J. Org. Chem. 1991, 56, 553-561 553

Structure and Photoisomerization of (*E*)- and (*Z*)-Cinnamamides and Their Lewis Acid Complexes[1]

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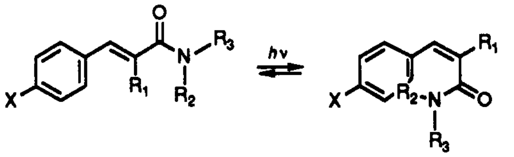
Received June 11, 1990

The spectroscopic properties and photoisomerization reactions of several (*E*)- and (*Z*)-cinnamamides have been investigated in the absence and presence of the strong Lewis acid BF_3. The (*E*)-cinnamamides are essentially planar and exist predominantly in the enone s-cis conformation, except in the case of the α-methyl tertiary amide which adopts the s-trans conformation in order to minimize nonbonded repulsion. The (*Z*)-cinnamamides exist predominantly in the highly nonplanar s-trans conformation. This unusual conformational preference is attributed to intramolecular charge transfer from the aromatic to amide functionality. Photoisomerization efficiencies are dependent upon N-alkylation, aromatic substitution, α-alkylation, solvent, and excitation wavelength. These effects are attributed to the existence of two lowest energy π,π^* singlet states (one reactive and one nonreactive) whose relative energies are dependent upon substitution. The cinnamamides form 1:1 complexes with BF_3 with equilibrium constants $>10^3$. Complexation alters both the electronic structure and photochemical behavior of the cinnamamides. Quantitative $E \rightarrow Z$ isomerization has been observed for the BF_3 complexes of two tertiary amides.

Introduction

The photoisomerization and photodimerization reactions of cinnamic esters have been the subject of numerous investigations, prompted at least in part by the application of their photodimerization in the early development of photo-cross-linkable polymers.[2-5] In contrast, investigations of the photochemistry of cinnamamides have been limited to the use of photochemical $E \rightarrow Z$ isomerization to prepare the *Z* isomers for pharmacological testing.[6,7] We have previously reported that strong Lewis acids such as BF_3 can serve as catalysts for selective $E \rightarrow Z$ isomerization, photodimerization, and cross-cycloaddition of cinnamic esters.[8,9] Since amides are stronger Lewis bases than esters, the cinnamamides appeared to be attractive candidates for further investigation. Preliminary studies of the noncomplexed (*E*)-cinnamamides revealed that their photoisomerization efficiencies are highly dependent upon both N-alkylation and aromatic substitution.[7] These results were attributed to the existence of two low-energy π,π^* singlet states (one reactive and one unreactive) whose relative energies are dependent upon the extent of N-alkylation and the nature of the aromatic substituent. We report here our detailed investigation of the structure and photochemistry of several (*E*)- and (*Z*)-cinnamamides (eq 1) and of their BF_3 complexes. Among the significant findings of this investigation are (a) a difference in enone configuration for *E* (s-cis) vs *Z* (s-trans) amides, (b) photoisomerization efficiencies that are dependent upon N-alkylation, α-alkylation, aromatic substitution, Lewis acid complexation, and excitation wavelength, and (c) the first example of quantitative $E \rightarrow Z$ isomerization of a Lewis acid complex.



(1)

	X	R_1	R_2	R_3
1	H	H	H	H
2	H	H	H	Me
3	H	H	Me	Me
4	H	Me	H	H
5	H	Me	H	Me
6	H	Me	Me	Me
7	CF_3	H	H	H
8	CF_3	H	Me	Me
9	OMe	H	H	H
10	OMe	H	Me	Me

Results and Discussion

Molecular and Electronic Structure. Crystal structures have been reported for (*E*)-cinnamamide and several of its derivatives.[10-12] The enone conformation is s-cis in all of the reported structures. The dihedral angles between the planes of the amide, olefin, and phenyl groups are dependent upon substitution. The angle between the amide and olefin planes is larger for the tertiary amide *N,N*-dimethyl-*p*-bromocinnamamide (15°) than for the secondary amide *N*-methylcinnamamide (5°) or the primary amide *p*-chlorocinnamamide (6°),[11] in accord with the anticipated nonbonded repulsion between the hydrogen atoms of the α-vinyl and *N*-methyl anti to the carbonyl oxygen. The angle between the vinyl and phenyl groups is smaller for the tertiary amide (4°) than for the secondary (19°) or primary amide (14°).[11] Crystal packing forces associated with the formation of hydrogen-bonded dimers from primary amides and hydrogen-bonded chains from secondary amides are presumed to be responsible for these distortions, which are too large to be attributed to nonbonded repulsion between the α-vinyl and ortho hydrogens. Crystal structures have not been reported for (*Z*)-cinnamamides. None of the (*Z*)-cinnamamides pre-

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[1] (a) Part 9 of our series Lewis Acid Catalysis of Photochemical Reactions. (b) For Part 8, see: Lewis, F. D.; Barancyk, S. V. *J. Am. Chem. Soc.* **1989**, *111*, 8653.

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Table I. ^{1}H NMR Chemical Shifts for Cinnamides and Their BF_3 Complexes[a]

amide	R_2	R_3	$R_1(H_\alpha)$	H_β	Ph
E-1	5.85		6.40	7.62	7.35
$+BF_3$	6.90		6.46	7.88	7.35
E-2	5.70	2.97	6.39	7.64	7.35
$+BF_3$	8.00	3.06, 3.23	6.69	8.05	7.40
E-3	3.15	3.05	6.89	7.68	7.40
$+BF_3$	3.28	3.37	6.84	7.69	7.50
E-4	6.00		2.20	7.50	7.40
$+BF_3$	*b*		2.02	7.95	7.40
E-5	6.25	2.87	2.02	7.30	7.30
$+BF_3$	7.35	3.10	2.15	8.45	7.35
E-6	3.05		2.02	6.05	7.30
$+BF_3$	3.20		2.10	6.65	7.30
E-10	3.10[c]		6.73	7.63	6.85, 7.45
$+BF_3$	3.30		6.65	7.80	6.87, 7.53
Z-2	5.08	2.75	5.94	6.81	7.35
$+BF_3$	7.67	2.90	6.07	7.20	7.37
Z-3	2.83	2.99	6.05	6.67	7.32
$+BF_3$	2.75	3.14	6.30	7.18	7.32
Z-8	2.85	2.90	6.23	7.53	6.80, 7.40
$+BF_3$	2.80	3.15	6.38	7.40	8.18, 7.50
Z-10	2.80[d]	2.95	5.83	6.53	6.75, 7.25
$+BF_3$	2.70	3.05	6.08	6.96	6.96

[a] Chemical shifts for 0.02 M amide in $CDCl_3$ vs TMS in the absence and presence of 1.0 equiv BF_3. [b] Broadened signal. [c] Methoxy singlet at δ 3.80 for free and complexed amide. [d] Methoxy singlet at δ 3.75 for free and complexed amide.

pared in the course of our investigation are crystalline.

The structures of the tertiary amides *E*-**3** and *E*-**6** in solution have been investigated by Kruk and Spaargaren[13] using ^{1}H NMR and IR spectroscopy. The assignment of the s-cis enone conformation for *E*-**3** and the s-trans conformation for *E*-**6** in solution is supported by the results of NOE experiments. Irradiation of the downfield *N*-methyl (anti to CO) of *E*-**3** results in a larger increase in the integrated intensity of H_α than does irradiation of the upfield (syn) *N*-methyl and no enhancement of H_β. In contrast, irradiation of the downfield *N*-methyl in *E*-**6** results in enhancement of H_β, but not the α-methyl. The absence of a significant NOE for either vinyl proton upon irradiation of *N*-methyl group of the secondary amide *E*-**2** supports the assignment of syn stereochemistry, as is normally observed for secondary amides.[14] The enone conformation of *E*-**2** and *E*-**1** cannot be reliably assigned on the basis of ^{1}H NMR data.

