oil, which was purified by chromatography on silica gel (dichloromethane solvent) yielding 3.7 g (40%) of **9**: ^{1}H NMR δ 1.5–1.9 (m, 4 H), 2.1 (q, 2 H), 4.2 (t, 2 H), 4.9–5.1 (m, 2 H), 5.5–6.0 (m, 1 H), 6.4 (d, 1 H), 7.1–7.5 (m, 5 H), 7.7 (d, 1 H).

Tin Tetrachloride–Bis((*E*)-ethyl cinnamate) ($SnCl_4$–$2C_6H_5CH{=}CHCOOC_2H_5$). Ethyl cinnamate (1.76 g, 0.01 mol) was transferred to a 10-mL volumetric flask and 5 mL of dichloromethane added. Under a dry N_2 atmosphere, $SnCl_4$ (1.30 g, 0.005 mol) was slowly syringed into the ethyl cinnamate solution. Hexane (5 mL) was added to induce precipitation of a white solid, which was filtered and rinsed several times with hexane. The residual solvent was removed under vacuum, yielding 2.90 g (0.0047 mol, 94%) of the complex. The complex was recrystallized from a 2:1 toluene/hexane mixture (crystallographic quality crystals were

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(24) Lewis, F. D.; Johnson, D. E. *J. Photochem.* **1977**, *7*, 421.

obtained by cooling the sealed solution slowly from 80 °C to room temperature over a 12-h period), yielding colorless rhombic plates: mp 145 °C. Anal. Calcd for $SnCl_4C_{22}H_{24}H_2$: C, 43.13; H, 3.92; Cl, 23.14. Found: C, 43.17; H, 3.90; Cl, 23.32. Chemical ionization mass spectroscopy yielded no parent ion 612; however, isotopic clusters centered at 577 and 507 are observed, which are indicative of loss of one and three chlorine atoms, respectively.

Irradiation of Solids and Oils. Thin films of the solid esters were prepared by transferring 0.001 mol of the respective ester to a 13 × 100 mm Pyrex tube. Solid samples were heated until the ester was in a liquid state, redistributed evenly on half of the tube, and allowed to recrystallize. Liquid samples were treated in a similar manner. BF_3 and $SnCl_4$ complexes were prepared as described and distributed on a single face of 13 × 100 mm Pyrex tubes with Kontes side arms. These samples were evacuated and sealed. Samples were irradiated with a 450-W medium-pressure lamp through a Pyrex filter at 0 °C. Liquid samples were irradiated in a horizontal position to ensure maximum light absorption. Lewis acid samples were quenched with water, and the organic material was extracted with dichloromethane, dried over $MgSO_4$, filtered, and concentrated. Samples were subjected to GC/MS and ^{1}H NMR analyses. Spectral data for the α-truxillates obtained from methyl and ethyl cinnamates, methyl *p*-methylcinnamate, and methyl *p*-chlorocinnamate are in agreement with published data.[23] Structure assignments for the other α-truxillates are based on spectral data, particularly the highly characteristic cyclobutane ring proton NMR signals.[23b]

Irradiation of the (*E*)-Ethyl Cinnamate–$SnCl_4$ Complex. The solid complex was irradiated for 12 h, yielding (*Z*)-ethyl cinnamate (<1%), (*E*)-ethyl cinnamate (14%), and the α-truxillate (85%): ^{1}H NMR ($CDCl_3$) δ 0.82 (t, J = 7 Hz, 6 H), 3.74 (q, J = 7 Hz, 4 H), 3.74–4.70 (m, 4 H), 7.30 (s, 10 H); mass spectrum, m/e 352, 176, 131 (M^+).

Irradiation of the (*E*)-Propyl Cinnamate–$SnCl_4$ Complex. The crystalline sample was irradiated for 4 h, yielding (*Z*)-propyl cinnamate (2%), (*E*)-propyl cinnamate (51%), and the corresponding α-truxillate (47%): ^{1}H NMR ($CDCl_3$) δ 0.80 (d, J = 7 Hz, 6 H), 1.55 (s, 4 H), 3.60 (t, J = 7 Hz, 4 H), 3.75–4.70 (m, 4 H), 7.30 (s, 10 H); mass spectrum, m/e 360, 180, 131 (M^+).

