

Lewis Acid Catalysis of Photochemical Reactions. 5. Selective Isomerization of Conjugated Butenoic and Dienoic Esters

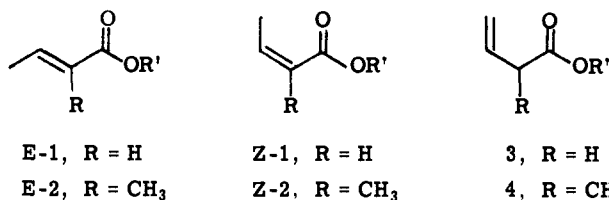
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Abstract: The effects of Lewis and Brønsted acids upon the photoisomerization reactions of several conjugated butenoic and dienoic esters have been investigated. Lewis acids inhibit the photochemical deconjugation of α,β - to β,γ -unsaturated butenoic esters and shift the photoequilibrium between *E* and *Z* isomers toward the *Z* isomer. As such, irradiation of *E* α,β -unsaturated esters in the presence of EtAlCl_2 provides a convenient method for the preparation of the thermodynamically less stable *Z* isomer. Irradiation of methyl (*E,E*)-2,4-hexadienoate and methyl (*E,E*)-5-phenyl-2,4-pentadienoate in the absence of added catalysts results in nonselective *E,Z* isomerization to give mixtures of all four stereoisomers in roughly comparable yields. In the presence of the Brønsted acid trifluoroacetic acid, quantitative conversion of methyl 2,4-hexadienoates to methyl 3,4-hexadienoate is observed. The acid serves as a catalyst for the thermal 1,3-hydrogen shift of an allenic enol ester formed via a photochemical 1,5-hydrogen shift of the conjugated esters. Irradiation of the ground-state complexes of the conjugated esters with the Lewis acids EtAlCl_2 or BF_3 results in selective *E,Z* isomerization about the α,β -double bond in methyl 2,4-hexadienoate and the γ,δ -double bond in methyl 5-phenyl-2,4-pentadienoate. The mechanistic bases for the observed effects of Lewis acids are selective excitation of the more strongly absorbing *E* complex and more efficient isomerization of the excited *E* vs. *Z* complex.

We recently reported that irradiation of α,β -unsaturated esters in the presence of Lewis acids results in the formation of photostationary states enriched in the thermodynamically less stable *Z* isomer.^{1,2} In the preceding paper in this issue, we report the results of our investigation of the effect of Lewis acids on the photoisomerization of cinnamic esters.¹ Selective *E* \rightarrow *Z* photoisomerization is observed to occur upon irradiation of ground-state ester/Lewis acid complexes. Selective isomerization is found to result from stronger long-wavelength absorption of the *E* vs. *Z* complex, higher quantum yields for isomerization of the *E* vs. *Z* complex, and larger equilibrium constants for formation of the *E* vs. *Z* complex.

Photoisomerization of butenoic³⁻⁶ and dienoic esters^{7,8} is more complicated than photoisomerization of cinnamic esters due to the occurrence of photodeconjugation of α,β -unsaturated to β,γ -unsaturated esters as well as *E,Z* photoisomerization. For example, irradiation of the isomeric (*E*)- and (*Z*)-2-butenate esters (crotonate, (*E*)-1, and isocrotonate, (*Z*)-1) and (*E*)- and (*Z*)-2-methyl-2-butenate esters (tiglate, (*E*)-2, and angelate, (*Z*)-2) is known to result in reversible *E,Z* isomerization and irreversible deconjugation to the 3-butenate esters 3 and 4.³⁻⁶



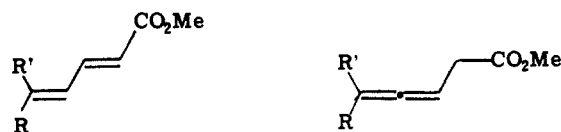
The photochemistry of conjugated dienoic acids and esters has received relatively little attention. Irradiation of methyl (*E*)-5-

Table I. Optimum *E* \rightarrow *Z* Conversions^a and Isomerization Quantum Yields^b for Butenoic Esters^a

Lewis acid, mol equiv	(<i>E</i>)-1/ AlCl_3	(<i>E</i>)-2/ AlCl_3	(<i>E</i>)-2/ EtAlCl_2	$\Phi_{E,Z}$	$\Phi_{Z,E}$
0	49	50	49	0.48	0.19
0.25	75	82	72	0.75	0.25
0.50	71	83	84	0.74	0.25
0.75	68	82	85	0.70	0.25
1.0	65	75	86	0.68	0.25
1.25			84	0.68	0.24

^a Percent conversion in dichloromethane solutions of 0.01 M ester irradiated at 254 nm. ^b Quantum yields for isomerization of (*E*)-2 \rightarrow (*Z*)-2 and (*Z*)-2 \rightarrow (*E*)-2 in the presence of added EtAlCl_2 .

methyl-2,4-hexadienoate ((*E*)-5) has not been reported, while previous investigations of the photochemistries of methyl (*E*)-*E*-2,4-hexadienoate (methyl sorbate, (*E,E*)-6) and methyl (*E*-



(*E*)-5-phenyl-2,4-pentadienoate ((*E,E*)-7) and their parent acids are limited to brief reports of the deconjugation of 2,4-hexadienoic acid and its methyl ester to their 3,4 isomers (9),⁷ the isomerization of (*E,E*)-5-phenyl-2,4-pentadienoic acid to its *Z,E* isomer,^{8a} and the solid-state photodimerization of the parent acids of (*E,E*)-6 and 7.^{8b}

We report here the results of our investigations of the photoisomerization of the butenoic esters 1 and 2 and the dienoic esters 5-7 in the absence and presence of Lewis acids. Irradiation of the ground-state complexes of α,β -unsaturated (*E*)-1 and (*E*)-2 with Lewis acids such as AlCl_3 or BF_3 results in the formation of photostationary states enriched in the *Z* isomer and inhibition of photochemical deconjugation of α,β - to β,γ -unsaturated esters.^{1,2,9} Irradiation of the ground-state complexes of the dienoic esters (*E*)-5 and (*E*)-6 with EtAlCl_2 results in selective *E,Z* isomerization of the α,β -double bond, while irradiation of the ground-state complex of (*E*)-7 with BF_3 results in selective *E,Z* isomerization of the γ,δ -double bond. Irradiation of 5 or 6 in the

(1) Part 3: Lewis F. D.; Oxman, J. D.; Gibson, L. L.; Lackritz, H. S.; Quillen, S. L. *J. Am. Chem. Soc.*, preceding paper in this issue.

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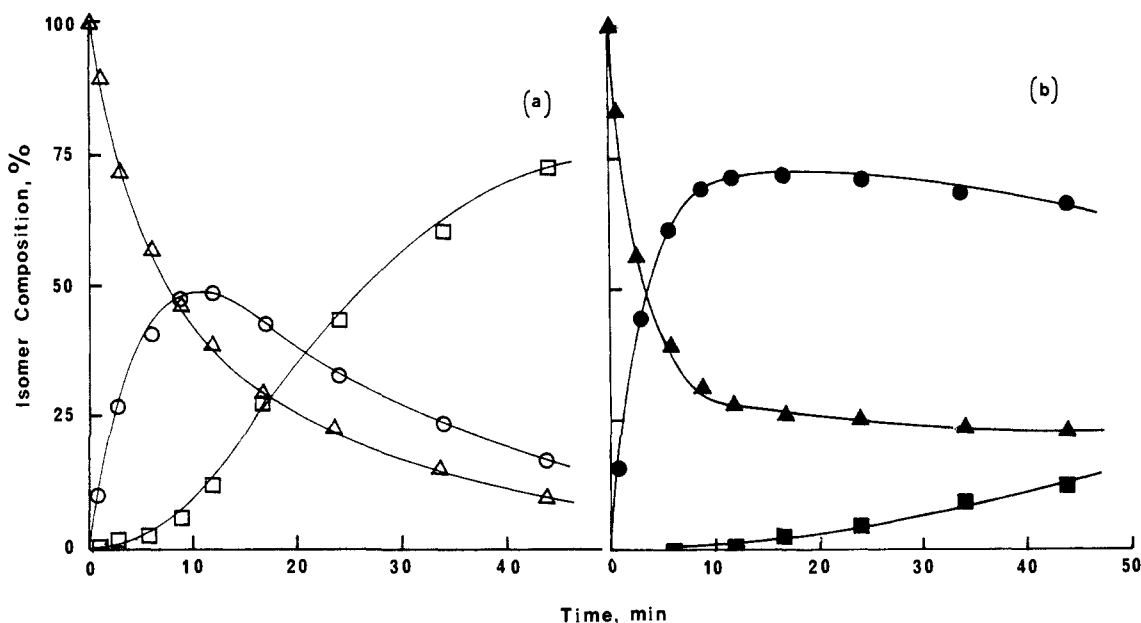


Figure 1. Composition of the isomer mixture vs. irradiation time for isomerization of 0.01 M (*E*)-1 (Δ) to (*Z*)-1 (\circ) and 3 (\square) in the absence (a) and presence (b) of 0.01 M EtAlCl_2 .