The *N*-methyl signals of *Z*-**2** and *Z*-**3** appear at higher field than those of their *E* isomers (Table I). This observation is suggestive of an enone s-trans conformation in which the *N*-methyl groups lie in the shielding region of the aromatic ring. Support for this suggestion is provided by the results of NOE studies. Irradiation of either methyl group in *Z*-**3** results in a ca. 7% enhancement of the aromatic proton signal and no change in the vinyl protons. Similar results are observed for *Z*-**2**.

The existence of *Z*-**2** and *Z*-**3** in an s-trans conformation was unexpected as both the (*E*)- and (*Z*)-cinnamic esters, like most conjugated enones, exist in the s-cis conformation.[8] The preference for the s-trans conformation may reflect an attractive interaction between the amide nitrogen and benzene p orbitals, which has previously been proposed to account for the intermolecular interaction of simple amides with aromatic solvents[15] and the intramolecular interaction in *N*,*N*-dimethyl-3-phenylpropionamide.[16]

Table II. IR Absorption Data for Cinnamides and Their BF_3 Complexes[a]

amide	free amide C=O	free amide C=C	rel int ϵ(C=O)/ϵ(C=C)	complexed amide C=O	complexed amide C=C
E-1	1682	1662	1.5	1657	1625
E-2	1668	1622	1.8	1647	1605
E-3	1650	1610	1.0	1637	1605
E-4	1675	1630	3.0	1665	1635
E-5	1665	1635	2.0		
E-6	1628		15.0		
E-7	1770	1650			
E-8	1650	1610			
E-9	1682	1636			
E-10	1652	1605			
Z-1	1673	1620	3.0	1655	1615
Z-2	1660	1620	6.0	1637	1615
Z-3	1630	1615	15.0	1612	
Z-4	1685	1645	3.0		
Z-5	1665	1638	6.0		
Z-6	1635		10.0	1628	
Z-10	1630				

[a] Frequencies (cm^{-1}) for 0.02 M amide in $CHCl_3$ solution.

Table III. UV Absorption Data for Cinnamides and Their BF_3 Complexes[a]

amide	free amide λ_{max}	free amide $\epsilon_{\lambda_{max}}$	complexed amide λ_{max}	complexed amide $\epsilon_{\lambda_{max}}$	ΔE, kcal/mol
E-1	273	19000	300	24500	9.5
Z-1	255	8800	290	8800	13.6
E-2	272	34000	396	33000	8.5
Z-2	255	11000	267	8000	5.1
E-3	277	20000	311	24000	11.2
Z-3	253	12000	261	7600	3.4
E-4	262	23000	292	27000	11.3
Z-4	254	22000	274	12000	8.2
E-5	260	18000	284	14600	9.3
Z-5	256	8300			
E-6	254	16500	258	13000	1.7
E-7	268	28000	288	35000	7.4
E-8	270	34000			
E-10	292	24100	347	28300	15.5
Z-10	272	19000	288	12000	5.8

[a] Data for 5×10^{-5} M amide in CH_2Cl_2 solution.

The barrier to amide rotation for *E*-**3** determined from variable-temperature NMR data is 16.3 kcal/mol and the coalescence temperature is 309 K, similar to previously reported values.[17] The smaller value for this and other conjugated amides vs saturated amides is attributed to the weakening of amide resonance due to competing enone resonance.[14] The barrier to amide rotation for *Z*-**3** is 18.7 kcal/mol and the coalescence temperature is 359 K. The larger barrier for *Z*-**3** vs *E*-**3** is consistent with either steric hindrance to rotation or decreased enone resonance for the highly nonplanar *Z*-**3**.

Since ^{1}H NMR does not distinguish between the s-cis and s-trans enone conformations of *E* or *Z* primary and *E* secondary cinnamamides, the use of IR spectroscopy was investigated. The assignment of enone conformation based upon the frequency and relative intensities of the enone C=O and C=C stretch for a series of benzyl ketones was described by Kronenberg and Havinga.[18] Planar s-cis enones were found to have lower ϵ(C=O)/ϵ(C=C) ratios

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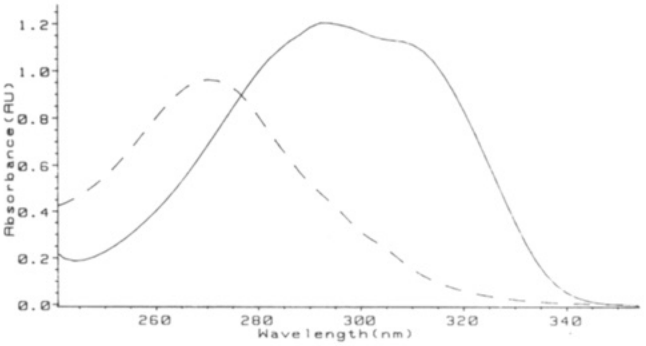

Figure 1. Ultraviolet absorption spectra of 5×10^{-5} M (*E*)-*N*,*N*-dimethyl-*p*-methoxycinnamamide, *E*-**10** (solid line), and its *Z* isomer (broken line).

than nonplanar s-trans enones. This method has previously been applied to the assignment of enone conformation in *E*-**3** and *E*-**6**.[13] Our data for the (*E*)-cinnamamides (Table II) indicates that they occur predominantly in the s-cis conformation, except in the case of *E*-**6** for which nonbonded repulsion between the α-methyl and anti *N*-methyl groups destabilizes the s-cis conformation. All of the (*Z*)-cinnamamides (and *E*-**6**) occur predominantly in the s-trans conformation.

UV absorption spectral data for the (*E*)- and (*Z*)-cinnamamides is summarized in Table III. As is the case for cinnamic acids and esters, the long-wavelength maximum occurs at longer wavelength and has greater intensity for the *E* vs *Z* isomers.[8,19] This band is assigned by Fueno et al.[19] to a styrene-like allowed ($^1A_1$) π,π^* transition, and the difference between isomers is attributed to the nonplanarity of the *Z* isomer. This assignment is consistent with the shift in λ_{max} to shorter wavelength with electron-withdrawing trifluoromethyl substituents and to longer wavelength with electron-releasing methoxy substituents and also with the relative insensitivity of λ_{max} to solvent polarity. The substituent-induced shifts are similar to those for cinnamic esters[8] and are smaller for *Z* vs *E* isomers, in accord with the nonplanarity of the *Z* isomers. The absorption spectra (*E*)- and (*Z*)-*N*,*N*-dimethyl-*p*-methoxycinnamamide (*E*- and *Z*-**10**) are shown in Figure 1. A long-wavelength shoulder is observed for the (*E*)-methoxy derivatives *E*-**10** and *E*-**9**. The long-wavelength bands of the other (*E*)-cinnamamides are generally symmetric, while those of the *Z* isomers exhibit tailing to long wavelengths. This is particularly evident in the case of *Z*-**10** for which absorption beyond 400 nm imparts a pale green color to concentrated solutions. The increase in intensity of the long-wavelength tails of the tertiary *Z* amides with electron-donating substituents (*Z*-**8** < *Z*-**3** < *Z*-**10**) suggests that these tails may arise from an intramolecular charge transfer transition.

