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Allenyl(vinyl)methane Photochemistry. Photochemistry of Methyl 4,4-Dimethyl-2,5,6-heptatrienoate Derivatives

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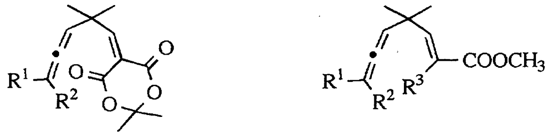
Both the direct and sensitized photolyses of [2-(1,2-propadienyl)-substituted alkylidene]malonates gave mainly intramolecular [2+2] cycloadducts. On the other hand, the direct irradiation of methyl (*E*)-4,4-dimethyl-2,5,6-heptatrienoate (**3a**) competitively underwent *E*–*Z* geometric isomerization and intramolecular [2+2] cycloaddition, though prolonged irradiation led to [2+2] cycloadducts as main products. For methyl (*E*)-4,4,7-trimethyl-2,5,6-octatrienoate (**3b**), the intramolecular [2+2] cycloaddition occurred under both direct and sensitized irradiation and the *E*–*Z* geometric isomerization scarcely occurred. In these allenyl(vinyl)methanes under direct irradiation, the 1,2-propadienyl-substituted esters gave a 1,2-propadienylcyclopropane or (2-ethenylidenecyclopropyl)acetate as a minor product. When **3b** was irradiated in the presence of hydrogen selenide in toluene, cyclopentenes were formed. The formation of the cyclopentenes indicated that the biradical intermediate is a cyclopentane-1,3-diyl radical. By MO calculations of the model compounds for the chromophores of the esters, it is suggested that the preferential initial bond for the 1,2-butadienyl- or 3-methyl-1,2-butadienyl-substituted esters is between the C_6 (allene center carbon) and C_2 (α-carbon), while 1,2-propadienyl-substituted esters can also be bonded between the C_5 and C_3 (β-carbon).

It is generally known that the di-π-methane rearrangement of acyclic divinylmethanes concertedly occurs via a singlet excited state on either vinyl chromophore.[1] In the photochemistry of allenyl(styryl)methanes, these compounds were expected to undergo a di-π-methane rearrangement, though this was a side reaction in direct photolyses, and an intramolecular [2+2] cycloaddition mainly took place.[2] On the other hand, Zimmerman et al. reported that the direct and sensitized photolyses of the divinylmethane substituted methoxycarbonyl groups at the geminal position gave different regioisomeric vinylcyclopropanes.[3,4] Such a regioselective di-π-methane rearrangement by multiplicity control of the divinylmethanes is interesting. We then noted the photochemistry of allenyl(vinyl)methanes in which the vinyl is an electron-deficient alkene, and recently reported on the photochemistry of 5-[2-(1,2-propadienyl)-substituted alkylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione, γ-allenyl-substituted alkylidene Meldrum's acids **1** (Chart 1).[5] Because the methylene Meldrum's acid chromophore is a strong electron acceptor,[6] the UV-absorption spectra showed that these compounds formed an intramolecular CT complex between the allenyl moiety and the methylene Meldrum's acid.[5] The direct photolyses of **1** gave (2-alkenylidenecyclopropyl)acetate mainly via a singlet CT excited state, while in the acetone-sensitized photolyses, the intramolecular [2+2] cycloaddition took place from the triplet excited state of the methylene Meldrum's acid chromophore to afford bicyclo[2.1.0]pentanes. Thus, the photochemistry of **1** suggested the participation of the CT excited state and presented the possibility of novel multiplicity control in the photochemistry of the divinylmethanes.



1: R^1, R^2=H, CH$_3$

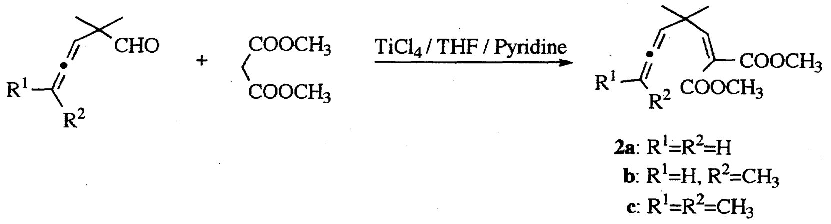
2: R^1, R^2=H, Me, R^3=COOCH$_3$
3: R^1, R^2=H, Me, R^3=H

Chart 1.

Newly prepared methyl 4,4-dimethyl-2,5,6-heptatrienoates, **2**[7] and **3**, are also expected to undergo formation of the intramolecular CT complex. However, because the α,β-unsaturated esters involving the alkylidenemalonates are less electron-deficient alkenes than the methylene Meldrum's acids,[6] it is considered that the intramolecular CT complexation in **2** and **3** is less than that in **1**. Therefore, the photoreaction is expected via a π–π* transition state, except for the CT excited state, of the acyclic allenyl(vinyl)methanes in which the vinyl is an α,β-unsaturated ester.[8] In the results, these esters **2** and **3** in both the direct and sensitized photolyses gave mainly intramolecular [2+2] cycloadducts. We now report herein the photochemistry of **2** and **3** and the reaction mechanism.

Results

Preparation of the Esters. The preparation of [2-(1,2-propadienyl)-substituted alkylidene]malonate has been reported by Black and Landor.[9] However, because this synthetic method gave the allenic ester in low yield, the diesters **2a**—**c** were prepared readily by Knoevenagel condensation of dimethyl malonate with allenic aldehydes using the procedure of Lehnert (Scheme 1).[10]



2a: R^1=R^2=H
b: R^1=H, R^2=CH_3
c: R^1=R^2=CH_3

Scheme 1.

On the other hand, the monoesters **3a**,**b**, which are *E*-forms, were prepared by the reaction of methyl diethoxyphosphorylacetate with the allenic aldehyde using sodium methoxide in DMF (Scheme 2).

UV-Absorption Spectra of the Esters. The UV-absorption spectra of **2a**—**c** and **3a**,**b** in hexane are shown in Figs. 1 and 2, respectively. In analogy with **1**, the diesters **2a**—**c** and monoesters, **3a** and **3b**, exhibited CT bands as shoulder absorption in the ranges of 225—275 nm and of 225—265 nm, respectively. Their CT bands showed bathchromic shifts in the order **2a** < **2b** < **2c** and **3a** < **3b** due to the hyperconjugation by the terminal methyl group(s) of the allenyl moiety, though these appeared at a shorter wavelength than those of **1** (250—320 nm).[5]

Irradiation of the Esters. Upon direct irradiation at room temperature under an argon atmosphere, the diesters **2a**—**c** in hexane underwent mainly an intramolecular [2+2] cycloaddition to give bicyclo[2.1.0]pentanes **4a**—**c**, and, in the case of **2a**, (1,2-propadieneyl)cylclopropane **5** was obtained as a minor product (Scheme 3). The same was obtained from direct photolyses in acetonitrile. The yields of the photoproducts are described in Table 1.

The monoester **3a** in the direct photolysis competitively underwent intramolecular [2+2] cycloaddition and *E*–*Z* geometric isomerization (Scheme 4). After prolonged irradiation, [2+2] cycloadducts **6a** were mainly produced, and a (2-ethenylidenecyclopropyl)acetate **7** was obtained as a minor product (Table 1). A *Z*-form **8a** was obtained in 15% yield when **3a** was consumed to 50% in hexane. On the other hand, in the direct photolysis of **3b**, [2+2] cycloadducts **6b** were mainly formed, and the *E*–*Z* geometric isomerization of **3b** to **8b** scarcely occurred; **8b** reached a maximum 3% yield by monitoring on GLC, and its amount decreased upon prolonged irradiation. After evaporation of the solvents, the residue in the reaction of **3a** or **3b** was examined by medium-pressure silica-gel chromatography to give [2+2] cycloadducts **6a** or **6b**, whose ^{1}H NMR spectra showed the presence of *cis*- and *trans*-stereoisomers. The stereoisomers **6a-*c*** and **6a-*t*** were isolated by further medium-pressure silica-gel chromatography, though attempts to separate **6b-*c***

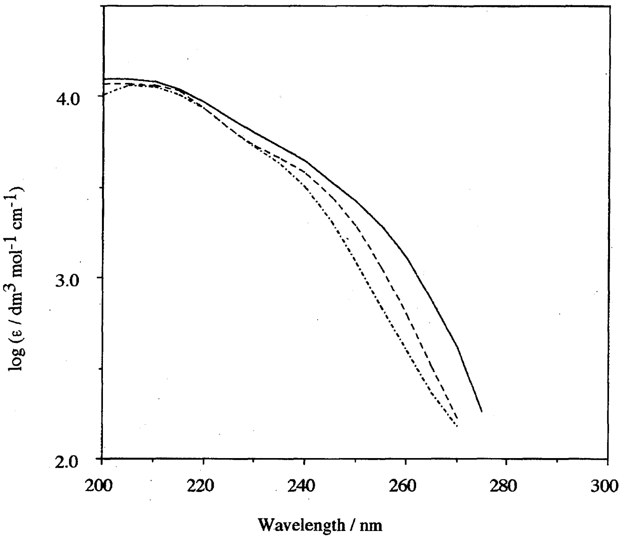


Fig. 1. UV-absorption spectra of **2a**—**c** in hexane (**2a**: – • –; **2b**: - - -; **2c**: —).