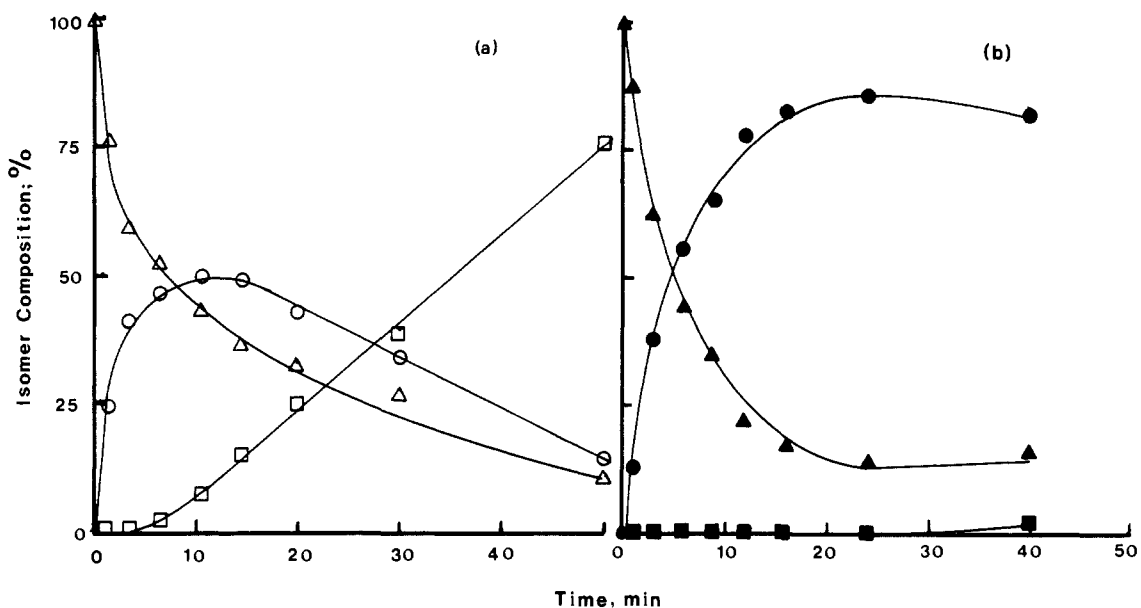


Figure 2. Composition of the isomer mixture vs. irradiation time for isomerization of 0.01 M (*E*)-2 (Δ) to (*Z*)-2 (\circ) and 4 (\square) in the absence (a) and presence (b) of 0.01 M EtAlCl_2 .

presence of Lewis and Brønsted acids or bases results in quantitative conversion to the nonconjugated allenic esters **8** and **9**. These results serve to further extend the scope of Lewis acid catalysis in organic photochemistry.

Results

Irradiation of Butenoic Esters. Irradiation of the esters (*E*)-1 and (*E*)-2 (0.01 M dichloromethane solution, 254-nm excitation), in the absence of Lewis acid, results in the formation of esters (*Z*)-1 and (*Z*)-2 and the β,γ -unsaturated esters **3** and **4**. Irradiation of the ester (*Z*)-2 results in the formation of (*E*)-2 and **4**. The progress of these reactions with time (as determined by GC analysis) is shown in Figures 1a–3a. Continued irradiation results in complete conversion of the *E* and *Z* α,β -unsaturated esters **1** and **2** to the β,γ -unsaturated esters **3** and **4**. Similar results have previously been reported for the irradiation of these esters in the absence of Lewis acid.^{4,5}

Irradiation of esters (*E*)-1 and (*E*)-2 or (*Z*)-2 in the presence of the Lewis acids AlCl_3 or EtAlCl_2 in dichloromethane solution results in conversion to photostationary-state mixtures of *E* and *Z* isomers prior to extensive formation of the β,γ -unsaturated esters

3 and **4**. The progress of these reactions with time is shown in Figures 1b–3b. The effect of Lewis acid concentration upon the photostationary-state isomer composition is reported in Table I. Optimum conversions of (*E*)-1 to (*Z*)-1 and (*E*)-2 to (*Z*)-2 are obtained with ca. 0.25–0.50 mol equiv of AlCl_3 or EtAlCl_2 and decrease at higher concentrations of AlCl_3 but not EtAlCl_2 . More concentrated (0.05 M) solutions of esters (*E*)-1 and (*E*)-2 required longer irradiation periods to attain equilibria but reached the same photostationary states. In a typical preparative irradiation, 0.64 g (5 mM) of ester (*E*)-2 and 0.31 g (2.5 mM) of AlCl_3 in 100 mL of dichloromethane were irradiated for 3.5 h to produce a mixture consisting of 81% (*Z*)-2, 18% (*E*)-2, and 1% **4**. Spinning band distillation afforded a sample of (*Z*)-2 containing 1% (*E*)-2 by GC analysis.

Irradiation of Methyl (*E*)-5-Methyl-2,4-hexadienoate. Irradiation of 0.02 M *E* or *Z* methyl 5-methyl-2,4-hexadienoate ((*E* or *Z*)-5) in dichloromethane solution results in the formation of photostationary states containing 60% (*Z*)-5 (254-nm light) and 40% (*Z*)-5 (254-nm light). No methyl 5-methyl-3,4-hexadienoate (**8**) was formed upon prolonged irradiation at either wavelength. Irradiation of (*E*)- or (*Z*)-5 at 254 nm in the presence of 1 mol

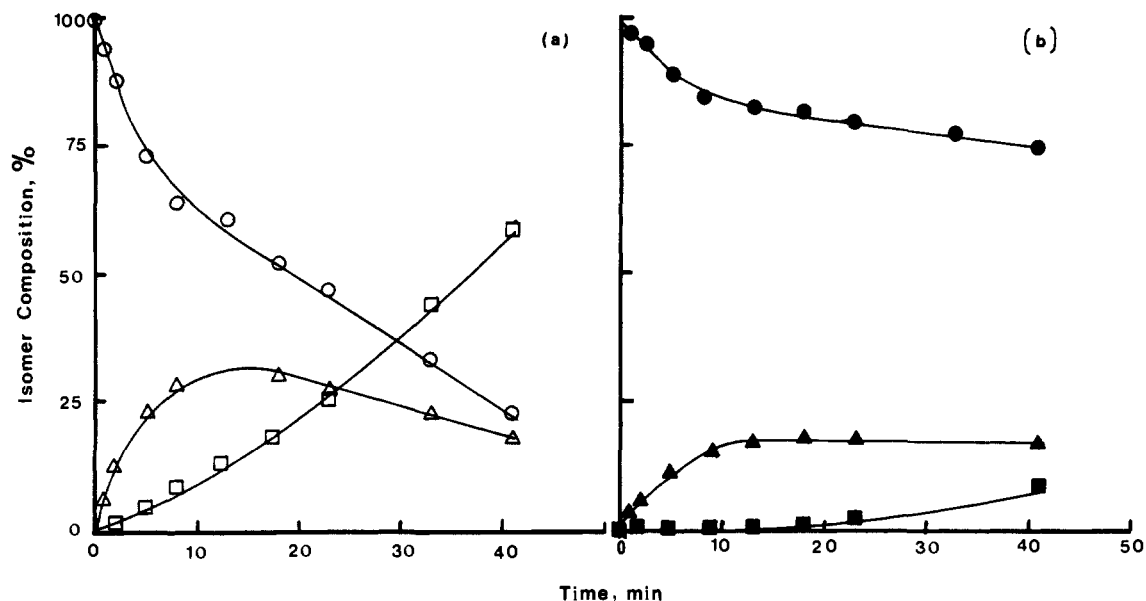


Figure 3. Composition of the isomer mixture vs. irradiation time for isomerization of 0.01 M (*Z*)-2 (O) to (*E*)-2 (Δ) and 4 (□) in the absence (a) and presence (b) of 0.01 M EtAlCl₂.