α-Alkylation results in a shift of the long-wavelength absorption band of the (*E*)-cinnamamides to higher energy, presumably due to decreased planarity. The largest shift is observed for *E*-**6** (vs *E*-**3**), in which nonbonded repulsion between the α-methyl and dimethylamino group results in a change in enone conformation from s-cis to s-trans.[13] In comparison, the shifts observed for the (*Z*)-cinnamamides are insignificant. Evidently, α-alkylation has little additional effect on the conformation of the highly nonplanar *Z* isomers.

Table IV. Frontier Orbital Energies (hartrees)

amide	n_O	π_N	π_S	π^*
E-1	−0.3183	−0.2976	−0.2531	0.2014
H⁺	–	−0.6003	−0.4013	−0.0518
E-2	−0.3177	−0.2816	−0.2531	0.2013
H⁺	–	−0.5741	−0.3966	−0.0450
E-3	−0.3144	−0.2683	−0.2510	0.2017
H⁺	–	−0.5030	−0.3932	−0.0390

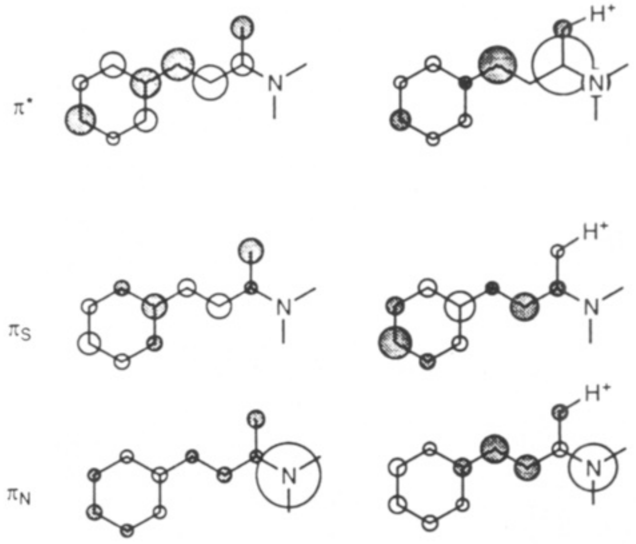

Figure 2. Frontier molecular orbitals of *N*,*N*-dimethylcinnamamide, *E*-**3**, and its protonated form.

N-Alkylation has little effect upon λ_{max} for either *E* or *Z* isomers. Values of λ_{max} are also relatively insensitive to solvent polarity. For example the value of λ_{max} for *E*-**3** is 273 nm in C_6H_{12}, 274 nm in CH_3CN, and 278 nm in CH_3OH. The largest solvent-induced shift is that for *E*-**10** (310 nm in CH_3OH vs 287 nm in C_6H_{12}). Primary and secondary amides are known to form hydrogen-bonded dimers and networks, respectively,[20] yet values of λ_{max} are independent of concentration. The insensitivity of the long wavelength absorption band to N-alkylation or hydrogen bonding is consistent with the assignment of the long-wavelength absorption band to a styrene-like π,π^* transition. While linear Beer's law plots are observed for all the cinnamamides, the long-wavelength tails of the primary and secondary (but not tertiary) amides display curved Beer's law plots, suggesting that another transition of low oscillator strength may contribute to these tails.

The cinnamamides are nonfluorescent at room temperature in solution and only weakly luminescent at 77 K in rigid glasses. Methyl cinnamate is weakly fluorescent in solution and its short lifetime (τ < 3 ps) is attributed to rapid internal conversion from the originally populated π,π^* singlet state to a lower energy n,π^* singlet state.[5]

In order to obtain further information about the electronic structure of the cinnamamides, restricted Hartree–Fock calculations were performed for *E*-**1**–**3** and *Z*-**1**–**3** at the STO-3G level using the GAUSSIAN 86 program package with optimization of molecular geometry.[21] Energy minimization was obtained for planar structures for *E*-**1**–**3**. The orbital eigenvalues for the three highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbital (LUMO) are reported in Table IV and the orbital coefficients presented pictorially in Figure 2.

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Table V. Quantum Yields and Photostationary States[a]

				PSS	
amide	Φ_{254}	Φ_{313}	Φ_{313} (BF_3)	% Z_{313}	% Z_{313} (BF_3)
E-1	0.26	0.25	1.0	56	45
E-2	0.08	0.03	0.35	40	69
E-3	0.04	0.01	0.55	85	100
E-4	0.33	0.20			
E-5	0.22	0.22			
E-6	0.10	0.01			
E-7	0.11	0.07	0.60	50	74
E-8	–	0.01		70	100
E-9	–	0.51			
E-10	0.05	0.27	0.68	80	76
Z-1	0.21	0.17	0.40		
Z-2	0.19	0.27	0.31		
Z-3	0.37	0.04	<0.01		
Z-4	0.24	0.11			
Z-5	0.22	0.40			
Z-6	–	0.2[b]			
Z-7	–	0.2[b]			
Z-8	0.40	0.53	<0.01		
Z-10	0.33	0.32	0.21		

[a] Data for 0.02 M amides containing <1% isomeric impurity in CH_2Cl_2 solution. [b] Data for amides containing ca. 5% isomeric impurity.

The LUMO (π^*) and one of the HOMO's (π_S) are styrene-like orbitals similar to those previously reported for methyl cinnamate.[9] The other HOMOs are the carbonyl oxygen lone pair (n_O) and an orbital mainly localized on nitrogen (π_N). The ordering of HOMO energies ($\pi_S > \pi_N > n_O$) for *E*-1 is the same as that previously assigned on the basis of its photoelectron spectrum.[22]

N-Alkylation does not significantly change the orbital coefficients or energies of the n_O, π_S, or π^* orbitals; however, it results in an increase in the energy of the π_N orbital (Table IV), as previously observed by Turner and coworkers[23] for simple amides. N-Methylation of formamide causes the π_N orbital to move above n_O and dimethylation causes this energy gap to widen. For the cinnamamides, the separation between the π_S and π_N orbitals decreases with N-alkylation to the point where their energies are essentially the same for *E*-3. Calculations with a larger basis set would be necessary to more accurately determine the relative energies of these orbitals.

GAUSSIAN 86 calculations were also conducted for the s-trans conformations of *Z*-1–3. The frontier orbital energies and orbital coefficients differ only minimally from those of the *E* isomers and thus are not reported. Energy minimization for *Z*-3 was obtained for a structure in which the dihedral angle between the phenyl, vinyl, and amide groups are both ca. 20°. The s-trans and s-cis conformations of *Z*-3 were calculated to have essentially the same total energy, the somewhat larger nuclear repulsion energy for the s-trans isomer being compensated for by larger (attractive) electronic energy.

Photoisomerization. Irradiation of the (*E*)- or (*Z*)-cinnamamides in solution results in isomerization to steady state mixtures of the *E* and *Z* isomers without competing photodimerization, even at relatively high concentrations (>0.1 M). Photodimerization has been observed in the solid state.[24] Quantum yields for photoisomerization (Φ_i) and photostationary states obtained using 313- or 254-nm irradiation of dilute (<0.1 M) dichloromethane solutions are summarized in Table V. The observed photostationary states are in good agreement with values calculated from the quantum yield and 313-nm absorption data. The photostationary states are all enriched in the *Z* isomers when compared to the thermal *E*,*Z* equilibria obtained by *p*-toluenesulfonic acid catalyzed isomerization.