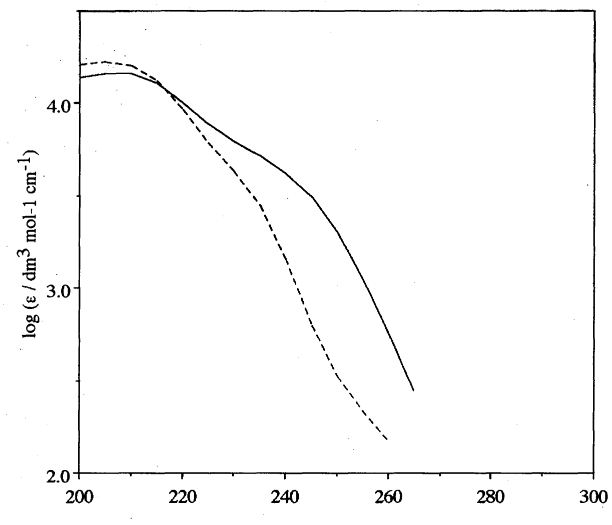
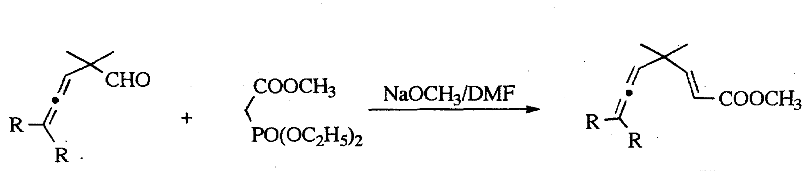
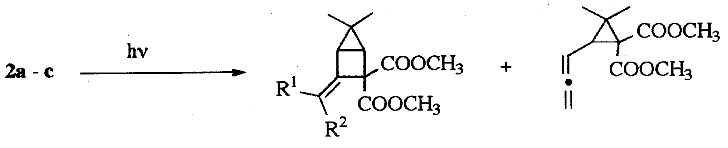


Fig. 2. UV-absorption spectra of **3a** and **3b** in hexane (**3a**: - - -; **3c**: —).



3a: R=H
b: R=CH_3

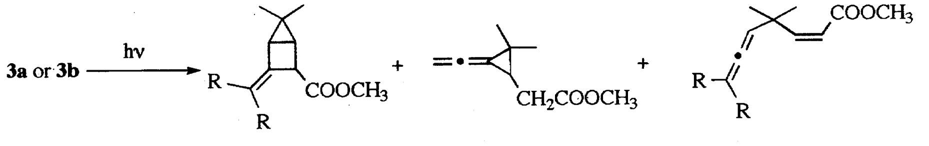
Scheme 2.



4a: $R^1=R^2=H$
b-*E*: $R^1=CH_3$, $R^2=H$
b-*Z*: $R^1=H$, $R^2=CH_3$
c: $R^1=R^2=CH_3$

5

Scheme 3.



6a: R=H
b: $R=CH_3$

7

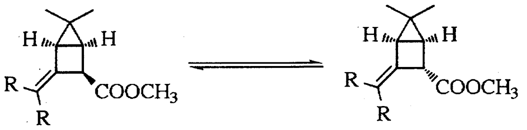
8a: R=H
b: $R=CH_3$

Scheme 4.

Table 1. Direct and Acetone-Sensitized Photolyses of **2a**—**c** and **3a**,**b**

Substrate	Solvent	Time/h	Product (Isolated yield/%)[a]
2a	Hexane	73[b]	**4a** (55) **5** (10)
	MeCN	56[b]	(53) (9)
	Acetone	20[c,d]	(50)
		2.7[e,f]	(17)
2b	Hexane	24[b]	**4b-*E*** (38), **4b-*Z*** (36)
	MeCN	24[b]	(33), (29)
	Acetone	6.5[c]	(52), (26)
2c	Hexane	20[b]	**4c** (59)
	MeCN	25[b]	(65)
	Acetone	11[b]	(56)
3a	Hexane	15[b]	**6a** (44) **7** (10)
		6[b,g]	(52) (0.6) **8a** (15)
	MeCN	15[b]	(72) (10)
	Acetone	3[c]	(31)
3b	Hexane	14[b]	**6b** (65)
		14.5[h,i]	(50) **8b** (2)
	MeCN	13[b]	(74)
	Acetone	4[c]	(40)

a) Photoproducts were isolated using a medium-pressure silica-gel chromatograph equipped with an RI detector. b) Using a 6-W low-pressure mercury lamp with a quartz jacket at room temperature under an argon atmosphere. c) Using a 100-W high-pressure mercury lamp with a Pyrex jacket at room temperature under an argon atmosphere. d) **2a** was consumed to 74%. e) Using a 450-W high pressure mercury lamp with a Pyrex jacket at room temperature under an argon atmosphere. f) **2a** was consumed to over 99%. g) **3a** was consumed to 50%. h) Using a 6-W low-pressure mercury lamp with a quartz jacket under an oxygen atmosphere. i) **3b** was consumed to 47%.



6a-*c*: R=H
b-*c*: $R=CH_3$

6a-*t*: R=H
b-*t*: $R=CH_3$

Scheme 5.

and **6b-*t*** were unsuccessful. The isolated adduct **6a-*c*** or **6a-*t*** was isomerized at room temperature to the respective stereoisomer to yield an equilibrated mixture of *cis* : *trans* = 18 : 82 (Scheme 5).

The acetone-sensitized photolyses of **2a**—**c** gave the [2+2] cycloadducts **4a**—**c** (Table 1). After prolonged irradiation, however, the yields of **4a**—**c** decreased gradually due to their decomposition by acetone-sensitization. The yield of **4a** was 17% at 99% conversion of **2a**, although it was 50% at 74% conversion. Moreover, in the case of the sensitization of **2b**, although the ratio of **4b-*E*** : **4b-*Z*** was 55 : 45 at 3% conversion, it was found to be 68 : 32 when the conversion was 97%.

The acetone-sensitization of **3a** or **3b** afforded **6a** or **6b**. The *Z*-form **8a** during the acetone-sensitization of **3a** reached a maximum 13% yield according to GLC, while, in a manner similar to the photolysis of **3a**, **8b** was present as a trace amount (< 1%).

Quantitative Studies: Quantum Yields. The quantum yields for the isomerizations of the diesters **2a**—**c** and the monoesters **3a**,**b** during the direct photolyses are described in Tables 2 and 3. The 1,2-butadienyl- or 3-methyl-1,2-butadienyl-substituted esters **2b**,**c** and **3b** underwent [2+2] cycloaddition more than did the 1,2-propadienyl-substituted esters **2a** and **3a**. The quantum yields for the cycloaddition decreased by 20—30% when oxygen was used as a quencher, though quenching effects by 2-methyl-1,3-butadiene or 2,3-butanedione were not observed. The quantum yields of the *E*-form **3a** to **7** are trace amounts, whereas those of the *Z*-form **8a** to **7** were determined to be as 0.035 in hexane and as 0.025 in acetonitrile under an argon atmosphere.

The quantum yields for the intramolecular [2+2] cycloaddition in the presence of several sensitizers with different triplet energies are also described in Tables 2 and 3. In hexane and in acetonitrile, the intramolecular [2+2] cycloaddition of **2a**—**c** was sensitized by acetone (E_{T} = 334—377 kJ mol^{-1}) or acetophenone (E_{T} = 310 kJ mol^{-1}). In the case of using benzophenone (E_{T} = 288 kJ mol^{-1}), the sensitizing effect was hardly detectable in hexane. However, benzophe-

Table 2. Quantum Yields for the Isomerization of **2a**—**c** in the Direct and Sensitized Photolyses

Substrate	Solvent	Atmosphere	Sensitizer	Quantum Yield	
			Concn/mol dm^3	Φ_{add}[a]	Φ_{di}[b]
2a	Hexane[c,d]	Ar	None	0.051	0.008
		O_2		0.038	0.008
	MeCN[c,d]	Ar		0.049	0.006
		O_2		0.049	0.006
	Hexane[e,f]	Ar	Acetone (1.0)	0.044	0.007
			Acetopheneone (0.1)	0.063	
			Benzophenone	< 0.0001	
	MeCN[e,f]		Acetone (1.0)	0.075	
			Acetophenone (0.1)	0.080	
			Benzophenone (0.1)	0.032	
2b	Hexane[c,d]	Ar	None	0.097 (E),	0.084 (Z)
		O_2		0.068,	0.054
	MeCN[c,d]	Ar		0.092,	0.073
		O_2		0.064,	0.049
	Hexane[e,f]	Ar	Acetone (1.0)	0.13,	0.10
			Acetophenone (0.1)	0.11,	0.095
			Benzophenone (0.1)	< 0.0001,	0.0001
	MeCN[e,f]	Ar	Acetone (1.0)	0.15,	0.13
			Acetophenone (1.0)	0.13,	0.10
			Benzophenone (1.0)	0.030,	0.021
2c	Hexane[c,d]	Ar	None	0.15	
		O_2		0.10	
	MeCN[c,d]	Ar		0.11	
		O_2		0.089	
	Hexane[e,f]	Ar	Acetone (1.0)	0.11	
			Acetophenone (0.1)	0.10	
			Benzophenone (0.1)	< 0.0001	
	MeCN[e,f]		Acetone (1.0)	0.12	
			Acetophenone (0.1)	0.10	
			Benzophenone (0.1)	0.007	

a) Quantum yields for the intramolecular [2+2] cycloaddition. b) Quantum yields for the di-π-methane rearrangement. c) A 6-W low-pressure mercury lamp with a quartz filter was used as a 254 nm irradiation source. d) The light intensity was determined by tris (oxalato)ferrate(III) actinometry. e) A 450-W high-pressure mercury lamp through a combination of a K_2CrO_4 solution and a Pyrex filter was used as a 313 nm irradiation source. f) The light intensity was determined by stilbene actinometry.

none shows a sensitizing effect for the [2+2] cycloaddition in acetonitrile, though the quantum yields had smaller values than those obtained using acetone or acetophenone. Furthermore, in both solvents, neither 2-benzoylpyridine (E_T = 279 kJ mol^{-1}) nor 2-acetylnaphthalene (E_T = 247 kJ mol^{-1}) had a sensitizing effect.