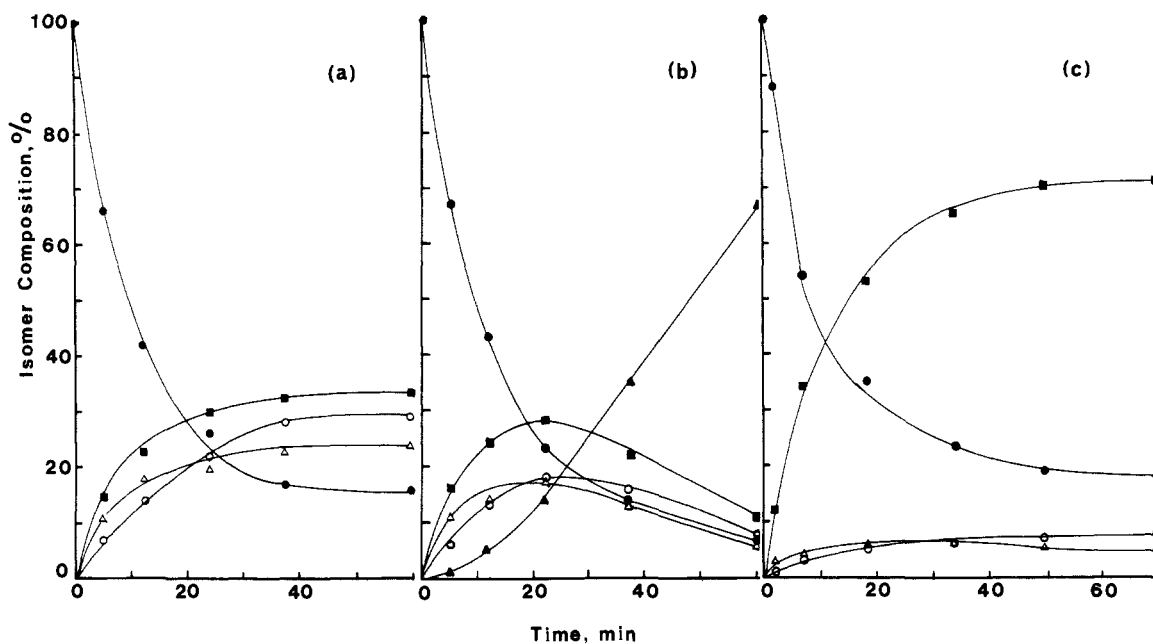


Figure 4. Composition of the isomer mixture vs. time for 254-nm irradiation of 0.02 M (*E,E*)-6 (●) to yield (*Z,E*)-6 (■), (*E,Z*)-6 (Δ), (*Z,Z*)-6 (○), and 9 (▲) (a) in the absence of catalyst, (b) in the presence of 0.005 M trifluoroacetic acid, and (c) in the presence of 0.015 M EtAlCl₂.

equiv of tetramethylpiperidine (TMP) results in reversible *E,Z* isomerization followed by quantitative and irreversible deconjugation to yield **8**, which was characterized by its IR, NMR, and mass spectra. Irradiation of (*Z*)-**5** yielded, at low conversions, (*E*)-**5** and **8** in a ratio of ca. 10/1. Irradiation of (*Z*)-**5** and TMP at 313 resulted in much less efficient deconjugation, the initial ratio of (*E*)-**5** to **8** being >50.

Irradiation of (*E*)-**5** at 313 nm in the presence of 1.0 mol equiv of BF₃·OEt₂ or 0.75 mol equiv of EtAlCl₂ results exclusively in *E,Z* isomerization, yielding photostationary states containing 59% (*Z*)-**5** and 45% (*Z*)-**5**, respectively (Table II). Lower conversions of (*E*)-**5** to (*Z*)-**5** were obtained using 2.0 or 3.0 mol equiv of BF₃·OEt₂. Preparative irradiation of (*E*)-**5** with BF₃·OEt₂ followed by column chromatography afforded pure (*Z*)-**5**, which was characterized by its NMR and mass spectra.

Irradiation of Methyl (*E,E*)-2,4-Hexadienoate. Irradiation of 0.02 M methyl (*E,E*)-2,4-hexadienoate ((*E,E*)-**6**) in dichloromethane solution with 254-nm light affords a mixture of the four possible *E,Z* isomers. Preparative-scale irradiation followed by

Table II. Isomer Mixtures Obtained upon Irradiation of Dienoic Esters^a

ester	additive	λ _{ex} , nm	<i>E</i> or <i>E,E</i>	<i>Z</i> or <i>Z,E</i>	<i>E,Z</i>	<i>Z,Z</i>	allene
<i>(E)</i> - 5	none	254	40	60			0
	TMP ^b	254	0	0			100
	none	313	70	30			0
	TMP ^b	313	70	30			0
<i>(E,E)</i> - 6	EtAlCl ₂ ^c	313	55	45			0
	BF ₃ ·OEt ₂ ^d	313	41	59			0
	none	254	16	33	23	28	0
<i>(E,E)</i> - 7	TMP ^b	254	0	0	0	0	100
	EtAlCl ₂ ^c	313	17	71	4	8	0
	none	313	18	16	34	32	0
<i>(E,E)</i> - 8	BF ₃ ·OEt ₂ ^{d,e}	313	24	18	46	12	0
	BF ₃ ·OEt ₂ ^{d,f}	313	16	17	38	29	0

^a Optimum conversions for irradiation of 0.02 M ester. Ester **5** has only one isomerizable double bond. ^b Tetramethylpiperidine, 0.02 M. ^c EtAlCl₂, 0.015 M. ^d BF₃·OEt₂, 0.02 M. ^e Irradiation time, 180-min. ^f Irradiation time, 620-min.

chromatography on silica gel provided samples of the *E,Z*, *Z,E*, and *Z,Z* isomers, which were characterized by comparisons of their ultraviolet,¹⁰ NMR,¹¹ and mass spectra with available published data. The order of elution of these isomers (*Z,E*, *Z,Z*, *E,Z*, *E,E*) is the same when using analytical GC (5% SF 96 on Chromasorb G),¹² HPLC, and column chromatography on silica gel. The progress of this reaction with time is shown in Figure 4a. The mixture of isomers obtained after 1 h (Table II) does not change with further irradiation. This mixture is presumed to be the photostationary state; however, this has not been confirmed by irradiation of the other *E,Z* isomers. No methyl 3,4-hexadienoate (**9**) was obtained under these irradiation conditions, in agreement with Crowley's observations.⁷

Irradiation of (*E,E*)-**6** with 254-nm light in the presence of trifluoroacetic acid (TFA) or TMP results in isomerization to a mixture of *E,Z* isomers followed by quantitative and irreversible formation of **9**, which was characterized by its IR, NMR, and mass spectra. The progress of the isomerization of 0.02 M (*E,E*)-**6** in the presence of 0.005 M TFA is shown in Figure 4b. The conversions of (*E,E*)-**6** to **9** obtained with TFA or TMP represent a marked improvement over the 8% conversion obtained by Crowley⁷ using 10% formic acid in diethyl ether. No isomerization of (*E,E*)-**6** to **9** is observed upon 313-nm irradiation in the presence of TMP.

Irradiation of (*E,E*)-**6** with Pyrex-filtered light in the presence of 0.25–1.0 mol equiv of EtAlCl₂ or AlCl₃ results in an enhanced rate of isomerization and the selective formation of (*Z,E*)-**6** (Table II). Lower selectivity was observed when using 1.0 mol equiv of BF₃·OEt₂. The progress of isomerization of (*E,E*)-**6** with 0.75 mol equiv of EtAlCl₂ is shown in Figure 4c. Somewhat lower optimum conversions in (*E,E*)-**6** to (*Z,E*)-**6** are obtained when using 0.25 or 1.0 mol equiv of EtAlCl₂. Continued irradiation results in increased yields of (*E,Z*)-**6** and (*Z,Z*)-**6** at the expense of (*Z,E*)-**6**, but no deconjugation to yield **9**. Irradiation of (*E,E*)-**6** with 0.75 mol equiv of EtAlCl₂ or 1.0 mol equiv of BF₃·OEt₂ at 254 nm does result in the formation of **9**. No reaction is observed for solutions of **6** or **9** with EtAlCl₂ in the absence of light.

Irradiation of Methyl (*E,E*)-5-Phenyl-2,4-pentadienoate. Irradiation of 0.02 M methyl (*E,E*)-5-phenyl-2,4-pentadienoate ((*E,E*)-**7**) in dichloromethane solution with Pyrex-filtered light affords a mixture of the four possible *E,Z* isomers. Preparative thick-layer chromatography provided samples of (*E,Z*)-**7** and (*Z,Z*)-**7** of sufficient purity of structural assignments based on comparisons of their ¹H NMR with available published data.¹³ The *Z,E*, *E,Z*, and *Z,Z* isomers revert to (*E,E*)-**7** upon column chromatography on silica gel and the *Z,Z* isomer is thermally unstable under the conditions used for GC analysis (220 °C). Thus the photoisomerization of (*E,E*)-**7** was monitored by analytical HPLC. Monochromatic 313-nm irradiation of (*E,E*)-**7** leads initially to the formation of (*Z,E*)-**7** and (*E,Z*)-**7** and then, following an induction period, (*Z,Z*)-**7** is observed. The apparent photostationary state obtained after prolonged irradiation is reported in Table II. The structure of the unidentified isomer is assigned by the process of elimination and on the basis of its formation as a primary photoproduct as (*Z,E*)-**7**.