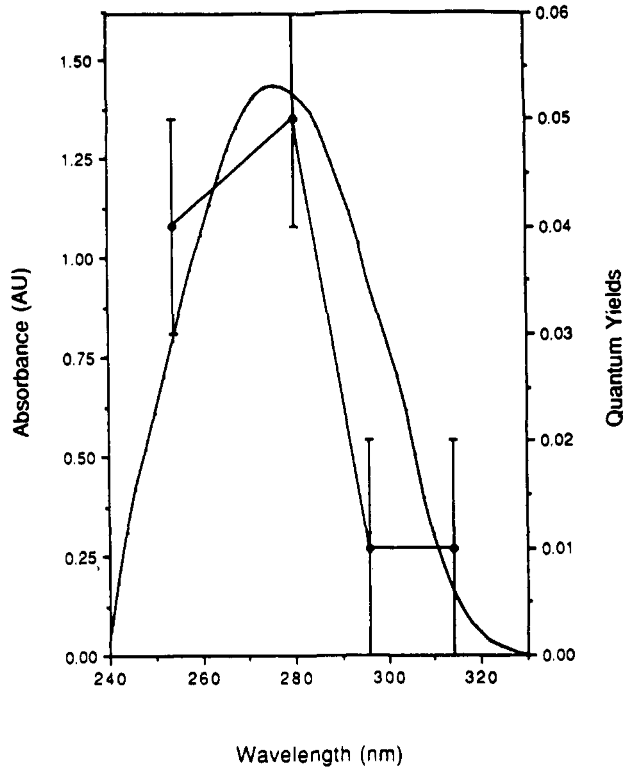

Figure 3. Wavelength dependence of the photoisomerization quantum yield for (*E*)-*N*,*N*-dimethylcinnamamide (*E*-3).

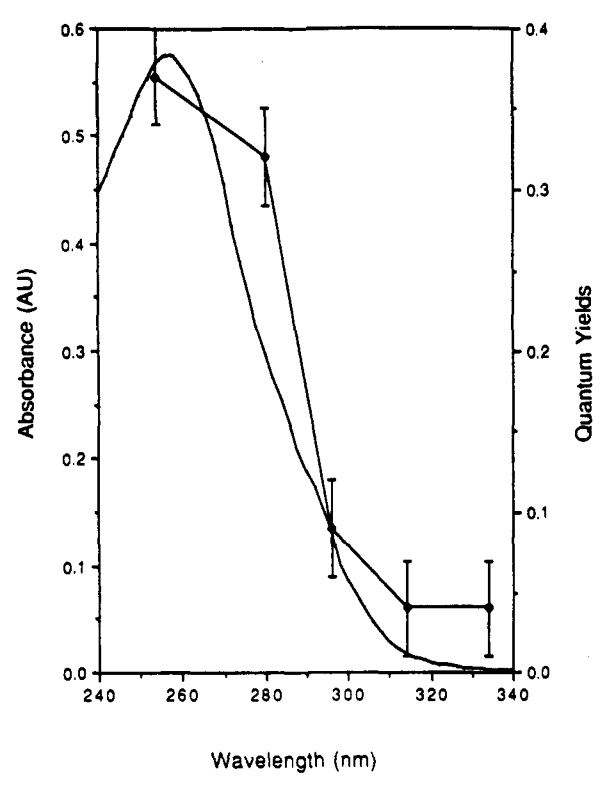

Figure 4. Wavelength dependence of the photoisomerization quantum yield for (*Z*)-*N*,*N*-dimethylcinnamamide (*Z*-3).

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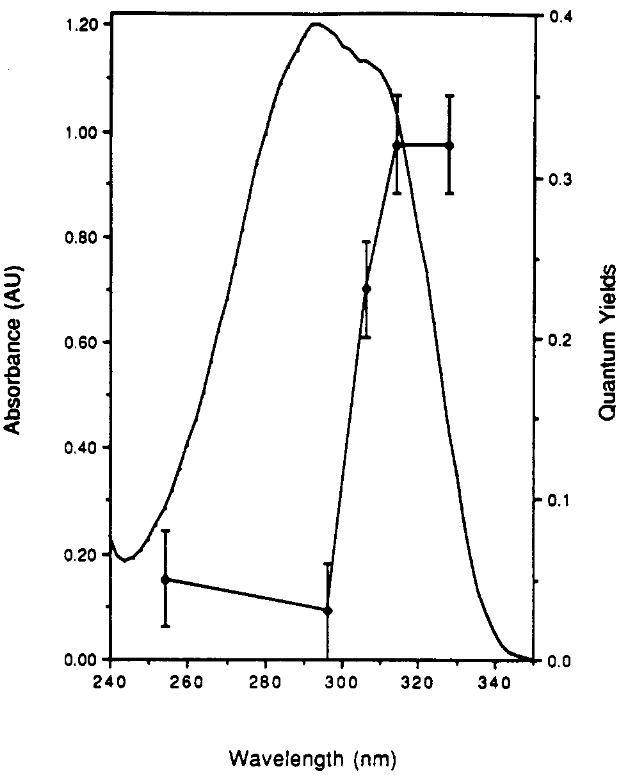

Figure 5. Wavelength dependence of the photoisomerization quantum yield for (*E*)-*N*,*N*-dimethyl-*p*-methoxycinnamamide (*E*-**10**).

Thermal equilibrium provided *Z* isomer contents of 7.5% for *Z*-**1**, 0.5% for *Z*-**2**, and <0.01% for *Z*-**3** and several other tertiary amides. The α-methyl tertiary amines *E*- and *Z*-**6** decompose in the presence of water or oxygen both in the absence and presence of light. The other amides possess good light and dark stability.

The wavelength dependence of Φ_i observed for most of the cinnamamides (Table V) was investigated over a wider range of wavelengths for several compounds. In the case of *E*-**3** and *Z*-**3**, Φ_i is observed to increase with decreasing irradiation wavelength (Figures 3 and 4), whereas for *E*-**10** Φ_i decreases with decreasing wavelength (Figure 5). The unusual wavelength dependence of Φ_i for *E*-**10** and the difference in absorption spectra for *E*-**10** vs *Z*-**10** (Figure 1) permits nearly quantitiative (>95%) conversion of *E*-**10** to *Z*-**10** upon monochromatic 328 nm irradiation and of *Z*-**10** to *E*-**10** upon 248-nm irradiation. This simple photochromic system has been recycled in dilute solution more than 10 times without fatigue and has been exploited in the development of a novel photoresponsive polymer.[25]

The solvent dependence of Φ_i has been investigated in the case of *E*- and *Z*-**10**. The value of Φ_i for *E*-**10** is distinctly higher in CH_3OH vs CH_2Cl_2 solution (0.74 vs 0.27), while that for *Z*-**10** is higher in CH_2Cl_2 (0.32) than in CH_3OH (0.27) or CH_3CN (0.16). Isomerization efficiencies and UV molar absorbance data for the cinnamamides are, in general, sensitive to the presence of small amounts of water or alcohols.