For the monoesters, **3a** and **3b**, it was found that acetone and acetophenone were good sensitizers for the intramolecular [2+2] cycloaddition. The quantum yields for the sensitized isomerizations were lower than those for direct ones, especially the *E*–*Z* geometric isomerization. Neither benzophenone, 2-benzoylpyridine, nor 2-acetylnaphthalene had a sensitizing effect.

Stereoisomers Ratios in the Photolyses of 3a,b and 8a. Table 4 gives the stereoisomer ratios of *cis*- and *trans*-[2+2] cycloadducts within 30% conversion of the monoesters **3a**,**b** or **8a** during the direct or sensitized photolyses in acetonitrile-d_3. Xanthone has a triplet energy of 311 kJ mol^{-1}, and was used as a sensitizer in these sensitizing experiments. Under the irradiation conditions of **3a** and **8a**, the ratios of **6a-*c*** and **6a-*t*** were both determined to be 18 : 82. The ratio of **6b-*c*** and **6b-*t*** during the direct photolysis of **3b** was observed to be 1 : 1, although the sensitization showed a 32 : 68 ratio.

An acetonitrile-d_3 solution of **3b** in a quartz NMR tube was irradiated at 0 °C using a 6-W low-pressure mercury lamp through a quartz filter. When **3b** was consumed to 95%, the ratio of **6b-*c*** and **6b-*t*** was determined to be 1 : 1. After a half volume of the reaction mixture was transferred to a Pyrex NMR tube in the presence of xanthone, the solution was further irradiated for 10 min at 0 °C by a 100-W high-pressure mercury lamp through a Pyrex filter. The ratio of **6b-*c*** and **6b-*t*** in the irradiated solution changed to 34 : 66. The residual half-volume solution was allowed to stand at 0 °C for 15 min in the dark and the stereoisomer ratio traced by NMR. After 7 d at room temperature, the stereoisomer ratio reached 18 : 82. These results are described in Table 5.

Trapping of Intermediates: Enol Intermediate. When a solution of the *Z*-form **8a** in methanol-d_1 was irradiated, GCMS analyses showed that the resulting **7** incorporated a deuterium at the α-position and that there were no products other than **3a** and **6a**.

Biradical Intermediate. The direct photolysis of

Table 3. Quantum Yields for the Isomerization of **3a**,**b** and **8a** in the Direct and Sensitized Photolyses

Substrate	Solvent	Atmosphere	Sensitizer	Quantum Yield		
			Concn/mol dm^3	Φ_{add}[a]	Φ_{ge}[b]	Φ_{alk}[c]
3a	Hexane[d,e]	Ar	None	0.34	0.34	< 0.0001
		O_2		0.14	0.37	< 0.0001
	MeCN[d,e]	Ar		0.45	0.35	< 0.0001
		O_2		0.21	0.38	< 0.0001
	Hexane[f,g]	Ar	Acetone (1.0)	0.10	0.053	
			Acetopheneone (0.1)	0.10	0.078	
	MeCN[f,g]		Acetone (1.0)	0.16	0.078	
			Acetophenone (0.1)	0.18	0.092	
3b	Hexane[d,e]	Ar	None	0.44	0.027	
		O_2		0.35	0.026	
	MeCN[d,e]	Ar		0.45	0.022	
				0.33	0.026	
	Hexane[f,g]	Ar	Acetone (1.0)	0.19	< 0.0001	
			Acetophenone (0.1)	0.14	< 0.0001	
	MeCN[f,g]		Acetone (1.0)	0.18	< 0.0001	
			Acetophenone (0.1)	0.15	< 0.0001	
8a	Hexane[d,e]	Ar	None	0.095	0.14	0.035
		O_2		0.067	0.15	0.034
	MeCN[d,e]	Ar		0.12	0.12	0.025
		O_2		0.074	0.15	0.026

a) Quantum yields for the intramolecular [2+2] cycloaddition. b) Quantum yields for the *E*–*Z* geometric isomerization. c) Quantum yields for the formation of **7**. d) A 6-W low-pressure mercury lamp with a quartz filter was used as a 254 nm irradiation source. e) The light intensity was determined by tris (oxalato)ferrate(III) actinometry. f) A 450-W high-pressure mercury lamp through a combination of a K_2CrO_4 solution and a Pyrex filter was used as a 313 nm irradiation. g) The light intensity was determined by stilbene actinometry.

Table 4. Stereoisomer Ratios of *cis*- and *trans*-Forms in the Direct or Sensitized Photolyses of **3a**,**b** and **8a** in Acetonitrile-d_3

Substrate	λ/nm	Additive	Conversion of ester/%	*cis* to *trans*[a]
3a	254[b]	None	20	18 : 82
8a			30	18 : 82
3b			27	50 : 50
3a	> 280[c]	Xanthone	28	19 : 81
8a			20	16 : 84
3b			21	32 : 68

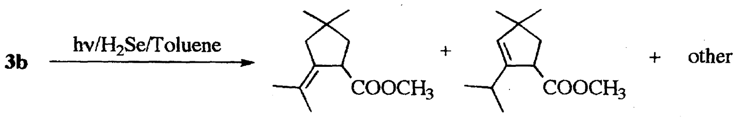
a) After irradiation, the ratio of stereoisomers was immediately determined by NMR. b) An acetonitrile-d_3 solution of the ester in a quartz NMR tube was irradiated for 1 h at room temperature under argon using a 6-W low-pressure mercury lamp through a quartz jacket. c) An acetonitrile-d_3 solution of a mixture of the esters and xanthone in a Pyrex NMR tube was irradiated for 10 min at room temperature under argon using a 100-W high-pressure mercury lamp through a Pyrex jacket.

Table 5. Change in the Ratio of **6b**-***c*** and **6b**-***t***

Irradiation time/h	Time at 0 °C/h	*cis* to *trans*[a]
4[b]	0	50 : 50
4[b]+0.17[c]	0	34 : 76
4[b]	0.25[b]	50 : 50
	4[d]	43 : 57
	6[d]	39 : 61
	7 days[e]	18 : 82

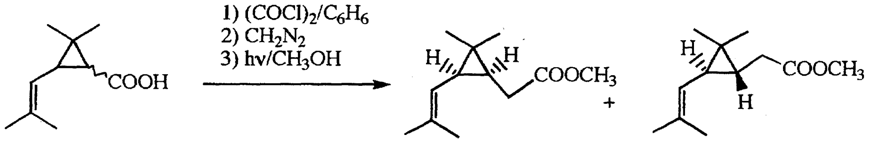
a) The ratios were determined by NMR. b) An acetonitrile-d_3 solution of **3b** in a quartz NMR tube was degassed with argon and then irradiated for 4 h at 0 °C using a 6-W low-pressure mercury lamp through a quartz filter. The ester **3b** was consumed to over 95%. c) A half portion was transferred to a Pyrex NMR tube in the presence of xanthone, and the mixture was degassed with argon and then irradiated for 10 min at 0 °C using a 100-W high-pressure mercury lamp through a Pyrex filter. d) The residual half portion was allowed to stand at 0 °C. e) The residual half portion was allowed to stand at room temperature.

the monoester **3b** in the presence of hydrogen selenide (**TOXIC**)[11] gave the [2+2] cycloadduct **6b** and several photoproducts. The GCMS spectra of the reaction mixture showed that the three main products have a molecular weight of *m*/*z* 196. Two of the three photoproducts corresponded with cyclopentenes **9a** and **10a** (Scheme 6), which were prepared by the Pd/C-hydrogenation of **6b** in methanol.[12] The ratio of **9a**, **10a**, and another product was 1 : 2.7 : 5.3 by GLC. Another photoproduct differed with *cis*- and *trans*-cyclopropaneacetates which are the trapping products **11a** and **12a** of the 1,4-biradical derived by bonding between the 3- and 5-positions of **3b**. The cyclopropaneacetates **11a** and **12a** were prepared according to the published procedure (Scheme 7).[13] Xanthone sensitization of **3b** in the presence of hydrogen selenide in toluene also produced **9a**, **10a**, and another product (1 : 1.8 : 1.8 ratio). We carried out the preparative scale of the photolysis of **3b** with hydrogen selenide in toluene, although isolation of the photoproducts failed due to cutting off the irradiation source by the deposition of a large amount of selenium. Hence, the structure of the another compound could not be determined.



9a **10a**

Scheme 6.



11a **12a**

Scheme 7.

Discussion

Stereochemistry of the Photoproducts. The stereochemistry of the resulting geometric isomers, **4b**-*E* and **4b**-*Z*, in the photolyses of **2b** was assigned on the basis of the effects of adding a lanthanide-induced shift (LIS) reagent [Yb(fod)$_3$] on the ^{1}H NMR spectra. The LIS's of the protons of the adducts increase linearly with the molar ratio [Yb(fod)$_3$/adduct] (Table 6). The stereochemistry of the adducts was readily determined by the ratio slopes of their ethylidene moieties; i.e., the relative shift of methyl protons in the ethylidene moiety of **4b**-*E* is smaller than that of **4b**-*Z*, whereas that of the methine proton (=CH) is the opposite.

The stereochemistry of the *cis*- and *trans*-adducts was determined from the signals of the 1- and 2-methine protons in the bicyclo[2.1.0]pentane ring. It has been reported that the coupling constants between the 1- and 2-methine protons of the reported bicyclo[2.1.0]pentanes are J_{trans} = ca. 0 Hz and J_{cis} = 4—5 Hz, respectively.[14] The 1-methine proton of the *trans*-form **6a**-*t* or **6b**-*t* appears as a doublet–doublet by coupling with the 2- and 4-methine protons, while that of *cis*-form **6a**-*c* or **6b**-*c* appears as a doublet.