Irradiation of 0.02 M (*E,E*)-**7** in the presence of 0.33–1.0 mol equiv of BF₃·OEt₂ in dichloromethane solution with monochromatic 313-nm light also results in the formation of a mixture of four *E,Z* isomers. The initial rate of isomerization and the *E,Z*/*Z,E* isomer ratio are both observed to increase in the presence of BF₃·OEt₂; however, the isomer ratio obtained following prolonged irradiation is similar to that obtained in the absence of BF₃·OEt₂ (Table II). Lower selectivity was observed when using 1.0 mol equiv of EtAlCl₂. Similar isomer ratios were obtained

Table III. ¹H NMR Chemical Shifts (ppm) for Esters (*E*)-**2** and (*Z*)-**2** and Their EtAlCl₂ Complexes in CDCl₃ Solution

proton	<i>(E)</i> - 2 / EtAlCl ₂			<i>(Z)</i> - 2 / EtAlCl ₂		
	<i>(E)</i> - 2	EtAlCl ₂	Δδ	<i>(Z)</i> - 2	EtAlCl ₂	Δδ
α-CH ₃	1.80	1.90	0.10	1.90	2.03	0.13
β-H	6.77	7.37	0.60	5.98	6.63	0.65
β-CH ₃	1.75	1.93	0.18	1.93	2.03	0.10
O-CH ₂ -CH ₃	4.13	4.53	0.40	4.17	4.73	0.56
O-CH ₂ -CH ₃	1.25	1.45	0.20	1.30	1.50	0.20

Table IV. UV Absorption Data for Conjugated Esters and Their Lewis Acid Complexes^a

ester	λ _{max}	ε _{max}	ε ₂₅₄	ε ₃₁₃
<i>(E)</i> - 1	202	14 000	400	
<i>(E)</i> - 1 /EtAlCl ₂	230	4 600	2 600	
<i>(Z)</i> - 1	206	14 000		
<i>(E)</i> - 2	216	10 500	200	
<i>(E)</i> - 2 /EtAlCl ₂	245	3 300	2 830	
<i>(Z)</i> - 2	213	10 400	400	
<i>(Z)</i> - 2 /EtAlCl ₂	245 (sh)	1 900	1 800	
<i>(E)</i> - 5	275	27 900	14 100	400
<i>(E)</i> - 5 /BF ₃	275	22 100	11 800	1 200
<i>(Z)</i> - 5	278	17 250	7 850	700
<i>(Z)</i> - 5 /BF ₃	278	14 550	6 550	975
<i>(E,E)</i> - 6	259	26 000		
<i>(E,E)</i> - 6 /EtAlCl ₂	301	23 000		16 500
<i>(Z,E)</i> - 6	262	20 000		
<i>(Z,E)</i> - 6 /EtAlCl ₂	300 (sh)	8 100		7 500
<i>(Z,Z)</i> - 6	264	16 800		
<i>(Z,Z)</i> - 6 /EtAlCl ₂	300 (sh)	3 800		3 500
<i>(E,E)</i> - 7	309	31 540		
<i>(E,E)</i> - 7 /BF ₃	352	32 000		

^a Data for hexane solutions of **1** and **2** and dichloromethane solutions of **5**–**7** and all Lewis acid complexes.

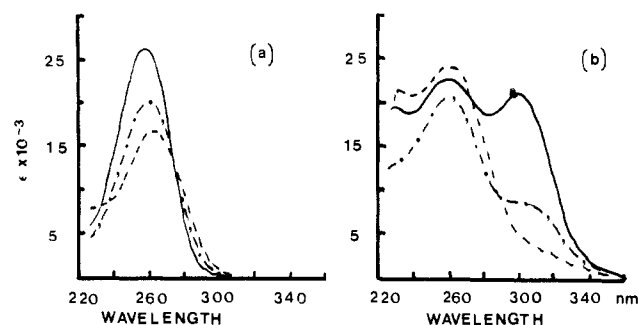


Figure 5. Absorption spectra of 2×10^{-5} M (*E,E*)-**6** (---), (*Z,E*)-**6** (-·-·-), and (*Z,Z*)-**6** (—) in dichloromethane solution in the absence (a) and presence (b) of 4×10^{-5} M EtAlCl₂.

by using 313, 365, and 435-nm excitation.

Spectroscopic Studies and Quantum Yields. The complexes of esters (*E*)-**2** and (*Z*)-**2** with EtAlCl₂ were characterized by ¹H NMR and UV spectroscopies. Chemical shift data for free and complexed (1.0 mol equiv) 0.5 M ester in CDCl₃ solution are given in Table III. No significant changes in coupling constants are observed upon addition of EtAlCl₂. Ultraviolet absorption spectral data for esters (*E*)-**2** and (*Z*)-**2** in hexane solution and for their complexes with EtAlCl₂ in dichloromethane solution are summarized in Table IV. Similar spectral changes are observed upon addition of AlCl₃ to (*E*)-**1** or (*E*)-**2**. Neither AlCl₃ nor EtAlCl₂ absorb appreciably above the 236-nm dichloromethane cutoff; thus the long-wavelength absorption bands observed upon addition of these Lewis acids to the α,β-unsaturated esters are attributed to the formation of a Lewis acid–ester complex.

The absorption spectra of the hexadienoate esters (*E,E*)-**6**, (*Z,E*)-**6**, and (*Z,Z*)-**6** in dichloromethane solution in the absence and presence of 2.0 mol equiv of EtAlCl₂ are shown in Figure 5a and 5b, respectively. Additional EtAlCl₂ caused little change in the appearance of the spectra; thus the spectra in Figure 5b are assumed to be those of the fully complexed ester. Absorption spectral data for the free and complexed esters are given in Table

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Table V. Quantum Yield Data for Isomerization of Dienoic Esters

ester	Lewis acid, mol equiv	$\Phi_{E,E}^a$	$\Phi_{Z,E}$	$\Phi_{E,Z}$
<i>(E,E)</i> -6	0.5 EtAlCl ₂		0.76	0.11
	0.75		0.73	0.10
	1.0		0.70	0.09
<i>(E,E)</i> -7	none	0.42	0.17	0.20
	1.0 BF ₃ ·OEt ₂	1.00	0.30	0.70

^aLoss of starting material.

IV. Data for the free butenoic and dienoic esters are in good agreement with published values.¹⁰

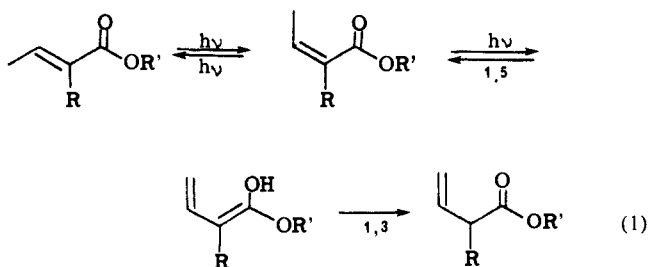
Quantum yields for the isomerization of esters (*E*)-2 and (*Z*)-2 (<10% conversion) with and without added Lewis acid are given in Table I. The *E* → *Z* isomerization quantum yield ($\Phi_{E,Z}$) increases from 0.48 to 0.75 upon addition of 0.25 mol equiv of EtAlCl₂ and decreases slightly at higher Lewis acid concentrations. The *Z* → *E* isomerization quantum yield ($\Phi_{Z,E}$) increases from 0.19 to 0.25 upon addition of 0.25 mol equiv of EtAlCl₂ and remains unchanged at higher Lewis acid concentrations. The quantum yield for formation of the deconjugated ester 4 from (*Z*)-2 ($\Phi_{\beta,\gamma}$) in the absence of Lewis acid is 0.01 ± 0.005. Quantum yields decrease rapidly with increasing conversion due to the reversible nature of the isomerization process. This may account for the lower values reported by Borrell and Holmes.⁵

Quantum yields for the photoisomerization of the (*E,E*)-6/EtAlCl₂ complex and free and complexed (*E,E*)-7 in dichloromethane solution were determined by using monochromatic 313-nm light. Conversions of (*E,E*)-6 and (*E,E*)-7 to their *E,Z* and *Z,E* isomers were <10%. At these low conversions, formation of *Z,Z* isomers could not be detected. The absorbance of free (*E,E*)-6 under these conditions is too low to permit quantum yield measurements. Values for the isomerization of (*E,E*)-6 and (*E,E*)-7 to their *Z,E* and *E,Z* isomers are summarized in Table V. Values for isomerization of (*E,E*)-6 decrease slightly with increasing EtAlCl₂ concentration.

The effect of other Lewis acids upon the absorption spectrum and photoisomerization of ester (*E*)-2 was briefly investigated. Addition of BF₃·OEt₂ (0.25–1.25 equiv) had little effect on either the absorption spectrum of (*Z*)-2 or its photoisomerization to (*Z*)-2 and 4. SnCl₄ absorbs strongly at 254 nm and decomposes upon irradiation at this wavelength. Irradiation of (*E*)-2 with SnCl₄ (0.25–1.25 equiv) results in diminished efficiency of (*E*)-2 to (*Z*)-2 and 4 and the formation of several unidentified products. Lewis acids including BF₃·OEt₂, EtAlCl₂, and SnCl₄ have little effect on either the absorption spectra or photoisomerization of dimethyl fumarate or dimethyl muconate.