Irradiation of the (*E*)-Methyl *p*-Methylcinnamate–$SnCl_4$ Complex. The solid complex was irradiated for 8 h. Analysis of the sample showed less than 1% (*Z*)-methyl *p*-methylcinnamate, (*E*)-methyl *p*-methylcinnamate (18%), and a single dimer that was characterized as the corresponding α-truxillate (81%): ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6 H); 3.33 (s, 6 H), 3.70–4.70 (m, 4 H), 7.15 (s, 8 H).

Irradiation of (*E*)-Methyl *p*-(Trifluoromethyl)cinnamate. The crystalline film was irradiated for 8 h. The film maintained its crystalline integrity during the entire irradiation. Examination of the sample showed a mixture composed of the *Z* (17%) and *E* (31%) isomers and a single dimer (67%) identified as the α-truxillate: ^{1}H NMR ($CDCl_3$) δ 3.35 (s, 6 H), 3.70–4.75 (m, 4 H), 7.10–7.80 (m, 8 H).

Irradiation of the Methyl α-Methylcinnamate–$SnCl_4$ Complex. The solid complex was irradiated for 4.5 h. Analysis of the sample by GC showed starting ester (75%) and a single dimer (23%) identified as the α-truxillate: mass spectrum, m/e 352, 176, 161, 91 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H), 3.54 (s, 6 H), 4.40 (s, 2 H), 7.27 (s, 2 H).

Irradiation of the Methyl 2-Idenoate–$SnCl_4$ Complex. The solid complex was irradiated for 24 h, yielding recovered starting material (61%) and a single dimeric species that was identified as the syn head-to-tail dimer: ^{1}H NMR ($CDCL_3$) δ 3.28 (s, 6 H), 3.62 (s, 4 H), 4.25 (s, 2 H), 7.20 (s, 8 H): mass spectrum, m/e 348, 229, 228, 174 (M^+), 146, 143, 129, 115.

Solution Photodimerization of Methyl Cinnamate With $BF_3 \cdot OEt_2$. (*Z*)-Methyl cinnamate (1.62 g, 0.01 mol) and $BF_3 \cdot OEt_2$ (1.0 mL, 0.0075 mol) were transferred to a 0.05-L volumetric flask and made to volume with dichloromethane under N_2. The sample was transferred to a Pyrex annulus and irradiated for 30 h with a 450-W lamp. Examination of the irradiated solution by GC showed that 85% of the cinnamate had been consumed and that several photoproducts had been formed. Further irradiation yielded no increase in product formation. The solution was extracted with 0.01 L of water, the aqueous layer discarded, and the organic layer dried over $MgSO_4$. The organics were concentrated and subjected to flash chromatographic separation on silica gel (60 × 4 cm column) with a 2% ethyl acetate/hexane solvent mixture. Early fractions contained (*Z*)- and (*E*)-methyl cinnamate. Further elution (≈3–4 L) yielded four truxillate dimers (α, peri, ν, ϵ) followed by four truxinate dimers (δ, neo, ξ, β). Total dimer yield was 1.20 g (0.75 mol, 75%). Mass spectra of the cyclodimers provided a means of distinguishing between truxinate and truxillate dimers.[3a] Cyclobutanes readily undergo fragmentation in a retro [2 + 2] fashion. While truxillates can undergo only symmetrical cleavage, truxinates yield products of both symmetrical and asymmetrical cleavage. In the latter mode, the ion $CH_3OOCCH{=}CHCO^+$ is produced, with a mass peak m/e 113, in a region uncluttered by other fragments. This mass peak in the fragmentation pattern of the cyclodimer is therefore diagnostic for the heat-to-head configuration of the substituents.

^{1}H NMR spectra of the α-truxillate and the δ-, neo-, β-, and ξ-truxinates were obtained and identified by comparison with literature data and authentic samples.[23] The other three isomeric truxillates were characterized by consideration of the chemical shifts of the ester methyl groups and cyclobutyl protons. The observed chemical shift of a methyl ester group adjacent to a single phenyl group is approximately δ = 3.30 ± 0.05 ppm as observed for the α- and ν-truxillates and the neo-, β-, and ξ-truxinates. The methyl chemical shift δ = 3.70 ± 0.05 ppm as observed for the ϵ-truxillate and δ-, neo-, and ξ-truxinates is indicative of a β-trans phenyl group. The assignment of the peri isomer is based on a single ester methyl resonance, which is unusually far upfield (δ 3.08), suggestive of shielding by two β-cis phenyl groups. The α-, peri-, ν-, and ϵ-truxillates and the δ- and β-truxinates each displayed two nonequivalent methyl groups, as expected. Mass spectral and ^{1}H NMR data are summarized in Table IV.