Irradiation of several of the amides in oxygenated solution results in neither a decrease in isomerization efficiency nor the formation of oxygenated products. Similarly, irradiation in the presence of high concentrations (>1 M) of the triplet quenchers 1,3-pentadiene or 1,3-cyclohexadiene does not diminish the quantum yield. Thus isomerization must occur via a short-lived singlet or triplet state. Triplet-sensitized irradiation (Michler's ketone, 366-nm irradiation) of *E*-**1** and *Z*-**10** results in values of $\Phi_i = 0.26$ and 0.07, respectively, similar to the values for direct irradiation. However, triplet-sensitized irradiation of either *E*-**3** or *E*-**10** results in values of $\Phi_i = 0.51$, significantly higher than those for direct irradiation. These results indicate that intersystem crossing cannot be highly efficient in the case of *E*-**3** or *E*-**10**. While the possible occurrence of intersystem crossing in the other cinnamamides cannot be excluded, we propose that isomerization occurs via a short-lived singlet state, as previously proposed for the cinnamic esters.[5] This assignment is consistent with the absence of photodimerization in solution.

We previously suggested that the decrease in Φ_i upon N-alkylation of the (*E*)-cinnamamides *E*-**1**–**3** might result from a change in the relative energies of the two lowest energy π,π^* excited states, identified as π_S,π^* and π_N,π^* to indicate the involvement of a HOMO localized on styrene or nitrogen, respectively (Figure 2).[7] The π_S,π^* state would be expected to isomerize efficiently, as it does in the case of the cinnamic esters,[8] whereas the π_N,π^* state retains a higher C=C bond order and thus should resist isomerization. N-Alkylation results in an increase in the energy of the π_N but not the π_S orbital (Table IV) and thus might be responsible for the lower values of Φ_i for *E*-**2** or *E*-**3** vs *E*-**1** (Table V).

Support for the two singlet hypothesis is provided by the effect of aromatic substituents upon photoisomerization efficiencies: viz the marked increase in Φ_i for *E*-**10** vs *E*-**3** and decrease in Φ_i for *E*-**7** vs *E*-**1**. Introduction of a *p*-methoxy substituent should raise the energy of the π_S but not the π_N orbital, possibly resulting in a change in configuration of the lowest singlet state. A shift of the π_S,π^* state to lower energy is supported by the red-shifted absorption band of *E*-**10** vs *E*-**3**. Conversely, a *p*-trifluoromethyl substituent should lower the energy of the π_S but not the π_N orbital, leading to a decrease in isomerization efficiency for *E*-**7** vs *E*-**1**. Relatively minor substituent effects on Φ_i are observed for *E*-**9** vs *E*-**1** (both lowest π_S,π^*) or *E*-**6** vs *E*-**3** (both lowest π_N,π^*). α-Alkylation of the (E)-cinnamamides has little effect upon Φ_i except in the case of the secondary amide *E*-**5** vs *E*-**2**. It is possible that α-alkylation, like N-alkylation or aromatic substitution, can alter the relative energies of the lowest singlet states; however, this possibility has not been fully explored.

Further evidence for a two singlet hypothesis is provided by the wavelength dependence of Φ_i (Table V, Figures 3–5). Irradiation of *E*-**3** (or *E*-**2**) in the long-wavelength region of its absorption band results in less efficient isomerization than does irradiation near the band maximum. In contrast, moderately efficient isomerization of *E*-**1** is observed upon irradiation at either 313 or 254 nm. The wavelength dependence of Φ_i for *E*-**3** requires that isomerization via an upper singlet state populated by short wavelength irradiation compete with internal conversion to the lower energy singlet state populated by long wavelength irradiation. In view of the low value of Φ_i at 254 nm (0.04 ± 0.01), <10% of the upper singlet is required to isomerize in competition with internal conversion. The larger value of Φ_i for *Z*-**3** at 254 vs 313 nm (Figure 4) requires that >30% of the upper singlet isomerize in competition with internal conversion. In contrast to the wavelength dependence of Φ_i for *E*- and *Z*-**3**, the behavior of *E*-**10** (Figure 5) requires that nonradiative decay of an upper singlet state populated by short-wavelength irradiation compete efficiently with internal conversion to a lower singlet state

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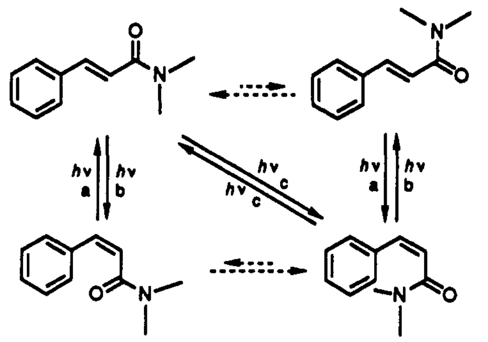
Scheme I



populated by long wavelength irradiation.

Photoisomerization efficiencies of the (*Z*)-cinnamamides are, in general, less sensitive to N-alkylation, aromatic substitution, α-alkylation, or excitation wavelength than are those of their *E* isomers (Table V). Moderately high values of Φ_i are observed except in the case of the long-wavelength ($\lambda > 290$ nm) irradiation of *Z*-**3** (Figure 5). A decrease in Φ_i is also observed when *Z*-**10** is irradiated in the weak long-wavelength tail of its absorption ($\Phi_i = 0.12$ at 366 nm). We have tentatively assigned the long-wavelength tails of the tertiary *Z* amides to an intramolecular arene-to-amide charge-transfer transition.

The wavelength dependence of Φ_i for several of the cinnamamides adds to a growing list of enones known to undergo wavelength-dependent unimolecular isomerization reactions.[5,26] In most of these cases, the upper and lower singlet states are assigned π,π^* and n,π^* configurations, respectively, and wavelength dependence results from upper singlet processes which are sufficiently rapid to compete with internal conversion to the lowest singlet. In the case of the (*E*)-cinnamamides the upper and lower singlets are assigned to π_N,π^* and π_S,π^* states whose relative energies are dependent upon N-alkylation and aromatic substitution.

An interesting feature of the photochemistry of the cinnamamides is the change in both C=C configuration and enone conformation. As described above, all of the (*E*)-cinnamamides except *E*-**6** are predominantly s-cis while all of the (*Z*)-cinnamamides are s-trans. As shown in Scheme I, in which solid lines designate photochemical and dashed lines thermal processes, there are three possible mechanisms (paths a–c) which would account for the occurrence of both configurational and conformational isomerization. Excitation of the less stable ground-state conformer (path a) can be ruled out by the high quantum yields observed for some of the amides. The low value of Φ_i for the only s-trans (*E*)-amide, *E*-**6**, indicates that there is no special advantage to configurational isomerization without accompanying conformational isomerization. We cannot at present distinguish between photoinduced *E*,*Z* isomerization followed by fast thermal conformational isomerization (path b) and the occurrence of both processes on the excited state potential energy surface (path c). Path c is a simple analogue of the hula-twist mechanism proposed by Liu et al.[27] for the photoisomerization of bathorhodopsin in sterically confined (protein) environments.

Molecular and Electronic Structure of BF_3 Complexes. Spectroscopic studies of the molecular complexes formed between amides and various Lewis acids have established that complexation involves the amide oxygen rather than nitrogen lone pair.[28] IR spectral data for several 1:1 cinnamamide–BF_3 (0.02 M) complexes in chloroform solution is summarized in Table II. One equivalent of BF_3 is sufficient to achieve maximum frequency shifts and precipitate formation occurs upon addition of more BF_3. The larger shifts to lower frequency observed for the C=O vs C=C stretch for the complexed vs noncomplexed amides is consistent with complexation at oxygen. The relative intensities of the C=O and C=C stretches are similar for complexed and noncomplexed amides, indicating that the enone conformation does not change upon complexation. For the (*E*)-cinnamamides *E*-**1**–**3** the value of $\Delta\nu$ for complexed vs noncomplexed C=O decreases with N-alkylation while the opposite trend is observed for the (*Z*)-cinnamamides.