Discussion

Photoisomerization of Butenoic Esters. The mechanism of photoisomerization of methyl (*E*)- and (*Z*)-methyl-2-butenoate (1) and methyl 2-methyl-2-butenoate (2) has previously been investigated by Barltrop and Willis⁴ and by Borrell and Holmes,⁵ respectively. Their investigations established that *E,Z* isomerization occurs upon direct or triplet-sensitized isomerization but that deconjugation occurs only upon direct irradiation. *E,Z* isomerization was proposed to occur via a π,π^* excited-state (triplet or singlet) and deconjugation via an n,π^* singlet-state 1,5-sigmatropic hydrogen shift of the *Z* isomer to yield a dienol which can reketonize to yield either the 2- or 3-butenoate ester (eq 1).



Our results for the photoisomerization of the noncomplexed α,β -unsaturated esters 1 and 2 are consistent with the established

reaction mechanism. The quantum yields for *E,Z* isomerization of (*E*)- and (*Z*)-2 (Table I) are higher than previously reported;⁵ however, the sum of the quantum yields for isomerization and deconjugation ($\Phi_{E,Z} = 0.48$, $\Phi_{Z,E} = 0.19$, $\Phi_{\beta,\gamma} = 0.01$, $\Phi_{\text{total}} = 0.68$) is less than unity. Thus one or more nonradiative decay pathways compete with isomerization.¹⁴ Borrell and Holmes⁵ observed an increase in isomerization quantum yield with increasing temperature, indicative of a small thermal barrier to twisting about the excited-state C=C bond. Weedon and co-workers^{6c} recently reported a 5-fold increase in the rate of formation of 4 upon irradiation of (*E*)-2 in the presence of the base 1,2-dimethylimidazole. This increase is attributed to an increased rate for the catalyzed 1,3-hydrogen shift vs. concerted 1,5-hydrogen shift of the dienol intermediate formed upon γ -hydrogen abstraction (eq 1). A 5-fold increase in our measured value for $\Phi_{\beta,\gamma}$ can account for only part of the observed inefficiency in *E,Z* isomerization.

The photostationary state for 254-nm irradiation of (*E*)- and (*Z*)-2, calculated using eq 2 and the data in Figure 5 and Table IV, is predicted to be 69% *Z* and 31% *E*. Due to competing deconjugation, the optimum conversion observed for *E* → *Z* isomerization (Figure 2a) is 50% and for *Z* → *E* isomerization (Figure 3a) is 28%.

$$\frac{[Z]}{[E]} = \frac{\Phi_{E,Z} \epsilon_E}{\Phi_{Z,E} \epsilon_Z} \quad (2)$$

Irradiation of the α,β -unsaturated esters 1 and 2 in the presence of the Lewis acids AlCl₃ or EtAlCl₂ has a pronounced effect upon isomer ratios (Figures 1–3). The optimum conversion of the (*E*)-1 to (*Z*)-1 and (*E*)-2 to (*Z*)-2 isomers increases from 49% to 71% and from 49% to 86%, respectively. Furthermore deconjugation to form the β,γ -unsaturated esters 3 and 4 is not observed until after the *E,Z* isomers attain a photostationary state, even in the case of ester (*Z*)-2 which has the *Z* configuration necessary for deconjugation (Figure 3b).

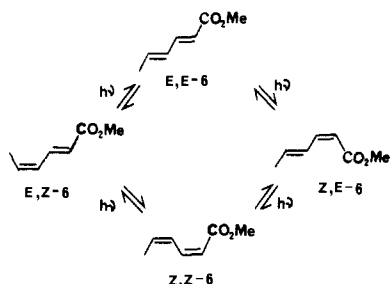
Our investigation of the effects of Lewis acids upon the photoisomerization of cinnamic esters established that three factors are responsible for enhanced *E* → *Z* isomerization: (1) stronger long-wavelength absorption for the *E* vs. *Z* complex; (2) more efficient isomerization of the *E* vs. *Z* complex; and (3) larger equilibrium constants for complexation of the *E* vs. *Z* ester.¹ The photostationary state for (*E*)- and (*Z*)-2 is independent of EtAlCl₂ concentration (0.5–1.25 mol equiv, Table I), indicating that preferential complexation of the *E* vs. *Z* ester may not occur in the case of (*E*)- and (*Z*)-2. The photostationary state calculated by using eq 2 for (*E*)- and (*Z*)-2 in the presence of 1.0 mol equiv of EtAlCl₂ is 91% *Z* and 9% *E*, slightly larger than the observed values, 85% *Z* for (*E*)-2 and 84% *Z* for (*Z*)-2 (Figures 2b and 3b). The reasonable agreement between the calculated and observed photostationary state obtained upon irradiation in the absence and presence of 1.0 mol equiv of EtAlCl₂ indicates that changes in absorption spectra and isomerization quantum yields can account for the change in photostationary state.

The esters of propenoic acid and its α - and β -alkyl derivatives are known to form 1:1 complexes with boron and aluminum halides in which the carbonyl oxygen serves as the Lewis base.¹⁵ An equilibrium constant of 8 ± 0.5 is reported for the formation of the AlCl₃ complex of ethyl propenoate.^{15b} The similar chemical shift differences ($\Delta\delta$) observed for both the ethoxy and β -H protons of (*E*)- and (*Z*)-2 upon complexation with EtAlCl₂ (Table III) indicate that the two esters form complexes with similar equilibrium constants and local anisotropy. While EtAlCl₂ complexation has a qualitatively similar effect on the NMR spectra of (*E*)- and (*Z*)-2, this is not the case for their UV absorption spectra (Table IV). The complex of (*E*)-2 displays a strong red-shifted absorption band, while that of (*Z*)-2 displays a weaker shoulder. This comparison may reflect a difference in planarity

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(15) (a) Brunn, J.; Radeaglia, R.; Lewansheck, B.; Peust, S. *Z. Phys. Chem. (Leipzig)* **1977**, *25*, 681. (b) Brunn, J.; Beck, C. *Z. Chem.* **1977**, *17*, 296. (c) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1981**, *60*, 801.

Scheme I



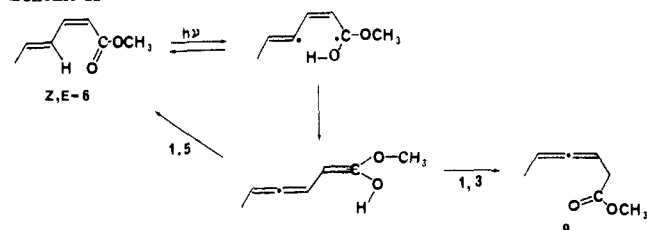
of the Lewis acid complexes of (*E*)- and (*Z*)-**2** or differences in the equilibrium between *s*-cis and *s*-trans conformers. The *s*-cis/*s*-trans conformer ratios (determined by IR spectroscopy) of ester (*E*)-**1** and 2-methylpropionate are reported to be 0.65 and 0.12, respectively, indicative of the destabilizing effect of an α -methyl substituent on the *s*-cis conformation.¹⁶ Childs et al.^{15c} have observed that Lewis acid complexes of β,γ -unsaturated carbonyl compounds can exist in two or more conformations. Thus the absorption spectra of both the free and complexed esters are probably due to mixtures of ground-state conformers.

The quantum yields of *E,Z* isomerization of (*E*)- and (*Z*)-**2** increase in the presence of EtAlCl_2 (Table I). The sum of the isomerization quantum yields in the presence of 0.25 or 0.50 mol equiv of EtAlCl_2 is 1.0 ± 0.05 , consistent with the efficient formation of a common twisted intermediate¹⁴ from the EtAlCl_2 complex of (*E*)- or (*Z*)-**2**, which decays to (*E*)- and (*Z*)-**2** with a ratio of ca. 1/3. The increase in the $\Phi_{Z,E}$ upon complexation is modest (0.19–0.25) compared to the increase in $\Phi_{E,Z}$ (0.48–0.75). The increase in $\Phi_{Z,E}$ parallels the decreased γ -hydrogen abstraction efficiency of (*Z*)-**2**. Lewis acid complexation at the carbonyl oxygen would be expected to lower the energy of the oxygen nonbonding electrons and hence raise the energy of the n,π^* state relative to the π,π^* state. Borrell and Holmes⁵ proposed that the inefficiency in singlet-state *E,Z* isomerization of (*E*)- and (*Z*)-**2** is due to a barrier to twisting about the central double bond which results from crossing of $S_1(n,\pi^*)$ and $S_2(\pi,\pi^*)$. A lowest energy π,π^* state for the Lewis acid complex would account for both the increased *E,Z* isomerization efficiency and the absence of γ -hydrogen abstraction from (*Z*)-**2**. Of course the absence of γ -hydrogen abstraction can also be rationalized on simple steric or conformational grounds. γ -Hydrogen abstraction requires an *s*-cis conformation of the enone chromophore, which may be disfavored by Lewis acid complexation.^{1,17}