The structures of the other photoproducts were readily established from spectroscopic data and microanalyses or HRMS.

Photochemistry of the Esters. Generally, the acyclic α,β-unsaturated esters undergo bond rotation, viz., energy-wasting *E*–*Z* geometric isomerization, under both direct and sensitized conditions.[15] We had expected that **3a** and **3b** would undergo the *E*–*Z* geometric isomerization. Based on the quantum yields for the isomerization of **3a** (Table 3), the [2+2] cycloaddition and *E*–*Z* geometric isomerization of **3a** competed under direct irradiation, although the former reaction predominantly occurred under sensitization. In the case of **3b**, in both direct and sensitized photolyses the [2+2] cycloaddition mainly occurs. Allenes are good alkenes which undergo intra- and intermolecular photocycloaddition with cycloalkenones.[16] Recently, the photochemical intermolecular [2+2] cycloaddition of the excited triplet allene to enone has been proposed by Froese et al.[17] However, we consider that the intramolecular [2+2] cycloaddition of these allenyl(vinyl)methanes takes place via an excited state of the vinyl chromophore. The triplet energies of **2a**—**c** are estimated to be ca. 300 kJ mol^{-1} in hexane based on the sensitizing effects and; further, those in acetonitrile have a lower energy (ca. 10 kJ mol^{-1}) than that in hexane. The triplet energies of **3a** and **3b** are also estimated to be ca. 300 kJ mol^{-1} in both solvents. These estimated values are close to the reported triplet energies of the α,β-unsaturated esters.[18] Hence, in analogy with the photochemistry of **1**,[5] the [2+2] cycloaddition during the sensitized irradiation of **2a**—**c** and **3a**,**b** occurs from the triplet excited state of the vinyl chromophore. In the direct photolyses, it was expected that 2-methyl-1,2-butadiene and 2,3-butanedione could be effectively quenched in the [2+2] cycloaddition of their esters based on the estimated triplet energies. However, the quenching effects were not found. Furthermore, the quantum yields for the [2+2] cycloaddition decrease (ca. 20—30%) in oxygen, but it seems that oxygen acts as a chemical quencher rather than a physical one. If the [2+2] cycloaddition of the esters during the direct irradiation takes place via a triplet pathway only, the rate of its reaction is larger than that of diffusion control by the solvents used, and should be above 10^{10} M s^{-1} (1 M = 1 mol dm^{-3}). Furthermore, if a concerted [2+2] cycloaddition of allenes with alkenes occurs, the stereoselevtive cycloaddition might be expected in the photolyses of the mono esters, **3a** and **3b**.[19,20] However, either direct or sensitized photolyses of **3a** and **3b** gave a *cis*- and *trans*-[2+2] cycloadduct mixture; hence, the [2+2] cycloaddition of these esters should proceed via a biradical mechanism. Photochemical intra- or intermolec-

Table 6. Relative Shifts of the Protons of **4b**-*E* and **4b**-*Z* in LIS Experiments

Adduct	1-CH	4-CH	5-Me	5-Me	=CH$_3$	=H	COOMe	COOMe
4b-*Z*	1	0.50	0.18	0.53	0.63	0.47	0.60	0.61
4b-*E*	1	0.63	0.22	0.57	0.25	1.06	0.56	0.54

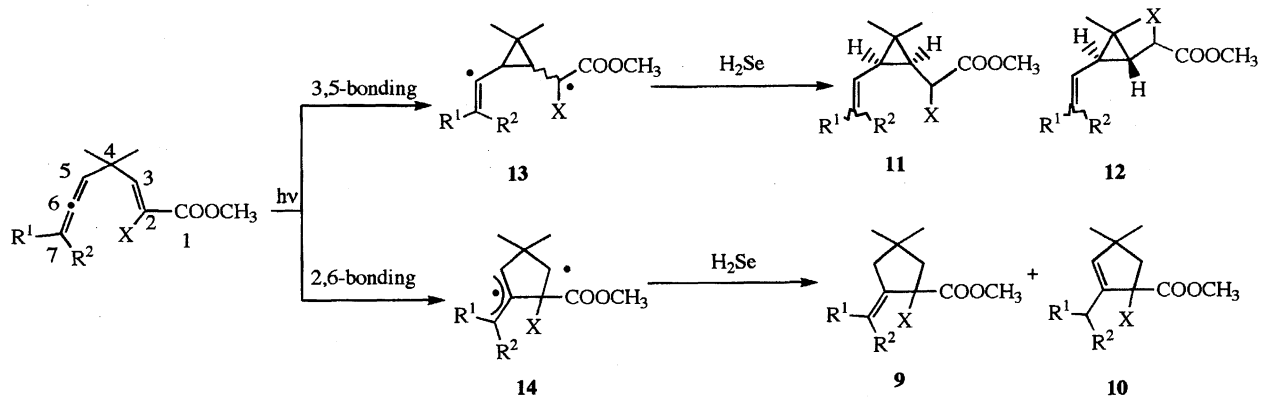
ular [2+2] cycloaddition of cycloalkenone with alkenes has been explained as the Corey–de Mayo mechanism involving the triplet exciplex,[21—23] but was recently proposed as the Bauslaugh–Schuster–Weedon biradical mechanism.[22—25] As shown in Table 4, either direct or sensitized irradiation of **3a** is stereoselective: i.e., the *trans*-adduct **6a**-*t* is a main product. However, the direct photolysis of **3b** gave a 1 : 1 mixture of **6b**-*t* : **6b**-*c*. Furthermore, although the adducts **6b**-*t* and **6b**-*c* certainly underwent the sensitized *cis–trans* isomerization, at the low conversion of **3b** the formation of **6b**-*t* was preferred under the sensitized condition. These results suggest that the [2+2] cycloadducts were also produced from the singlet excited state, except for the triplet one. A consideration of a tendency for the ratio of the adducts on the direct and sensitized photolyses is described elsewhere.

Hydrogen selenide is known to be a good radical hydrogenating reagent.[23—25] From the trapping of a biradical intermediate by hydrogen selenide in the photolysis of cyclopentenone with allene,[23a,24] Weedon et al. reported that the terminal carbon, rather than the center carbon of 1,2-propadiene, initially bonds to the α-carbon of the cyclopentenone.[24] If these allenyl esters underwent the [2+2] cycloaddition according to this reported mechanism, the resulting intermediates are *cis*- and *trans*-1,4-biradicals **13**. On the other hand, the "rule of five" for the intramolecular [2+2] cycloaddition of a cycloalkenone with a terminal alkene was verified by the trapping experiment of the biradical intermediate with hydrogen selenide.[25] In our previous report,[5] we have proposed that the [2+2] cycloaddition of **1** initially bonds between the allene center carbon and the α-carbon of the methylene Meldrum's acid moiety by the "rule of five" to yield a cyclopentane-1,3-diyl radical **14**. If considerable biradicals **13** and **14** were trapped with hydrogen selenide, four possible products **9**—**12** would be formed (Scheme 8). The trapping products from the photochemistry of **3b** in the presence of hydrogen selenide can be prepared readily by other synthetic methods. The cyclopentenes, **9a** and **10a**, were prepared by Pd/C hydrogenation of **6b**. Isobutenylcyclopropaneacetates, **11a** and **12a**, were also prepared according to the published procedure (Scheme 7).[13] By GCMS and GLC analyses of the resulting products in the photochemistry of **3b** in the presence of hydrogen selenide, the formation of **9a** and **10a** was observed, but not that of **11a** and **12a**. This result indicates that the intermediate for the [2+2] cycloaddition is the cyclopentane-1,3-diyl radical **14**.

On the other hand, direct photolyses of the 1,2-propadienyl-substituted ester, **2a** or **3a**, afforded the 1,2-propadienylcyclopropane **5** or the (2-ethenylidenecyclopropyl)acetate **7**, which were derived from the 1,4-biradical intermediate **13**. For **2a** and **3a**, it is considered that the 3,5- and 2,6-bonding in the photolyses occurs competitively.

Such a difference by the allene-substituent would be explained as follows. It is known that several radicals add to a terminal carbon of 1,2-propadiene and mono-alkyl-substituted allene rather than to their center carbons.[26] However, in the cases of di-, tri-, and tetra-alkyl-substituted allenes, the radicals attack the center carbon rather than the terminal carbon because of the orbital coefficients of each C=C=C bond, steric effects, and the stability of the resulting radical adduct.[26,27] From the results of PM3 MO calculations for the ground state of **15a**—**c**, **16**, and **17** as models of the chromophores of **2a**—**c** and **3a**,**b** (Fig. 3), the energy levels of HOMO's and LUMO's suggest that the intramolecular [2+2] cycloaddition of these allenyl(vinyl)methanes occurs from a HOMO–HOMO interaction between the allene and the unsaturated ester moieties. For the di- and tri-alkyl-substituted allenes, **15b** and **15c**, the HOMO levels are at the C_1–C_2 bond. The MO coefficients of the C_1 and C_2 of **15c** in HOMO are both 0.60, while the MO coefficient of C_2 of **15b** is lower than that of C_1, but its difference is 0.03. In addition, the MO coefficient of the β-carbon of **16** or **17** is lower than that of the α-carbons, though its difference is also slight (Fig. 3). Taking account of the structures of these allenyl(vinyl)methanes, it is considered that the intramolecular [2+2] cycloaddition of **2b**,**c** and **3b** takes place from interaction between the MO's of the α-carbon (C_2) and of the allene center carbon (C_6). However, for the monoalkyl-substituted allene **15a**, the HOMO level lies at the C_2–C_3 bond and the MO coefficient of C_3 is larger than that of C_2. This result indicates that both the interactions of the C_2–C_6 and of the C_3–C_5 of **2a** or **3a** are possible; hence, photoproducts **5** and **7** were derived via bonding of the C_3–C_5 (Scheme 8).