^{1}H NMR data for several cinnamamide–BF_3 complexes (0.02 M) in dichloromethane solution is summarized in Table II. As observed in the IR spectral studies, 1 equiv of BF_3 is sufficient to attain complete complexation. Use of 0.5 equiv of BF_3 results in the observation of signals for both complexed and noncomplexed amide, indicative of slow exchange of BF_3 on the NMR time scale. In our previous studies of cinnamic ester–BF_3 complexes,[8] only the time-averaged signals of complexed and noncomplexed esters could be observed. Complexation does result in an increase in the barrier to amide rotation ($\Delta G^* = 17.8$ kcal/mol, $T_c = 336$ K for *E*-**3**–BF_3 and $\Delta G^* > 20$ kcal/mol for *Z*-**3**–BF_3) as previously observed for *N*,*N*-dimethylformamide and benzamide and their Lewis acid complexes.[29]

Complexation of the cinnamamides results in large down-field shifts of the N-H and N-Me protons, and variable shifts for the vinyl protons. The smallest vinyl shifts are observed for the *E* tertiary amides which also display the smallest C=O frequency shift upon complexation. Complexation is known to result in a change in enone conformation from s-cis to s-trans in some cases.[8,30] However, NOE studies of *E*- and *Z*-**3**–BF_3 indicate that complexation does not change the enone conformation.

The observation of slow exchange for the cinnamamide–BF_3 complexes facilitates the pairwise determination of relative equilibrium constants for two amides present in a 1:1 ratio with 0.5 equiv of BF_3 (based on total amide). The relative Lewis base strength for the (*E*)-cinnamamides decreases with N-alkylation (*E*-**1** > *E*-**2** > *E*-**3**). This trend is opposite that reported for the Brønsted base strengths of acetamides and benzamides, which increase with N-alkylation.[31] Steric rather than inductive effects apparently control the Lewis basicity of the cinnamamides, as has previously been observed for other Lewis acid–base complexes.[32] A further indication of the steric requirements of Lewis acid complexation is provided by the observation of two *N*-methyl signals in the ^{1}H NMR

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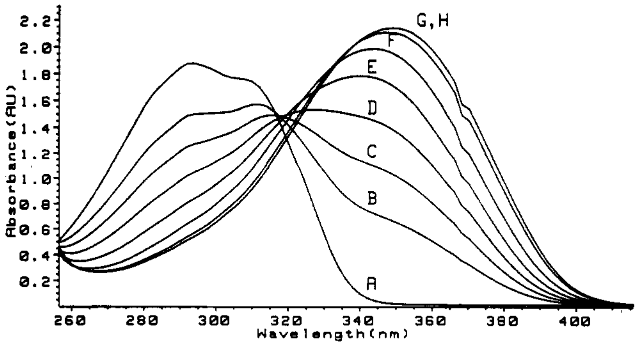

Figure 6. Ultraviolet absorption spectra of 5 × 10^{-5} M (*E*)-*N*,*N*-dimethyl-*p*-methoxycinnamamide (*E*-**10**) in the presence of 0 (A), 0.25 (B), 0.5 (C), 0.75 (D), 1.0 (E), 1.5 (F), 2.0 (G), 2.5 (H), and 3.0 (I) equiv of BF_3–OEt_2.

spectrum of *E*-**2** (Table II), which we assign to the syn and anti amide conformers. Evidently, the steric demands of complexation counterbalance the normal preference for the syn conformation in secondary amides.[14] An alternative explanation for the spectrum of *E*-**2**–BF_3 based upon complexation of BF_3 either syn or anti to nitrogen is inconsistent with the observation of a single set of vinyl signals and the low barrier anticipated for the interconversion of such conformers.[30]

Relative equilibrium constants for cinnamamide complex formation are essentially independent of configuration or aromatic substitution. In contrast, larger equilibrium constants were observed for (*E*)- vs (*Z*)-cinnamic esters and for cinnamic esters substituted with electron-donating vs electron-withdrawing groups.[8] Diminished sensitivity to aromatic substituents has previously been reported for complexation of BF_3 with benzamides vs benzaldehydes.[33] This difference was attributed to the diminished importance of aryl resonance for the more basic amide vs aldehyde carbonyl group.

Addition of BF_3 to dichloromethane solutions of the cinnamamides (10^{-4} M) results in the appearance of a single red-shifted absorption band. As illustrated for *E*-**10** in Figure 6, the absorption bands for complexed *E* amides are symmetric and more intense than those of the noncomplexed amides. Absorption bands for the complexed *Z* amides are skewed toward longer wavelength and less intense than those of the noncomplexed amides. Well-defined isosbestic points are observed for most of the amides, *E*-**10** representing a worst case in this respect. In the case of the primary and secondary cinnamamides, 1 equiv of BF_3 is sufficient to attain complete complexation and plots of absorbance at the λ_{max} for the complex vs added BF_3–OEt have the appearance of simple titration curves. While this prevents the use of the Benesi–Hildebrand[34] method to determine equilibrium constants, we estimate values of $K_{eq} > 10^4$ for all of the primary and secondary amides. Values of $K_{eq} > 10^3$ have previously been reported for the complexes of several *N*,*N*-dimethylamides with triethylaluminum.[28b] In the case of the tertiary amides such as *E*-**10** 2–3 equiv of BF_3 are necessary to obtain full complexation (Figure 2), in accord with the lower values of K_{eq} for tertiary vs primary or secondary amines observed by means of NMR.

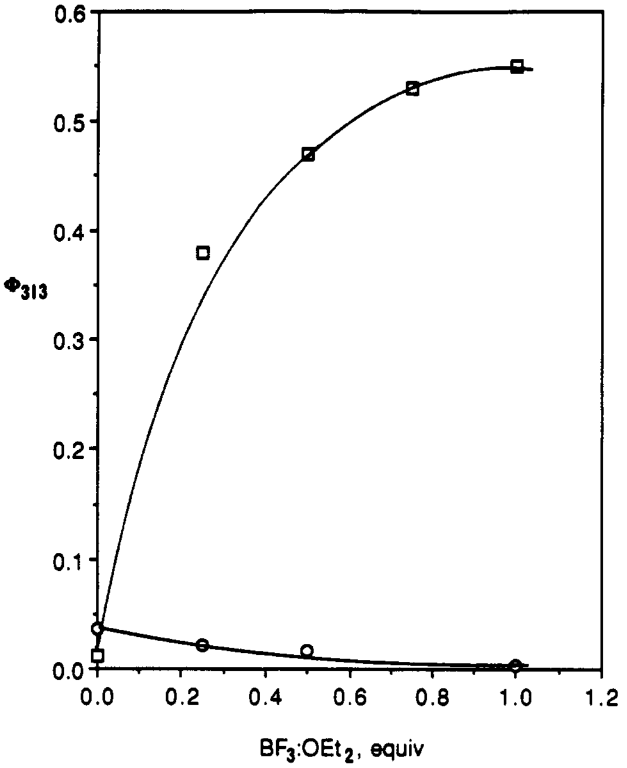

Figure 7. Effect of added BF_3–OEt_2 upon the photoisomerization quantum yields of (*E*)-*N*,*N*-dimethylcinnamamide (*E*-**3**, □) and its *Z* isomer (○).