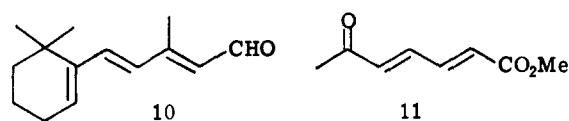
Photoisomerization of Dienoic Esters. Direct irradiation of the conjugated dienoic ester **5** in the absence of added acid or base catalyst results in *E,Z* isomerization, while irradiation of **6** or **7** results in the formation of mixtures of all four possible *E,Z* isomers. The observation of an induction period or slower initial rate of formation for the *Z,Z* isomers vs. the *E,Z* and *Z,E* isomers (Figure 4a) indicates that isomerization occurs via the sequential one-bond, one-photon mechanism¹⁴ shown in Scheme I for **6**. Detailed analysis of the isomer ratios obtained upon irradiation of (*E,E*)-**6** would require knowledge of the quantum yields for each of the steps in Scheme I as well as the extinction coefficients of each isomer.^{18,19} For esters **5** and **6**, isomer ratios appear to be largely determined by extinction coefficients (Table IV), the less strongly absorbing isomers being formed in preference to more strongly absorbing isomers.

The initial ratio of isomers (*Z,E*)-**6**/*(E,Z)*-**6** = 1.4, and (*Z,E*)-**7**/*(E,Z)*-**7** = 0.85 indicates that the isomerization process is not highly regioselective. Slightly higher selectivity is reported for photoisomerization at the α,β - vs. γ,δ -bond of (*E,E*)-**3**,**5**-

Scheme II



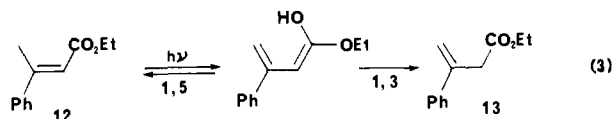
heptadienone.¹⁸ The photostationary states obtained upon prolonged irradiation of (*E,E*)-**6** and **7** (Table II) contain all four isomers in amounts ranging from 16% to 34% and contain significant amounts of the *Z,Z* isomers. Curiously, the *Z,Z* isomer is absent in Kluge and Lillya's investigations of the photoisomerization of conjugated dienones¹⁸ but is present in the photostationary state obtained upon direct irradiation of the trienal **10**^{20a} and 6-oxo-2,4-heptadienoic acid (**11**).^{20b} Variable yields of *Z,Z* isomers from photoisomerization of conjugated $\alpha,\beta,\gamma,\delta$ -unsaturated carbonyl compounds may reflect their facile thermal or catalyzed isomerization.^{20b}



The photoisomerization of (*E,E*)-**6** to the nonconjugated allene **9** was originally observed by Crowley⁷ to occur in low yield in the presence of formic acid. We have obtained quantitative conversions of **5** to **8** and of **6** to **9** in the presence of a Brønsted acid (trifluoroacetic acid, TFA) or base (tetramethylpiperidine, TMP). The TFA-catalyzed formation of **9** (Figure 4b) displays an induction period suggestive of its formation via a photochemical 1,5-hydrogen shift from an α,β -*Z* isomer (*Z,E* or *Z,Z*) to yield an allenic enol ester which can reketonize to yield either the original conjugated methyl 2,4-hexadienoate or the nonconjugated 3,4-hexadienoate (Scheme II). No induction period is observed for the TMP-catalyzed formation of **8** from (*Z*)-**5**. Reketonization involves a thermally allowed 1,5-hydrogen shift, while allene formation involves a forbidden 1,3 shift and requires the presence of acid or base catalysts. We have not observed the formation of an allene from (*E,E*)-**7** but cannot exclude the possibility that it is formed but is unstable under the conditions of irradiation or product isolation.

The acid- or base-catalyzed isomerization of the dienoic esters **5** and **6** to the nonconjugated allenes **8** and **9** occurs in competition with *E,Z* isomerization. Irradiation of (*Z*)-**5** at 254 nm in the presence of TMP results in an initial ratio of (*E*)-**5**/**8** of ~ 10 , while 313-nm irradiation results in a ratio > 50 . A similar wavelength dependence is observed for the formation of **9** from (*E,E*)-**6**. The more efficient formation of allene products upon 254-nm vs. 313-nm irradiation suggests that population of an upper (presumably η,π^*) excited state is required for γ -hydrogen abstraction, while *E,Z* isomerization is the predominant reaction of the lowest π,π^* excited state. Added TMP does not perturb the photostationary state obtained from **5** upon 313-nm irradiation.

Weedon et al.^{6c} have recently reported substantially enhanced rates and yields of photochemical deconjugation of α,β -unsaturated esters to their β,γ isomers in the presence of the base catalyst 1,2-dimethylimidazole. The behavior of ethyl 3-phenyl-2-butenate (**12**) is analogous to that of (*E,E*)-**6** in that no photodeconjugation occurs in the absence of 1,2-dimethylimidazole, while an 85% isolated yield of **13** is obtained in its presence (eq 3). In



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the absence of catalysts, the dienols formed from **5**, **6**, and **12** reketonize exclusively to the thermodynamically more stable conjugated starting material. One notable difference between the reaction of **5** or **6** and simple α,β -unsaturated esters such as **1**, **2**, or **12** is the photochemical abstraction of a vinyl hydrogen in the former case vs. an allyl hydrogen in the latter. A nonplanar cyclic transition state for the hydrogen-transfer process would allow overlap of the γ -C-H bond with the α,β - π orbitals, thus lowering the transition-state energy. To our knowledge, there have been no additional examples of a 1,5-vinyl hydrogen shift to an excited carbonyl oxygen since the initial report by Crowley⁷ over 20 years ago.

Irradiation of esters **5**–**7** with 313-nm light in the presence of the Lewis acids EtAlCl₂ or BF₃ results in their conversion to mixtures of *E,Z* isomers different from those obtained in the absence of Lewis acid (Table II). For example, 313-nm irradiation of (*E*)-**5** in the presence of 1.0 mol equiv of BF₃·OEt₂ results in higher conversion to (*Z*)-**5** than obtained in the absence of BF₃ (59% vs. 30%). Under these conditions, the ester/Lewis acid complexes are the only light-absorbing species. The most notable effect of added Lewis acid is the increased conversion (71% vs. 33%) of (*E,E*)-**6** to its *Z,E* isomer. An even greater change in observed in the selectivity of formation of (*Z,E*)-**6** vs. (*E,Z*)-**6** at low conversions, the *Z,E/E,Z* ratio increasing from 1.4 to 7.8 upon addition of EtAlCl₂. Unfortunately, the reversible nature of these isomerization reactions prevents the high selectivity inherent in the isomerization quantum yields (Table III) from being realized in the photostationary states (Table II). The selectivity of formation of (*E,Z*)-**7** vs. (*Z,E*)-**7** from (*E,E*)-**7** is also enhanced by added Lewis acid, the ratio increasing from 1.2 to 2.3 upon addition of BF₃.

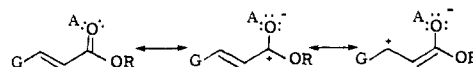
While isomerization of simple 1,4-dialkyl-substituted conjugated dienes is normally nonselective,^{14,18} selective isomerization has been observed when the terminal substituents differ in their electronic character.^{20,21} Selectivity in these cases can be attributed to substituent stabilization of one of the two possible allyl methylene or dipolar intermediates reached upon twisting about the two nonequivalent double bonds. Lewis acid complexation of the ester carbonyl oxygen might be expected to stabilize a dipolar intermediate (enolate, allyl cation), at the α,β bond, thus accounting for the increased selectivity for α,β vs. γ,δ isomerization from (*E,E*)-**6** upon complexation. However, this explanation does not account for selective γ,δ isomerization from (*E,E*)-**7**.

A further indication of a change in the excited-state potential energy surface for the complexed vs. noncomplexed esters is provided by the change in photoisomerization quantum yield for (*E,E*)-**7** (Table V). The observed value of $\Phi_{-E,E} = 1.0$ indicates that isomerization does not occur via equilibrated twisted intermediates which can decay to either reactant or product. It is, however, consistent with the dynamic model for *E,Z* photoisomerization proposed by Weiss and Warshel.^{1,22}

Concluding Remarks. In summary, we find that irradiation of the conjugated dienol esters **1** and **2** in the presence of the Lewis acids AlCl₃ or EtAlCl₂ results in photostationary states enriched in (*Z*)-**1** and (*Z*)-**2** and retards the formation of the β,γ -unsaturated esters **3** and **4**. This method constitutes an improvement over previous photochemical and nonphotochemical methods for preparing (*Z*)-**1** and (*Z*)-**2**²³ and has been applied by ourselves¹ and others⁹ to the preparation of numerous α,β -unsaturated carbonyl compounds.