The results of the trapping experiments and of the MO calculations suggest that the intramolecular [2+2] cycloaddition



Scheme 8.

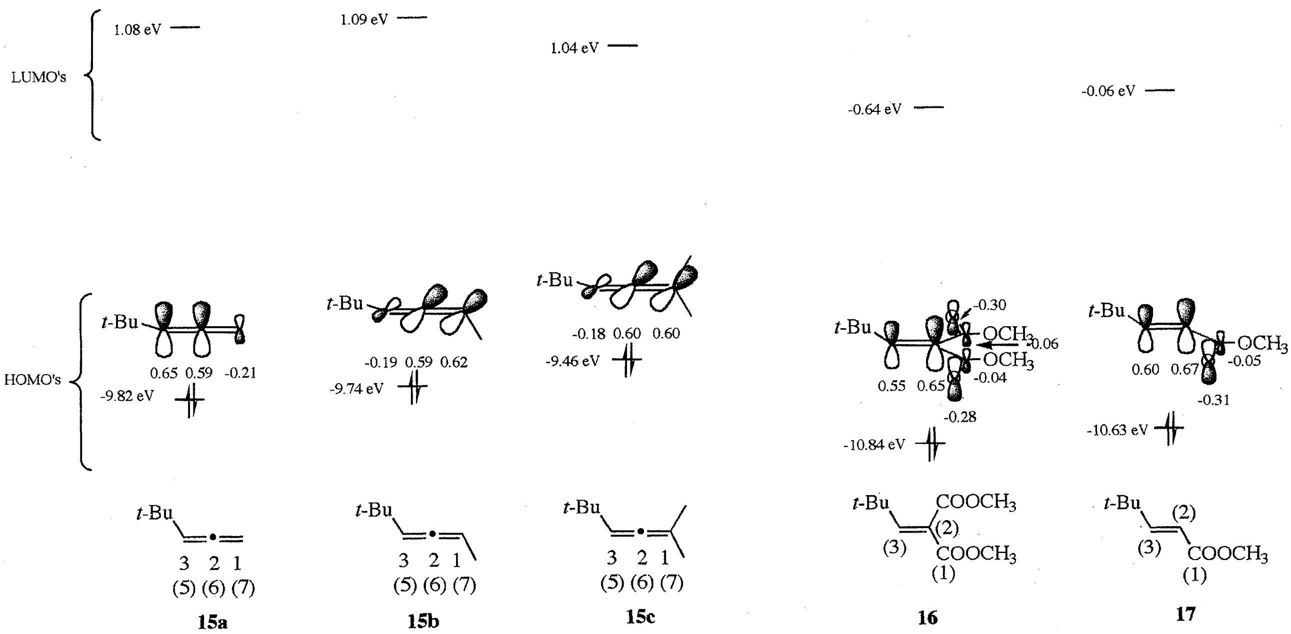
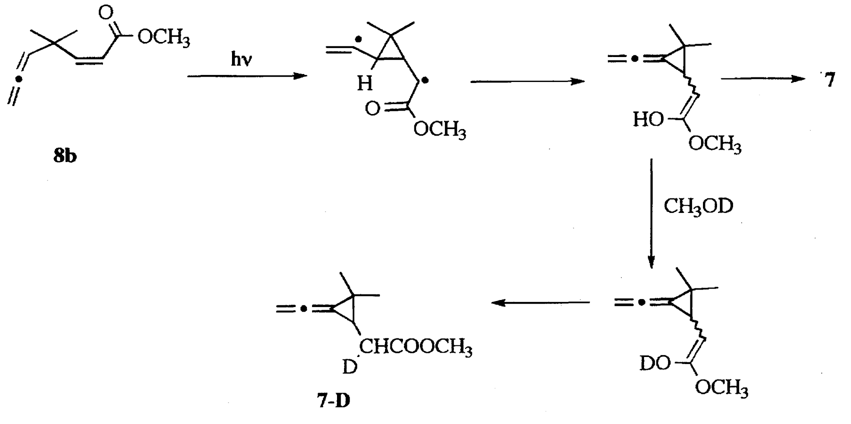


Fig. 3. Molecular orbital correlation diagrams of **15a**—**c**, **16**, and **17**: Number in parentheses corresponds with position in **2a**—**c** and **3a**,**b**.

of these esters apparently proceeds via the cyclopentane-1,3-diyl radical mechanism and, further, both the singlet and triplet state mechanisms exist. Because it has been reported that the lowest state of the cyclopentane-1,3-diyl radicals is a triplet and that the energy gap between the triplet and singlet of the *gem*-dimethyl substituted cyclopentane-1,3-diyl radical is small,[28] it seems that the resulting singlet cyclopentane-1,3-diyl radicals on the direct photolyses of these esters underwent spin inversion to yield the triplet cyclopentane-1,3-diyl radical and the differences of the ratio of **6b**-*t* and **6b**-*c* on the direct and sensitized photolyses of **3b** were found.

In these esters, the direct photolyses of **3a** gave the (1-ethenylidene)cyclopropane **7**; however the quantum yields of **3a** to **7** in both hexane and acetonitrile were trace amounts, whereas those of **8a** to **7** were obtained as 0.035 in hexane and 0.025 in acetonitrile. This suggests that **7** is derived from the singlet excited state of *Z*-form **8a**. It is considered that the reaction mechanism for the formation of **7** is similar to that of (1-alkenylidene)cyclopropanes in the direct photolyses of **1** in our previous report,[5] and involves an enol intermediate. In the photolysis of **8a** in methanol-d_1, the resulting **7** incorporated a deuterium at the α-position according to GCMS analysis. This strongly supports a reaction mechanism involving the enol intermediate, and it is considered that the intramolecular hydrogen transfer occurs from the *trans*-1,4-biradical intermediate (Scheme 9).

In conclusion, the preferential initial bond for the 1,2-butadienyl- or 3-methyl-1,2-butadienyl-substituted esters is between the C_6 (allene center carbon) and C_2 (α-carbon) to give the bicyclo[2.1.0]pentanes via the cyclopentane-1,3-diyl radical. On the other hand, 1,2-propadienyl-substituted esters bond between the C_5 and C_3 (β-carbon) to afford the 1,2-propadienylcyclopropane or (2-ethenylidenecyclopropyl)acetate. The triplet intramolecular [2+2] cycloaddition occurs from the excited state of the vinyl chromophore.



Scheme 9.

Experimental

Boiling points are uncorrected. The melting points were determined on a micro hot stage (Yazawa) and are uncorrected. IR spectra were taken with KBr disks or a liquid film inserted between NaCl plates using a BIO-RAD FTS-60A spectrophotometer. ^{1}H and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with a JEOL JNM-EX90 (89.45 MHz for ^{1}H and 22.40 MHz for ^{13}C) spectrometer using TMS as an internal standard. Low- and high-resolution mass spectra were obtained with a JEOL JMS-AX-500 spectrometer at an ionization voltage of 70 eV, and were acquired by a GC/MS analysis using a gas chromatograph equipped with a capillary column (OV-1, 0.24 mm×25 m). UV spectra were measured with a Shimadzu UV-160A spectrophotometer. Microanalyses were performed with a Perkin–Elmer 240C element analyzer. The purification and isolation of photoproducts were performed on a Kusano C.I.G. prepacked-column (silica-gel: grain size; 10 μm, 22 mm×100 mm glass column) equipped with a Shimadzu RID-2 detector. Gas chromatography analyses were performed on a Shimadzu GC-14A using a capillary column (OV-1, 0.24 mm×25 m).

Spectroscopic-grade hexane was washed with concn H_2SO_4, distilled, and stored over molecular sieves 4A. Spectroscopic-grade acetonitrile and the commercial acetone were stored over molecular sieves 4A. Commercial benzophenone and 2-benzoylpyridine were recrystallized twice from benzene/hexane. Commercial xanthone was recrystallized twice from 95% ethanol. The commercial acetophenone was distilled. Commercial Yb(fod)$_3$ was dried under reduced pressure at 60 °C. Aluminum selenide was purchased from Soekawa Rikagaku, Ltd.

Methyl *cis*- and *trans*-(2-isobutenyl-3,3-dimethylcyclopropyl)-acetates **11a** and **12a** were prepared according to the published procedure using chrysanthemic acid.[13]

General Procedure for 2a—c: The $TiCl_4$ method described by Lehnert was used.[10] A solution of $TiCl_4$ (25 cm^3, 0.21 mol) in CCl_4 (60 cm^3) was added dropwise under N_2 to dry THF (200 cm^3) with stirring and cooling at −10 °C. To the $TiCl_4$/THF suspension was added a solution of the allenic aldehyde[5] (0.1 mol) and dimethyl malonate (13.2 g, 0.1 mol) in THF (60 cm^3), and further, a mixture of pyridine (32 cm^3, 0.4 mol) and THF (60 cm^3) was added dropwise over 30 min. The mixture was stirred for 48 h at room temperature and then quenched with water (100 cm^3) and ether (100 cm^3). The layers were separated and the aqueous layer was extracted with ether (100 cm^3). The combined organic fractions were washed with sat. $NaHCO_3$, brine, and water, and dried over $MgSO_4$. After evaporation of the solvent, residue oil was distilled under reduced pressure to give the esters.