Irradiation of (*E*)-Methyl Cinnamate and (*E*)-2-Butene in the Presence of $BF_3 \cdot OEt_2$. Methyl cinnamate (0.37 g, 2.3 × 10^{-3} mol) was dissolved in 0.075 L of dichloromethane, and the resultant mixture was transferred to a 0.1-L Pyrex tube with a Kontes gas-tight valve and O-ring adapter. Boron trifloride etherate (1.35 mL, 3.45 × 10^{-3} mol) was syringed into the sample under a dry nitrogen atmosphere. The tube was connected to a gas-transfer line, the sample cooled to liquid nitrogen temperature, and (*E*)-2-butene (2.3 g, 4.1 × 10^{-2} mol) condensed into the vessel. The sample was irradiated at 0 °C for 48 h with a 450-W medium-pressure lamp in a Pyrex filter. Analysis of the reaction mixture by GC showed that 98% of the methyl cinnamate had been consumed and that two products were formed in a ratio of 0.77:1.0. The solution was quenched with water and the aqueous portion discarded, and the organics were dried over $MgSO_4$. The solution was concentrated, yielding 0.4 g of a yellow oil, and subjected to a preparative gas chromatographic separation. The short retention time product was determined to be the anti-adduct **6**: mass spectrum, m/e 218, 162, 131, 118 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.15 (d, J = 7.5 Hz, 6 H), 1.75–2.30 (m, 2 H), 2.60 (dd, $J_1 \approx J_2$ = 12 Hz, 1 H), 3.10 (dd, $J_1 \approx J_2$ = 12 Hz, 1 H), 3.68 (s, 3 H), 7.24 (s, 5 H); IR (neat) λ_{max} 3080, 3060, 3023, 2950, 2920, 2862, 1730, 1603, 1495, 1450, 1435, 1403*, 1373, 1240*, 1140* cm^{-1} (*characteristic of anti adduct).

The longer reaction time product was characterized as the syn-adduct **5**: mass spectrum, m/e 218, 162 (M^+), 131, 118 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.75 (d, J = 10 Hz, 3 H), 1.18 (d, J = 10 Hz, 3 H), 3.32 (m, 2 H), 3.58 (dd, $J_1 \approx J_2$ = 10 Hz, 1 H), 3.70 (s, 3 H), 4.07 (dd, $J_1 \approx J_2$ = 104, 1 H), 7.0–7.50 (m, 5 H); IR (neat) λ_{max} 3080, 3060, 3023, 2958, 2920, 2868, 1730, 1601, 1495, 1435, 1375, 1200‡, 1160‡, 750, 700 cm^{-1} (‡characteristic of syn adduct).

Irradiation of (*E*)-Methyl Cinnamate and (*Z*)-2-Butene in the Presence of $BF_3 \cdot OEt_2$. Methyl cinnamate (0.37 g, 2.3 × 10^{-3} mol), (*Z*)-2-butene (2.3 g, 4.1 × 10^{-2} mol), and $BF_3 \cdot OEt_2$ (1.35 mL, 3.5 × 10^{-3} mol) were combined in 0.075 L of dichloromethane as described in the previous procedure. Irradiation with a 450-W lamp for 72 h followed by analysis by GC indicated that 90% of the cinnamate had been consumed, yielding two products in a ratio of 1:9. Spectral characterization revealed that the minor (short retention time) product was the same as the (*E*)-2-butene adduct **6**. The longer reaction time species was found to be composed of two (*Z*)-2-butene adducts on the basis of GC/MS and NMR analyses of the isolated material. Further preparative separation was not achieved. Enhanced separation was achieved with capillary GC/MS, which suggested that two isomers were present in comparable amounts. Mixture of **7** and **8**: ^{1}H NMR δ 0.67 (d, J = 10 Hz, 3 H), 1.04 (d, J = 10 Hz, 9 H), 2.40–2.70 (m, 4 H), 2.80–4.10 (several dd, 4 H), 3.67 (s, 6 H), 7.17–7.25 (s, 10 H); IR (neat) λ_{max} 3080, 3060, 3025, 2960, 2930, 2875, 1760, 1600, 1500, 1495, 1450, 1435, 1380, 1345, 1330, 1250, 1100, 1070, 1045, 810, 745, 700 cm^{-1}.

Calculations. Semiempirical calculations employed the PPP model[25] and were carried out with a standard code.[26] Ab initio Hartree–Fock calculations[27] were done at the STO-3G (minimal basis set) level using the GAUSSIAN 77 program package.[28]

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