The observed UV shifts for most of the complexed vs noncomplexed (*E*)-amides (Table IV) lie in the range 7.4–15.5 kcal/mol, the largest shift being observed for the *p*-methoxy derivative *E*-**10** and the smallest for the *p*-trifluoromethyl derivative *E*-**8**. In the case of the severely nonplanar α-methyl tertiary amide *E*-**6** the shift is only 1.7 kcal/mol. These trends are analogous to those previously reported for the Lewis acid complexes of cinnamic esters.[8] The UV shifts for (*Z*)-amides decrease with N-alkylation from a value of 13.6 kcal/mol for *Z*-**1** to 3.4 kcal/mol for *Z*-**3**. This trend is most likely steric in origin, the planarity of the BF_3 complexes decreasing with N-alkylation. The absorption maxima of the BF_3 complexes are relatively insensitive to solvent polarity and no fluorescence can be observed at room temperature in solution.

Further information about the electronic structure of (*E*)-cinnamamide–BF_3 complexes is provided by the results of GAUSSIAN 86 calculations[21] in which H^+ is used as a model for BF_3 in order to control the size of the calculation. Frontier orbital energies are summarized in Table IV and the orbital coefficients in Figure 2. Protonation results in a decrease in energy for all the frontier orbitals, especially n_O, which can no longer be identified among the highest occupied orbitals, and π_N, which lies well below π_S, even for the tertiary amide *E*-**3**. The LUMO resembles π_2 of the allyl system rather than the styrene π^* of the noncomplexed amides. The calculated π_S, π^* energy gap is smaller for the complexed vs noncomplexed amide, in accord with the shift of the absorption band to longer wavelength upon complexation. Aromatic substituents have a larger effect on the absorption maxima of complexed vs noncomplexed amides, in accord with the greater extent of intramolecular charge transfer for the π_S,π^* state of the complexed amide (Figure 2).

Photoisomerization of BF_3 Complexes. Photoisomerization quantum yields and photostationary states for 313-nm irradiation of the cinnamamides in the presence of 1 equiv of BF_3–OEt_2 are reported in Table V. The amides are fully complexed under these conditions. Quantum yields are higher for complexed vs noncomplexed

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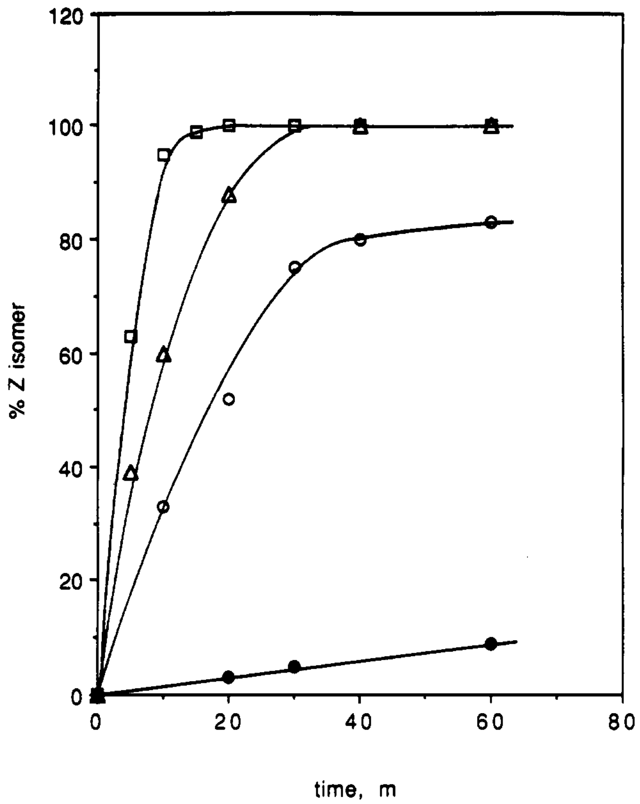

Figure 8. Conversion of (*E*)-*N*,*N*-dimethylcinnamamide (*E*-3) to its *Z* isomer in the presence of 0 (●), 0.1 (○), 0.5 (△), and 1.0 (□) equiv of BF_3–OEt_2.

amides except in the case of the *Z* tertiary amides, *Z*-3, *Z*-8, and *Z*-10. In the case of *Z*-3 and *Z*-8, the values of Φ_i are < 0.01 and the photostationary states consist of 100% *Z* isomer! The effect of added BF_3 on Φ_i for *E*-3 and *Z*-3 is illustrated in Figure 7. Addition of 0.25-equiv increments of BF_3 results in a continuous increase in Φ_i for *E*-3 and decrease in Φ_i for *Z*-3. The effect of added BF_3 on the rate of isomerization of *E*-3 is shown in Figure 8. The more rapid approach to the photostationary state for complexed vs noncomplexed *E*-3 reflects the increase in Φ_i upon complexation. The differences in absorption spectra and values of Φ_i for complexed vs noncomplexed amides are sufficiently large to allow quantitative conversion of *E*-3 to *Z*-3 using <0.5 equiv of BF_3.

The increase in Φ_i upon complexation for all of the (*E*)-amides and the primary and secondary (*Z*)-amides can be rationalized in terms of the changes in the frontier orbitals which occur upon protonation (Table IV and Figure 2). The π_S,π^* state is expected to be the lowest singlet state for all of the complexed amides and should isomerize efficiently due to its diminished C=C bond order. In the case of the primary amides *E*-1 and *Z*-1, the sum of the isomerization efficiencies exceeds 1.0, indicating the absence of a common, vibrationally equilibrated twisted intermediate. The only exceptions to efficient isomerization of the complexed amides are the tertiary (*Z*)-amides, *Z*-3 and *Z*-8. We suspect their photochemical behavior, like their spectroscopic properties, is related to their severe nonplanarity.

Concluding Remarks. The photoisomerization efficiency of the cinnamamides is remarkable in its dependence upon substitution, excitation wavelength, solvent, and complexation. The photochemical and photophysical behavior of the cinnamamides can be attributed to the existence of two low energy singlet π,π^* states, a reactive π_S,π^* state with a styrene-like HOMO, and an unreactive π_N,π^* state with an amide nonbonding π HOMO. N-Alkylation raises the energy of the π_N orbital relative to the π_S orbital, while aromatic substitution can either raise (electron donating substituents) or lower (electron-withdrawing substituents) the energy of the π_S orbital relative to the π_N orbital. Thus the electronic configuration of the lowest excited state is dependent upon the nature of substituents at either end of the conjugated molecule. The wavelength dependence of the photoisomerization efficiency requires that isomerization or nonradiative decay of upper singlet states compete with internal conversion to the lowest singlet state. Thus the configuration of the reactive state can in some cases be controlled by choice of excitation wavelength. Finally, complexation of the amides with BF_3 lowers the energy of the π_N orbital relative to the π_S orbital resulting in increased photoisomerization efficiency. This result serves to further extend the scope of the Lewis acid catalysis in organic photochemistry.[1,8,9]

Experimental Section

General Methods. ^1H NMR spectra of 0.02 M solutions of the cinnamamides in $CDCl_3$ containing tetramethylsilane internal standard were recorded using a Perkin-Elmer EM 390 spectrometer. Aliquots of BF_3–OEt_2 were introduced to nitrogen-purged solutions using a gas-tight microliter syringe. Chemical shift data for the free and complexed amides is summarized in Table I. Vinyl coupling constants for the (*E*)- and (*Z*)-cinnamamides were between 15 and 16 Hz and 12 and 13 Hz, respectively. Variable-temperature studies were conducted using a JEOL FX-90Q spectrometer. Amide rotational barriers were determined by the dynamic NMR method and free energies of activation calculated using the Eyring equation and the rates of C–N bond rotation at the coalescence temperature. NOE studies were conducted at −20 °C to minimize the effects of C–N bond rotation.