1,1-Bis(methoxycarbonyl)-3,3-dimethyl-1,4,5-hexatriene (2a): Yield 52%; colorless crystals; mp 45—46 °C (pentane); bp 90—95 °C (2.0 Torr; 1 Torr = 133.322 Pa); IR (KBr) 1956 (C=C=C), 1723 (ester), and 1645 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.24 (6H, s, 3-Me×2), 3.78 (3H, s, COOMe), 3.82 (3H, s, COOMe), 4.82 (2H, d, J = 6.6 Hz, H_2C=C=C), 5.17 (1H, dd, J = 5.8 and 7.0 Hz, HC=C=C), and 6.91 (1H, s, CH=C); ^{13}C NMR ($CDCl_3$) δ = 27.5 (2C, q, 3-Me), 37.0 (s, 3-C), 52,0 (q, OMe), 52.3 (q, OMe), 77.8 (t, 6-C), 97.3 (d, 4-C), 125.0 (s, 1-C), 153.2 (d, 2-C), 164.4 (s, CO), 166.5 (s, CO), and 207.0 (s, 5-C); MS *m/z* (rel intensity) 224 (M$^+$; 12), 165 (100), 164 (29), 161 (79), 160 (53), 133 (45), 105 (66), 91 (36), 78 (28), and 77 (30).

HRMS Found: *m/z* 224.1041. Calcd for $C_{12}H_{16}O_4$: M, 224.1049. Found: C, 64.01; H, 7.09%. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19%.

1,1-Bis(methoxycarbonyl)-3,3-dimethyl-1,4,5-heptatriene (2b): Yield 73%; colorless oil; bp 95—100 °C (2.8 Torr); IR (neat) 1964 (C=C=C), 1737 (ester), and 1643 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.22 (6H, s, 3-Me×2), 1.67 (3H, dd, J = 3.5 and 6.6 Hz, MeC=C=C), 3.77 (3H, s, COOMe), 3.79 (3H, s, COOMe), 5.10 (1H, dq, J = 3.5 and 6.6 Hz, MeCH=C=C$\underline{H}$), 5.24 (1H, dq, J = 6.6 and 6.6 Hz, MeC$\underline{H}$=C=CH), and 6.91 (1H, s, CH=C); ^{13}C NMR ($CDCl_3$) δ = 14.1 (q, 7-C), 27.5 (q, 3-Me), 27.7 (q, 3-Me), 37.7 (s, 3-C), 52.1 (q, OMe), 52.4 (q, OMe), 88.9 (d, 6-C), 97.6 (d, 4-C), 125.6 (s, 1-C), 153.8 (d, 2-C), 164.6 (s, CO), 166.8 (s, CO), and 203.4 (s, 5-C); MS *m/z* (rel intensity) 238 (M$^+$; 22), 191 (69), 182 (45), 180 (11), 179 (87), 175 (76), 176 (66), 159 (47), 153 (100), 147 (32), 146 (41), 125 (30), 119 (76), 91 (40), 77 (37), 59 (60), 53 (44), 41 (55), and 39 (37).

HRMS Found: *m/z* 238.1214. Calcd for $C_{13}H_{18}O_4$: M, 238.1205.

1,1-Bis(methoxycarbonyl)-3,3,6-trimethyl-1,4,5-heptatriene (2c): Yield 62%; colorless oil; bp 95—100 °C (2.5 Torr); IR (neat) 1969 (C=C=C), 1737 (ester), and 1643 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.19 (6H, s, 3-Me×2), 1.70 (6H, d, J = 3.1 Hz, (Me)$_2$C=C=C), 3.77 (3H, s, COOMe), 3.80 (3H, s, COOMe), 5.00 (1H, septet, J = 3.1 Hz, CH=C=C), and 6.92 (CH=C); ^{13}C NMR ($CDCl_3$) δ = 20.3 (2C, q, 6-Me), 27.5 (2C, q, 3-Me), 38.2 (s, 3-C), 52.0 (q, OMe), 52.3 (q, OMe), 96.2 (d, 4-C), 98.5 (s, 6-C), 125.4 (s, 1-C), 154.6 (d, 2-C), 164.7 (s, CO), 166.8 (s, CO), and 200.3 (s, 5-C); MS *m/z* (rel intensity) 252 (M$^+$; 25), 193 (44), 189 (55), 188 (66), 182 (44), 173 (41), 160 (29), 153 (79), 133 (44), 122 (100), 67 (51), 59 (30), 41 (79), and 39 (33).

HRMS Found: *m/z* 252.1386. Calcd $C_{14}H_{20}O_4$: M, 252.1362.

General Procedure for the Monoesters 3a and 3b: Methyl diethoxyphosphorylacetate (0.08 mol), prepared from the reaction of triethyl phosphonate with methyl chloroacetate, was dissolved in DMF (100 cm^3). To the solution was added NaOMe (0.07 mol). The mixture was stirred for 30 min under argon at room temperature and then added to a solution of allenic aldehyde (0.07 mol) in DMF (50 cm^3). The reaction mixture was stirred for 2 d at room temperature, and the reaction was quenched by water (100 cm^3). The aqueous solution was extracted with hexane (50 cm^3×2). The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. The residue oil was distilled under reduced pressure to give the monoesters.

Methyl (*E*)-4,4-Dimethyl-2,5,6-heptatrienoate (3a): Yield 15%; colorless oil; bp 50—60 °C (3 Torr); IR (neat) 1955 (C=C=C), 1727 (COO), and 1653 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.19 (6H, s, 4-Me×2), 3.73 (3H, s, COOMe), 4.80 (2H, d, J = 6.6 Hz, 7-H×2), 5.04 (1H, t, J = 4.5 Hz, 5-H), 5.79 (1H, d, J = 15.8 Hz, =CH), and 6.96 (1H, d, J = 15.8 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ = 27.0 (2C, q, 4-Me), 36.9 (s, 4-C), 51.4 (q, OMe), 77.6 (t, 7-C), 98.1 (d, 5-C), 117.5 (d), 156.6 (d), 167.3 (s, COO), and 206.9 (s, 6-C); MS *m/z* (rel intensity) 166 (M$^+$; 7), 151 (22), 127 (34), 107 (100), 106 (22), 95 (47), 91 (75), 79 (27), 67 (56), and 65 (20).

HRMS Found: *m/z* 166.1000. Calcd $C_{10}H_{14}O_2$: M, 166.0994.

Methyl (*E*)-4,4,7-Trimethyl-2,5,6-octatrienoate (3b): Yield 68%; colorless oil; bp 60—70 °C (3 Torr); IR (neat) 1961 (C=C=C), 1727 (COO), and 1651 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.16 (6H, s, 4-Me×2), 1.69 (6H, d, J = 2.6 Hz, C=C=CMe$_2$), 3.73 (3H, s, COOMe), 4.92 (1H, septet, J = 2.6 Hz, 5-H), 5.78 (1H, d, J = 15.8 Hz, =CH), and 6.97 (1H, d, J = 15.8 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ = 20.6 (q, 2C, 7-Me), 27.1 (q, 2C, 4-Me), 37.9 (s, 4-C), 51.2 (q, OMe), 97.1 (d, 5-C), 98.0 (s, 7-C), 116.8 (d), 157.3 (d), 168.0 (s, COO), and 200.3 (s, 6-C); MS *m/z* (rel intensity) 194 (M$^+$; 3), 135 (100), 128 (26), 127 (19), 95 (31), 67 (48), and 41 (38).

HRMS Found: *m/z* 194.1309. Calcd for $C_{12}H_{18}O_2$: M, 194.1307.

Direct Photolysis of 2a—c in Hexane or Acetonitrile: The typical procedure for the direct photolysis of **2a** in hexane was as follows. A solution of **2a** (901 mg, 40 mmol) in hexane (400 cm^3) was irradiated for 73 h under argon by a 6-W low-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the photoproducts were separated by medium-pressure silica-gel chromatography equipped an RI detector eluting with 8% EtOAc–hexane to give 2,2-bis(methoxycarbonyl)-5,5-dimethyl-3-methylenebicyclo[2.1.0]pentane (**4a**: 493 mg, 55%) and 1,1-bis(methoxycarbonyl)-3,3-dimethyl-2-propadienylcyclopropane (**5**: 91 mg, 10%).

4a: Colorless oil; IR (neat) 1739 (ester) and 1680 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 0.97 (3H, s, *exo*-5-Me), 1.03 (3H, s, *endo*-5-Me), 2.29 (1H, d, *J* = 5.6 Hz, 1-CH), 2.31 (1H, d, *J* = 5.6 Hz, 4-CH), 3.76 (3H, s, COOMe), 3.79 (3H, s, COOMe), 4.95 (1H, s, =CH), and 5.17 (1H, s, =CH); ^{13}C NMR ($CDCl_3$) δ = 16.7 (q, 5-Me), 23.9 (q, 5-Me), 26.7 (s, 5-C), 31.3 (d), 36.6 (d), 52.2 (q, OMe), 53.0 (q, OMe), 58.5 (s, 2-C), 107.8 (t, =CH_2), 142.9 (s, 3-C), 169.4 (s, COO), and 170.0 (s, COO); MS *m/z* (rel intensity) 224 (M$^+$; 14), 192 (19), 165 (56), 165 (100), 164 (87), 160 (44), 137 (29), 79 (28), 77 (30), 59 (60), 41 (23), and 39 (29).

HRMS Found: *m/z* 224.1048. Calcd for $C_{12}H_{16}O_4$: M, 224.1049.