Irradiation of the conjugated dienol esters **5**–**7** in the absence of acid or base catalysts results in nonselective isomerization to yield mixtures of all possible *E,Z* isomers. Irradiation of **5** or **6** in the presence of Brønsted acid or base catalysts results in quantitative conversion to the nonconjugated allene esters **8** and **9**. The role of the acid or base in this reaction is to catalyze the

Scheme III



thermal 1,3-hydrogen shift of an allenic enol ester which is a primary photoproduct of α,β -*Z* esters (*Z*)-**5** and (*Z,E*)- or (*Z,Z*)-**6**. Irradiation of the Lewis acid complexes (*E,E*)-**6**/EtAlCl₂ and (*E,E*)-**7**/BF₃ results in isomerization to mixtures of all four *E,Z* isomers with greater regioselectivity than is observed in the noncatalyzed reaction.

Ellis et al.²⁴ have recently reported that irradiation of *all-trans*-retinal in the presence of Eu(fod)₃ leads to the formation of 11-*cis*-retinals as well as the 13-*cis*- and 9-*cis*-retinals which are obtained upon irradiation in the absence of Lewis acid. Thus altered photoisomerization regioselectivity is also observed upon irradiation of complexed vs. noncomplexed retinal. While the factors which control the isomerization regioselectivity in dienes and polyenes are not fully understood, the ability to alter the selectivity of such reactions by the use of acid or base catalysts promises to expand the synthetic utility of the photoisomerization process.

As discussed in the preceding article in this issue, Lewis acid enhanced *E* → *Z* photoisomerization requires selective excitation of the Lewis acid complex. Thus a significant fraction of the α,β -unsaturated carbonyl compound must be in the complexed form and the complex must absorb strongly at the excitation frequency. The stability of the complex will depend both upon the donor basicity and the acceptor acidity. Based on simple charge delocalization arguments (Scheme III), butenoic esters should be weaker donors than dienol or cinnamic esters; fumaric and muconic esters should be still weaker donors. In accord with this prediction, we find that a stronger Lewis acid (EtAlCl₂) is needed to alter the absorption spectra and photoequilibrium of the butenoic vs. dienol or cinnamic esters (BF₃·OEt₂) and that neither the absorption spectra nor photoequilibrium of fumaric or muconic esters is affected by strong Lewis acids. Effective charge delocalization of the Lewis acid complex (Scheme III) also requires planarity of the extended π system. Thus the weaker long-wavelength absorption bands for *Z* vs. *E* complexes (Table IV) presumably reflect the nonplanarity of the *Z* complexes.

Experimental Section

General Methods. NMR spectra were obtained on a Varian CFT20 60-MHz spectrometer. Ultraviolet absorption spectra were obtained on a GCA/McPherson EU-700 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer and mass spectra on a Hewlett-Packard 5985 GC/MS. Irradiated solutions were analyzed on a Hewlett-Packard 5750 flame ionization gas chromatograph using a calibrated 11 ft (butenoic esters) or 6 ft (dienol esters) \times 1/8 in. column containing 5% SF-96 on Chromosorb G or a Beckman 100 HPLC using a 4.6 mm \times 25 cm Altex Ultraphere Si column.

Irradiations were conducted by using a Rayonet reactor with 254-nm lamps or a Hanovia 450-W medium-pressure mercury lamp in a water-cooled Pyrex lamp well. Monochromatic 313-nm irradiation was obtained by using a potassium chromate filter solution with the Hanovia lamp. Quantum yield and conversion vs. time measurements were carried out on a merry-go-round apparatus using potassium ferrioxalate (254 nm) or *trans*-stilbene²⁵ (313 nm) solution actinometers run in triplicate. Solutions of ester in dichloromethane contained in 13 mm o.d. quartz or Pyrex test tubes equipped with serum caps were bubbled with dry N₂. Lewis acid solutions were added by syringe under a N₂ atmosphere in a Kewaunee Scientific Products drybox.

Materials. Dichloromethane (Aldrich gold label) was distilled from phosphorus pentoxide, refluxed over calcium hydride, and distilled immediately prior to use. (*E*)-Methyl 2-butenate (Aldrich) was distilled prior to use. Ethyl (*E*)-2-methyl-2-butenate was prepared by esterification of the acid (Aldrich) and distilled under vacuum (bp 55 °C/11 torr, >99% pure by GC analysis; NMR, see Table II).

Ethyl (*Z*)-2-Methyl-2-butenate ((*Z*)-2**).** Ethyl (*E*)-2-methyl-2-butenate (0.64 g, 5×10^{-3} mol) and EtAlCl₂ (1.20 mL, 2.75×10^{-3} mol) or AlCl₃ (0.31 g, 2.2×10^{-3} mol) were dissolved in 0.25 L of dichloro-

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methane under a dry nitrogen atmosphere. The mixture was transferred to a Vycor irradiation vessel and irradiated for 3.5 h at 254 nm in a Rayonet reactor. The irradiated solution was extracted with water and dried over MgSO_4 . The solvent was removed under reduced pressure and the residue distilled on a spinning band column. The second fraction (bp 50 °C/11 torr) contained 99% pure (Z)-2 by GC analysis, 0.25 g (40%): NMR (Table II). The isolated yield could be improved by redistillation of less pure fractions. Attempted chromatography of (Z)-2 on silica gel resulted in its isomerization to (E)-2.

Methyl (E)-5-Methyl-2,4-hexadienoate ((E)-5). Reaction of 1-bromo-2-methyl-1-propene with methyl acrylate in the presence of triethylamine, triphenylphosphine, and palladium acetate according to the procedure of Dieck and Heck²⁶ afforded a pale-yellow oil: bp 89 °C/13 torr; ¹H NMR (CDCl_3) δ 1.90 (br s, 6 H), 3.73 (s, 3 H), 5.73 (d, $J_{\alpha\beta}$ = 15 Hz, H_α), 5.97 (d, $J_{\beta\gamma}$ = 10.5 Hz, H_γ), 7.56 (d of d, $J_{\alpha\beta}$ = 15, $J_{\beta\gamma}$ = 10.5 Hz, H_β).

Methyl (Z)-5-Methyl-2,4-hexadienoate ((Z)-5). Methyl (E)-5-methyl-2,4-hexadienoate (0.98 g, 7.0×10^{-3} mol) was dissolved in 0.1 L of dichloromethane and transferred to a Pyrex annulus. The annulus was sealed with a rubber septum and the solution degassed with N_2 for 5 min. The annulus was then placed in a drybox, and $\text{BF}_3 \cdot \text{OEt}_2$ (0.99 g, 7.0×10^{-3} mol) was added to the solution by syringe. The solution was irradiated with a 450-W medium-pressure Hanovia lamp in a Pyrex lamp well for 1.0 h until a photoequilibrium had been established. GC of the sample indicated 45% conversion to the title species. The $\text{BF}_3 \cdot \text{OEt}_2$ was extracted with water and the aqueous layer discarded. The organic layer was dried over MgSO_4 , concentrated, and subjected to column chromatographic separation on 30 g silica gel. Elution of the column with benzene/ CCl_4 yielded 0.20 g (20.4%) of pure Z isomer in the early fractions, followed by a mixture of the Z and E isomers and finally by pure E isomer: ¹H NMR (CDCl_3) δ 1.83 (s, 3 H), 1.93 (s, 3 H), 3.72 (s, 3 H), 5.77 (d, $J_{\alpha\beta}$ = 11.5 Hz, H_α), 6.88 (d of d, $J_{\alpha\beta}$ = 11.5, $J_{\beta\gamma}$ = 12 Hz, H_β), 7.17 (d, $J_{\beta\gamma}$ = 12 Hz, H_γ).

Methyl 5-Methyl-3,4-hexadienoate (8). A mixture of E (66%) and Z (34%) methyl 5-methyl-2,4-hexadienoate (0.14 g, 1×10^{-3} mol) and 2,2,6,6-tetramethylpiperidine (0.14 g, 1×10^{-3} mol) were dissolved in 0.1 L of dichloromethane and transferred to a Vycor flask. The flask was sealed with a rubber septum and the solution degassed with N_2 for 5 min. The solution was irradiated for 20.5 h with 254-nm light (RPR 2537-Å lamps) in a Rayonet reactor. Reaction progress was monitored by GC until only a single product peak was observed. The solution was then extracted 3 times with 5% HCl and 3 times with deionized water. The organic layers were dried over MgSO_4 , filtered, and concentrated, yielding 0.14 g (100%) of a dark-brown oil. The oil was dissolved in benzene and filtered through silica gel and the benzene removed by rotary evaporation, yielding 0.07 g (50%) of a bright-yellow oil: mass spectrum, m/e 140 (M^+); ¹H NMR (CDCl_3) δ 1.67 (s, 3 H), 1.70 (s, 3 H), 2.99 (d, J = 6 Hz, 2 H), 3.70 (s, 3 H), 5.10 (m, 1 H); IR (neat) 2980, 2950, 2910, 2860, 1975 (allenic stretch), 1740, 1635, 1435, 1415, 1365, 1425, 1260, 1205, 1160, 1020, 1010, 950, 765 cm^{-1} .