Infrared spectra of 0.02 M solutios of the cinnamamides and their BF_3 complexes in $CHCl_3$ were recorded in 1-mm pathlength NaCl cells using a Perkin-Elmer Model 286 double beam spectrometer. C=O and C=C stretching frequencies are reported in Table II.

Ultraviolet absorption spectra of 5×10^{-5} M solutions of the cinnamamides in CH_2Cl_2 were recorded in 1-cm path length quartz cuvettes using a Hewlett-Packard Model 8452A diode array spectrophotometer. Data for the free and complexed amides is reported in Table III. Beer's law plots were conducted for 10^{-2} to 10^{-4} M solutions using a 2-mm path length cuvette. Emission spectra were recorded using a Perkin-Elmer MPF-44A spectrophotometer in methylcyclohexane solution. No emission could be detected at room temperature and only weak emission was detected in the glassy state at 77 K for either the free or complexed amides.

Photoisomerization quantum yields were determined for 3-mL aliquots of 0.02 M solutions of cinnamamide in CH_2Cl_2 contained in 13 mm o.d. quartz or Pyrex test tubes purged with dry nitrogen for 5 min prior to irradiation. Samples were irradiated in triplicate, and each sample was analyzed in triplicate for isomer formation at <10% conversion by means of gas chromatography using a Hewlett-Packard 5890 FID-GC equipped with a 0.53 mm fused silica capillary column bonded with polydimethylsiloxane. Irradiation at 254 or 313 nm was performed on a merry-go-round appratus using respectively, the output of a Rayonet reactor or a Hanovia 450-W high-pressure mercury arc lamp with a potassium chromate solution filter. Variable-wavelength irradiations were conducted on an optical bench consisting of an Oriel 300-W high-pressure mercury arc lamp, a Bausch and Lomb 0.25-m high intensity monochrometer, and a thermostatted cell holder. Potassium ferrioxylate[35] and Aberchrome 540[36] were used as the primary actinometers. (*E*)-Stilbene (0.01 M in CH_2Cl_2) was used as a secondary actinometer and found to undergo isomerization with a quantum yield of 0.44 ± 0.02 over the range 254–313 nm.

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Materials. The (*E*)-cinnamamides were prepared from the cinnamic acids (Aldrich) via reaction of the acid chlorides with ammonia, methylamine, or dimethylamine and purified by recrystallization from hexane or chloroform or, for the noncrystalline *E*-**4–6**, silica gel chromatography. GC analysis indicated that all of the (*E*)-cinnamamides used in spectroscopic and photochemical studies were of >99% purity. Irradiation of the (*E*)-cinnamamides with the Pyrex-filtered output of a Hanovia 450-W high-pressure mercury arc provided isomer mixtures containing 50–75% *Z* isomer. Silica gel chromatography using chloroform eluant provided samples of the (*Z*)-cinnamamides containing <5% *E* impurity. In most cases, repeated chromatography provided samples containing <1% *E* impurity and these purified samples were used except as indicated in the footnotes to Table V. Both the *E* and *Z* isomers were fully characterized by means of their ^{1}H NMR and IR spectra and high-resolution mass spectroscopy.

Spectrophotometric grade dichloromethane (Aldrich) was refluxed over calcium hydride and freshly distilled prior to use in photochemical studies. Other solvents were spectral grade and used as received. BF_3–OEt_2 (Aldrich) was used as received until discolored and then distilled prior to use.

Acknowledgment. This work is supported by the National Science Foundation (CHE 8922835).

Supplementary Material Available: ^{1}H NMR, HRMS, and melting point data for solid compounds and ^{1}H NMR spectra of the (*E*)- and (*Z*)-cinnamamides and their BF_3 complexes (30 pages). Ordering information is given on any current masthead page.

Stereochemistry of [2 + 2] Photocycloaddition of Cyclic Enones to Alkenes: Structural and Mechanistic Considerations in Formation of Trans-Fused Cycloadducts

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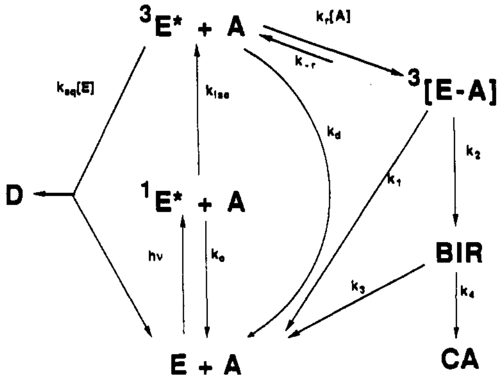
Received June 12, 1990

Photocycloaddition of 2-cyclohexenone to cyclopentene gives four [2 + 2] adducts, rather than only two as reported previously. Differentiation between the cis–anti–cis and cis–syn–cis structures was made on the basis of differences in ^{13}C chemical shifts in the two isomers. The structures of the two trans-fused adducts, which were not isolated, derive from their base-catalyzed epimerization to the corresponding cis-fused isomers. One trans-fused and one cis–fused cycloadduct are formed initially in a ratio of 2:1, respectively, upon photoaddition of testosterone acetate to cyclopentene, but this ratio changes in favor of the cis–fused isomer as the irradiation progresses due to secondary reactions. These adducts were identified by X-ray crystallography as the trans-fused (4α,5β) and cis-fused (4α,5α) structures. Epimerization of the trans-fused adduct in base led to isolation of the alternative cis-fused adduct (4β,5β) whose X-ray crystal structure was also determined. The X-ray structure of the oxime of the trans-fused photoadduct of 2-cyclohexenone and tetramethylethylene was also obtained for structural comparison with the steroid enone adducts. These are believed to be the first definitive structure determinations of trans-fused bicyclo[4.2.0]octan-2-ones. The assignments of ^{1}H NMR coupling constants to vicinal cis and trans protons on the cyclobutane ring are based on the relevant dihedral angles obtained from the X-ray structures and from molecular modeling. Mechanisms for the formation of trans-fused adducts from both planar and twisted cyclohexenone triplets are discussed.

The [2 + 2] photocycloaddition of cyclic enones to alkenes is arguably the most useful photochemical reaction to synthetic organic chemists, as a route to annelated products or products of subsequent cyclobutane fragmentation.[1] The synthetic utility of this reaction was first vividly demonstrated by Corey in his synthesis of the terpenoid caryophyllene, in which the natural product featuring trans fusion of a four- and nine-membered ring is produced by elaboration of a trans-fused adduct formed upon [2 + 2] photocycloaddition of cyclohexenone to isobutylene.[2] The mechanism generally used[1] to describe this reaction, formulated first by Corey[3] and later elaborated by de Mayo, is shown in Scheme I.[4] According to this mechanism, the lowest triplet state of the enone (initially thought[3] to be an n,π* triplet but now known to be a π,π* triplet)[5] reacts with the alkene to give an oriented π-complex or triplet exciplex, which then collapses to a triplet

Scheme I. The Corey–de Mayo Mechanism



E = enone, A = alkene, D = enone dimer, BIR = 1,4-biradical, CA = cycloadduct

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