5: Colorless oil; IR (neat) 1955 (C=C=C) and 1733 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ = 1.24 (3H, s, 3-Me), 1.30 (3H, s, 3-Me), 2.36 (1H, ddd, *J* = 1,4, 1,4, and 8.8 Hz, 2-CH), 3.72 (3H, s, COOMe), 3.73 (3H, s, COOMe), 4,79 (1H, dd, *J* = 1.4 and 7.6 Hz), 4.80 (1H, dd, *J* = 1.4 and 6.0 Hz), and 5.10 (1H, ddd, *J* = 6.0, 7.2, and 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ = 17.9 (q, 3-Me), 22.7 (q, 3-Me), 31.6 (s, 3-C), 35.6 (d, 2-C), 42.9 (s, 1-C), 52.2 (q, OMe), 52.5 (q, OMe), 76.0 (t, $H_2\underline{C}$=C=C), 84.9 (d, H$\underline{C}$=C=C), 167.5 (s, COO), 169.0 (s, COO), and 210.8 (s, =C=); MS *m/z* (rel intensity) 224 (M$^+$; 6), 192 (21), 165 (100), 164 (64), 161 (31), 160 (36), 153 (23), 133 (42), 106 (20), 105 (80), 91 (44), 79 (29), 77 (36), 73 (30), 59 (57), 53 (20), 41 (30), and 39 (33).

HRMS Found: *m/z* 224.1075. Calcd for $C_{12}H_{16}O_4$: M, 224.1049.

The yields and irradiation time of the photoproducts on the direct photolyses of **2a—c** in hexane or acetonitrile are described in Table 1. Spectroscopic data and the physical property of the photoproducts from **2b**,**c** are as follows.

(*E*)-3-Ethylidene-2,2-bis(methoxycarbonyl)-5,5-dimethylbicyclo[2.1.0]pentane (4b-*E*): Colorless crystals; mp 63 °C (pentane); IR (neat) 1740 (ester) and 1640 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.04 (3H, s, *exo*-5-Me), 1.06 (3H, s, *endo*-5-Me), 1.61 (3H, d, *J* = 7.0 Hz, $\underline{Me}$CH=), 2.22 (1H, d, *J* = 5.3 Hz, 1-CH), 2.28 (1H, d, *J* = 5.3 Hz, 4-CH), 3.71 (3H, s, COOMe), 3.74 (3H, s, COOMe), and 5.51 (1H, q, *J* = 7.0 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ = 12.7 (q, $\underline{Me}$CH=), 16.7 (q, 5-Me), 24.0 (q, 5-Me), 26.4 (s, 5-C), 30.7 (d), 34.3 (d), 52.1 (q, OMe), 52.8 (q, OMe), 57.8 (s, 2-C), 118.6 (d, =CH), 134.2 (s, 3-C), 169.6 (s, COO), and 170.3 (s, COO); MS *m/z* (rel intensity) 238 (M$^+$; 7), 179 (75), 178 (72), 174 (21), 163 (18), 147 (65), 146 (42), 120 (28), 119 (100), 105 (34), 91 (36), 77 (27), 59 (77), 54 (58), and 44 (18).

HRMS Found: *m/z* 238.1214. Calcd for $C_{13}H_{18}O_4$: M, 238.1205. Found: C, 65.24; H, 7.58%. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61%.

(*Z*)-3-Ethylidene-2,2-bis(methoxycarbonyl)-5,5-dimethylbicyclo[2.1.0]pentane (4b-*Z*) Colorless oil; IR (neat) 1737 (ester) and 1645 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 0.99 (3H, s, *exo*-5-Me), 1.09 (3H, s, *endo*-5-Me), 1.72 (3H, d, *J* = 7.0 Hz, $\underline{Me}$CH=), 2.17 (1H, d, *J* = 5.3 Hz, 1-CH), 2.25 (1H, d, *J* = 5.3 Hz, 4-CH), 3.74 (3H, s, COOMe), 3.77 (3H, s, COOMe), and 5.32 (1H, q, *J* = 7.0 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ = 13.0 (q, $\underline{Me}$CH=), 16.7 (q, 5-Me), 23.9 (q, 5-Me), 26.1 (s, 5-C), 30.7 (d), 36.5 (d), 52.0 (q, OMe), 52.6 (q, OMe), 58.5 (s, 2-C), 118.9 (d, =CH), 133.8 (s, 3-C), 169.9 (s, CO), and 170.4 (s, CO); MS *m/z* (rel intensity) 238 (M$^+$; 3), 179 (61), 178 (68), 163 (22), 147 (50), 146 (34), 120 (27), 119 (100), 105 (34), 91 (33), 79 (17), 77 (27), 62 (61), 59 (46), 53 (57), and 45 (16).

HRMS Found: *m/z* 238.1198. Calcd for $C_{13}H_{18}O_4$: M, 238.1205.

3-Isopropylidene-2,2-bis(methoxycarbonyl)-5,5-dimethylbicyclo[2.1.0]pentane (4c): Colorless oil; IR (neat) 1737 (ester) and 1640 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 1.01 (3H, s, *exo*-5-Me), 1.06 (3H, s, *endo*-5-Me), 1.59 (3H, s, *E*-Me), 1.73 (3H, s, *Z*-Me), 2.07 (1H, d, *J* = 5.3 Hz, 1-CH), 2.22 (1H, d, *J* = 5.3 Hz, 4-CH), 3.71 (3H, s, COOMe), and 3.74 (3H, s, COOMe); ^{13}C NMR ($CDCl_3$) δ = 16.7 (q, 5-Me), 19.0 (q, $\underline{Me}$C=), 19.3 (q, $\underline{Me}$C=), 24.0 (q, 5-Me), 26.0 (s, 5-C), 30.7 (d), 35.3 (d), 51.9 (q, OMe), 52.5 (q, OMe), 58.1 (s, 2-C), 126.6 (s), 127.1 (s), 170.4 (s, CO), and 170.8 (s, CO); MS *m/z* (rel intensity) 252 (M$^+$; 5), 193 (58), 192 (26), 177 (27), 173 (20), 161 (73), 160 (59), 134 (20), 133 (100), 119 (24), 117 (22), 105 (22), 91 (34), 73 (48), 59 (22), and 41 (32).

HRMS Found: *m/z* 252.1349. Calcd for $C_{14}H_{20}O_4$: M, 252.1362.

Stereochemistry of 4b-*E* and 4b-*Z*: The LIS was determined by a stepwise addition of Yb(fod)$_3$ to a solution of the adduct (ca. 35 mg) in $CDCl_3$ (0.30 cm^3). The LIS's of the protons of the adducts increased linearly with the molar ratio [Yb(fod)$_3$/adduct]. The ratio slopes are given in Table 6.

Acetone-Sensitized Photolysis of 2a—c: The typical procedure for the acetone-sensitized photolysis of **2a** was as follows. A solution of **2a** (899 mg, 4.00 mmol) in acetone (400 cm^3) was irradiated for 20 h under argon at room temperature by a 100-W high-pressure mercury lamp with a Pyrex jacket. After evaporation of the solvent, purification by medium-pressure silica-gel chromatography gave **4a** in 50% (451 mg) yield.

When an acetone solution (350 cm^3) of **2a** (787 mg, 3.51 mmol) was irradiated for 2.7 h using a 450-W high-pressure mercury lamp with a Pyrex jacket at room temperature under an argon atmosphere, **4a** was obtained in 17% (136 mg) yield: **2a** was consumed to over 99%. The spectral data for **4a** obtained here were identical with those measured from the direct irradiation of **2a**.

Analytical data for other products were also identical with those measured from the direct photolyses of **2b** and **2c** and the yields are shown in Table 1.

Direct Photolyses of 3a: A solution of **3a** (660 mg, 3.98 mmol) in hexane (400 cm^3) was irradiated for 15 h at room temperature under argon using a 6-W low-pressure mercury lamp with a quartz jacket. The reaction mixture was evaporated in vacuo and the residue oil was subjected to medium-pressure silica-gel chromatography (hexane/EtOAc: v/v 98 : 2). The first elution gave a mixture of *cis*- and *trans*-[2+2]adducts (480 mg, 72%) as a colorless oil. The isomers were further chromatographed using the same column under the cooling condition (0 °C) to isolate *cis*-2-methoxycarbonyl-5,5-dimethyl-2-methylenebicyclo[2.1.0]pentane (**6a-*c***) and its *trans*-isomer (**6a-*t***). Because the half-lifetime of the adduct **6a-*c*** at 30 °C has 225 min, those spectra were immediately measured.

6a-*c*: Colorless oil; IR (neat) 1737 (COO) and 1680 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ = 0.99 (3H, s, 5-Me), 1.05 (3H, s, 5-Me), 2.02 (1H, dd, *J* = 4.5 and 4.5 Hz, 1-CH), 2.17 (1H, br d, *J* = 4.5 Hz, 4-CH), 3.50—3.65 (1H, m, 2-CH), 3.68 (3H, s, COOMe), 4.84 (1H, d, *J* = 2.2 Hz, =CH), and 4.97 (1H, dd, *J* = 0.9 and 2.2 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ = 16.8 (q, 5-Me), 24.0 (s, 5-C), 25.7 (q, 5-Me), 28.1 (d, 1-C), 36.1 (d, 4-C), 44.0 (d, 2-C), 51.5 (q, OMe), 105.5 (t, $=CH_2$), 143.3 (s, 3-C), and 172.7 (s, CO).