Methyl (E,E)-2,4-Hexadienoate ((E,E)-6). Sorbic acid (7 g, 0.062 mol, Aldrich) was reacted with thionyl chloride followed by methanol. Following rotary evaporation, the residue was distilled under vacuum (bp 80 °C/20 torr) yielding a colorless liquid (7.4 g, 0.059 mol, 94%): mass spectrum, m/e 126 (M^+); ¹H NMR (CDCl_3) δ 1.84 (d, $J_{\beta\text{H}}$ = 7.0 Hz, $\delta\text{-CH}_3$), 3.72 (s, 3 H), 5.68 (d, $J_{\alpha\beta}$ = 16 Hz, H_α), 5.90–6.25 (m, H_γ and H_β), 7.17 (m, H_β).

Methyl (Z,E)-2,4-Hexadienoate ((Z,E)-6). Methyl (E,E)-2,4-hexadienoate (0.63 g, 5×10^{-3} mol) and AlCl_3 (0.34 g, 2.8×10^{-3} mol) were dissolved in 0.1 L of dichloromethane and transferred to a Pyrex annulus under nitrogen. The solution was irradiated with a 450-W medium-pressure Hanovia lamp in a Pyrex lamp well for 1.5 h until a photoequilibrium had been established. GC and HPLC of the sample indicated 71% conversion to the title species. The AlCl_3 was extracted with water and the aqueous layer discarded. The organic layer was dried over MgSO_4 , concentrated, and subjected to a flash chromatographic separation on 100 g of silver nitrate impregnated silica gel. Elution of the

column with hexane yielded 0.38 g (60%) of pure (Z,E)-6 in the early fractions followed by a mixture of the three other isomers: mass spectrum, m/e 126 (M^+); ¹H NMR (CDCl_3) δ 1.87 (d of d, $J_{\delta\text{CH}_3-\beta\text{H}}$ = 7.0, $J_{\delta\text{CH}_3-\gamma\text{H}}$ = 1.5 Hz, $\delta\text{-CH}_3$), 3.65 (s, 3 H), 5.48 (d, $J_{\alpha\beta}$ = 12 Hz, H_α), 5.99 (q of d, $J_{\delta\text{CH}_3-\beta\text{H}}$ = 7, $J_{\gamma\delta}$ = 15.7 Hz, H_δ), 6.47 (d of d, $J_{\alpha\beta}$ = 11.6, $J_{\beta\gamma}$ = 11.5 Hz, H_β), 7.39 (m, H_γ).

Methyl (E,Z)-2,4-Hexadienoate ((E,Z)-6) and Methyl (Z,Z)-2,4-Hexadienoate ((Z,Z)-6). Methyl (E,E)-2,4-hexadienoate (0.38 g, 3×10^{-3} mol) was dissolved in 0.1 L of dichloromethane, transferred to a Vycor vessel, and irradiated for 2 h with 254-nm light (RPA 254-nm lamps) in a Rayonet reactor. This yielded a photostationary-state mixture of the four isomeric hexadienoates composed of 16% E,E-6, 33% Z,E-6, 24% E,Z-6, and 27% (Z,Z)-6, respectively, based on GC and HPLC analysis. The sample was concentrated and subjected to flash chromatography on 100 g of 25% silver nitrate on silica gel, using hexane as the eluant. Early fractions yielded pure (Z,E)-6 (0.11 g, 30%). Continued elution afforded pure (Z,Z)-6 (0.05 g, 14%), followed by (E,Z)-6 contaminated by (E,E)- and (Z,Z)-6. The latter fractions were combined and rechromatographed twice, yielding an enriched sample of (E,Z)-6 with a purity (70%) sufficient for structural assignment. (E,Z)-6: mass spectrum, m/e 126 (M^+); ¹H NMR (CDCl_3) δ 1.85 (d of d, $J_{\delta\text{CH}_3-\beta\text{H}}$ = 9, $J_{\delta\text{CH}_3-\gamma\text{H}}$ = 1.5 Hz $\delta\text{-CH}_3$), 3.75 (s, 3 H), 5.60 (d, $J_{\alpha\beta}$ = 16 Hz, H_α), 5.75–6.20 (m, H_δ), 6.75–7.60 (m, H_β , H_γ). (Z,Z)-6: mass spectrum, m/e 126 (M^+); ¹H NMR (CDCl_3) δ 1.85 (d of d, $J_{\delta\text{CH}_3-\beta\text{H}}$ = 7.0, $J_{\gamma\text{H}}$ = 1.5 Hz, $\delta\text{-CH}_3$), 3.75 (s, 3 H), 5.60 (d, $J_{\alpha\beta}$ = 12 Hz, H_α), 5.75–6.20 (m, H_δ), 6.75–7.60 (m, H_β , H_γ).

Methyl 3,4-Hexadienoate (9). Methyl (E,E)-2,4-hexadienoate (0.38 g, 3.0×10^{-3} mol) and trifluoroacetic acid (0.68 g, 6.0×10^{-3} mol) were dissolved in 0.1 L of dichloromethane. The solutions were irradiated for 36 h with 254-nm light (RPR 2537-Å lamps) in a Vycor reaction vessel in a Rayonet reactor. Reaction progress was monitored by GC until only a single product peak was observed. The samples containing trifluoroacetic acid were extracted with 10% sodium bicarbonate. The organic layers were dried over MgSO_4 , filtered, and concentrated, yielding 0.36 g (100%) of a colorless liquid: mass spectrum, m/e 126 (M^+); ¹H NMR (CDCl_3) δ 1.56 (d of d, 3 H), 2.95 (d of d, 2 H), 3.67 (s, 3 H), 4.80–5.35 (m, 2 H); IR (neat) 2990, 2950, 2910, 2860, 1945 (allenic stretch), 1740, 1640, 1600, 1440, 1330, 1250, 1170, 940, 870 cm^{-1} .

Methyl (E,E)-5-Phenyl-2,4-pentadienoate ((E,E)-7). (E,E)-5-Phenyl-2,4-pentadienoic acid was prepared by the method of Bausal and Pandya,²⁷ mp 166–167 °C [lit.²⁷ mp 165–166 °C]. The acid was esterified (thionyl chloride, methanol), yielding a light-yellow solid which was vacuum sublimed. The resulting product was a white solid which was found to be >99% pure by GC analysis: mp 103 °C; mass spectrum, m/e 176 (M^+); ¹H NMR (CDCl_3) δ 3.73 (s, 3 H), 5.98 (d, J = 15 Hz, H_α), 6.65–7.00 (m, H_γ , H_δ), 7.25 (m, 5 H, aromatic), 7.25 (m, $J_{\alpha\beta}$ = 15 Hz, H_β).

Methyl (E,Z)-5-Phenyl-2,4-pentadienoate ((E,Z)-7) and Methyl (Z,Z)-5-Phenyl-2,4-pentadienoate ((Z,Z)-7). Methyl (E,E)-5-phenyl-2,4-pentadienoate (3.8 g, 0.02 mol) and 1 equiv of $\text{BF}_3 \cdot \text{OEt}_2$ were dissolved in 0.1 L of dichloromethane and transferred to a Pyrex annulus under nitrogen. The solution was irradiated for 24 h with 350-nm light (RPR 3500-Å lamps) in a Rayonet reactor. The irradiated solution was extracted with 10% sodium bicarbonate and dried over MgSO_4 and the solvent evaporated. The residue was repeatedly chromatographed on Woelm GF silica, 1000 μM thick-layer plates using 99% hexane–1% ethyl acetate elutant. Isolated material was analyzed by HPLC. In this manner, samples enriched in (E,Z)-7 (75%) and (Z,Z)-7 (70%) were obtained. (E,Z)-7: mass spectrum, m/e 176 (M^+); ¹H NMR (CDCl_3) δ 3.73 (s, 3 H), 6.10 (d, J = 15 Hz, H_α), 6.50 (m, H_γ), 6.89 (d, J = 12 Hz, H_β), 7.4 (m, 5 H, aromatic), 7.7–8.1 (m, H_δ). (Z,Z)-7: mass spectrum, m/e 176 (M^+); ¹H NMR (CDCl_3) δ 3.75 (s, 3 H), 5.85 (d, J = 12 Hz, H_α), 6.40 (d, J = 12 Hz, H_β), 6.55 (m, H_δ), 6.85 (m, H_γ), 7.3 (m, 5 H, aromatic).

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