6a-*t*: Colorless oil; IR (neat) 1738 (COO) and 1673 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ = 1.01 (3H, s, 5-Me), 1.16 (3H, s, 5-Me), 2.14 (1H, d, *J* = 4.9 Hz, 1-CH), 2.22 (1H, br d, *J* = 4.9 Hz, 4-CH), 3.08 (1H, dd, 2-CH, *J* = 1.8 and 1.8 Hz), 3.73 (3H, s, COOMe), 4.74 (1H, d, *J* = 2.2 Hz, =CH), and 4.78 (1H, br s, =CH); ^{13}C NMR (CDCl$_3$) δ = 15.6 (q, 5-Me), 23.7 (q, 5-Me), 26.1 (s, 5-C), 28.5 (d), 38.4 (d, 1-C), 45.1 (d, 4-C), 52.0 (q, OMe), 104.0 (t, $=CH_2$), 143.6 (s, 3-C), and 172.8 (s, CO); MS *m*/*z* (rel intensity) 166 (M$^+$; 6), 151 (10), 123 (11), 119 (10), 107 (100), 106 (29), 105 (16), 92 (17), 91 (82), 79 (31), 77 (11), 65 (14), 65 (22), 59 (15), 41 (34), and 38 (17).

HRMS Found: *m*/*z* 166.0970. Calcd for $C_{10}H_{14}O_2$: M, 166.0994.

The second elution gave methyl (2-ethenylidene-3,3-dimethylcyclopropyl)acetate (**7**) in 10% (64 mg) yield: colorless oil; IR (neat) 2012 (C=C=C), and 1741 cm^{-1} (COO); ^{1}H NMR (CDCl$_3$) δ = 1.22 (3H, s, 3-Me), 1.29 (3H, s, 3-Me), 1.8—2.2 (1H, m, 2-CH), 2.51 (1H, d, *J* = 7.6 Hz), 2.55 (1H, d, *J* = 7.6 Hz), 3.70 (3H, s, COOMe), and 4.76 (2H, d, *J* = 4.1 Hz, $=CH_2$); ^{13}C NMR (CDCl$_3$) δ = 19.1 (q, 3-Me), 25.9 (q, 3-Me), 28.5 (d, 2-CH), 33.4 (t, CH$_2$), 36.2 (s, 3-C), 51.7 (q, OMe), 76.7 (t, $=CH_2$), 89.0 (s, 1-C), 172.9 (s, CO), and 192.5 (s, =C=); MS *m*/*z* (rel intensity) 166 (M$^+$; 6), 151 (9). 135 (7), 123 (13), 119 (11), 108 (12), 107 (100), 106 (30), 105 (19), 92 (19), 91 (90), 79 (31), 77 (14), 65 (15), 59 (14), 53 (8), 41 (16), and 38 (17).

HRMS Found: *m*/*z* 166.0970. Calcd for $C_{10}H_{14}O_2$: M, 166.0994.

Methyl (*Z*)-4,4-Dimethyl-2,5,6-heptatrienoate (8a): A solution of **3a** (667 mg, 4.02 mmol) in hexane (400 cm^3) was irradiated for 6 h under argon using a 6-W low-pressure mercury lamp: **3a** was consumed to 50%. After evaporation of the solvent, the residue oil was subjected to medium-pressure silica-gel chromatography. A first elution gave **8a** in 15% (50 mg) yield as a colorless oil: IR (neat) 1956 (C=C=C), 1730 (COO), and 1637 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ = 1.30 (6H, s, 4-Me×2), 3.71 (3H, s, COOMe), 4.77 (2H, d, *J* = 6.7 Hz, 7-H), 5.47 (1H, d, *J* = 6.6 Hz, 5-H), 5.69 (1H, d, *J* = 12.9 Hz, CH=), and 6.04 (1H, d, *J* = 12.9 Hz, CH=); ^{13}C NMR (CDCl$_3$) δ = 28.4 (q, 2C, 4-Me), 36.7 (s, 4-C), 51.3 (q, OMe), 77.3 (t, 7-C), 99.2 (d, 5-C), 119.1 (d, 3-C), 152.2 (d, 2-C), 167.0 (s, CO), and 206.6 (s, 6-C); MS *m*/*z* (rel intensity) 166 (M$^+$; 5), 151 (50). 138 (14), 135 (17), 124 (22), 123 (15), 119 (12), 108 (13), 107 (100), 106 (17), 105 (20), 95 (43), 92 (20), 91 (90), 79 (35), 77 (15), 67 (44), 65 (22), 59 (18), 55 (11), 53 (17), 51 (11), 41 (33), and 38 (31).

HRMS Found: *m*/*z* 166.0986. Calcd for $C_{10}H_{14}O_2$: M, 166.0994.

A second elution gave a mixture of **3a** and **6a** (439 mg, **3a** : **6a** = 68 : 32). Further elution gave a mixture of **3a** and **7** (42 mg, **3a** : **7** = 78 : 22).

Photolysis of Methyl (*Z*)-4,4-Dimethyl-2,5,6-heptatrienoate in Methanol-d_1: A methanol-d_1 solution (1 cm^3) of **8a** (3.32 mg, 0.02 mmol) in a quartz NMR tube was degassed with argon and then irradiated for 24 h by a 6-W low-pressure mercury lamp through a quartz filter. The reaction mixture was analyzed by GCMS. No deuterations of **3a**, **6a**, and **8a** were detectable. The ion ratio of *m*/*z* 166 (M$^+$) and 167 (monodeuterated species) for **7** was 21 : 79. By the mass table analysis, deuterium was incorporated at the α-position of **7**.

Direct Photolysis of 3b: A solution of **3b** (780 mg, 4.03 mmol) in hexane (400 cm^3) was irradiated for 14 h under an argon atmosphere at room temperature using a 6-W low-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the residue oil was subjected to medium-pressure silica-gel chromatography using hexane–EtOAc (v/v, 98 : 2) as an eluent to give a mixture of *cis*- and *trans*-3-isopropylidene-2-methoxycarbonyl-5,5-dimethylbicyclo[2.1.0]pentane (**6b**) in 74% (580 mg, *cis* : *trans* = 18 : 82) yield: Colorless oil, IR (neat) 1737 (COO), and 1650 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ = 0.97 (0.54H, s, *cis*-5-Me), 0.99 (2.46H, s, *trans*-5-Me), 1.05 (0.56H, s, *cis*-5-Me), 1.08 (2.46H, s, *trans*-5-Me), 1.54 (2.46H, br s, *trans*-=-Me), 1.58 (2.46H, br s, *trans*-=-Me), 1.61 (0.54H, d, *J* = 1.8 Hz, *cis*-=-Me), 1.71 (0.54H, br s, *cis*-=-Me), 1.78 (0.82H, d, *J* = 5.3 Hz, *trans*-1-CH), 1.89 (0.18 H, dd, 4.9 and 4.9 Hz, *cis*-4-CH), 2.17 (0.82H, d, *J* = 5.3 Hz, *trans*-4-CH), 3.07 (0.82H, br s, *trans*-2-CH), 3.45—3.55 (0.18H, m, *cis*-2-CH), 3.68 (0.56H, s, *cis*-COOMe), and 3.71 (2.46H, s, *trans*-COOMe); ^{13}C NMR (CDCl$_3$) δ = 15.5 (q, *trans*-Me), 16.8 (q, *cis*-Me), 18.4 (q, *trans*-Me), 18.5 (q, *trans*-Me), 18.8 (q, *cis*-Me), 19.2 (q, *cis*-Me), 23.7 (q, *trans*-Me), 24.2 (q, *cis*-Me), 25.3 (s, *trans*-5-C), 26.2 (d, *trans*-1-C), 26.3 (s, *cis*-5-C), 27.0 (d, *cis*-1-C), 34.9 (d, *cis*-4-C), 36.0 (d, *trans*-4-C), 42.8 (d, *cis*-2-C), 43.9 (d, *trans*-2-C), 51.3 (q, *cis*-OMe), 51.5 (q, *trans*-OMe), 123.2 (s), 123.9 (s), 127.4 (s), 173.7 (s, *cis*-CO), 173.8 (s, *trans*-CO); MS *m*/*z* (rel intensity) 194 (M$^+$; 6), 147 (11), 136 (20), 135 (100), 120 (19), 119 (56), 105 (15), 91 (19), and 41 (12).

HRMS Found: *m*/*z* 194.1338. Calcd for $C_{12}H_{18}O_2$: M, 194.1307.

Methyl (*Z*)-4,4,7-Trimethyl-2,5,6-octatrienoate (8b): A solution of **3b** (788 mg, 4.06 mmol) in hexane (400 cm^3) was irradiated for 14.5 h under oxygen using a 6-W low pressure mercury lamp with a quartz jacket and **3b** was consumed to 47%. After evaporation of the solvent, the residue oil was subjected to medium-pressure silica-gel chromatography. The first elution gave **8b** in 2% (7 mg) yield as a colorless oil: IR (neat) 1967 (C=C=C), 1730 (COO), and 1636 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ = 1.26 (6H, s, 4-Me×2), 1.65 (6H, d, *J* = 4.0 Hz, 3-Me×2), 3.71 (3H, s, COOMe), 5.22 (1H, septet, *J* = 4.0 Hz, 5-H), 5.67 (1H, d, *J* = 12.8 Hz, CH=), and 6.04 (1H, d, *J* = 12.8 Hz, CH=); MS *m*/*z* (rel intensity) 194 (M$^+$; 11), 179 (21), 163 (13), 151 (22), 147 (20), 136 (15), 135 (91), 128 (12), 127 (17), 125 (13), 124 (97), 123 (16), 120 (19), 119 (59), 103 (14), 105 (25), 96 (15), 95 (100), 93 (22), 91 (23), 79 (15), 77 (16), 67 (67), 65 (13), 59 (15), 55 (12), 53 (13), 43 (17), 41 (52), 39 (20), and 32 (34).

HRMS Found: *m*/*z* 194.1341. Calcd for $C_{12}H_{18}O_2$: M, 194.1307.

The next elution gave a mixture of **3b** and **6b** (394 mg, **3b** : **6b** = 53 : 47).

Measurements of Quantum Yields: The quantum yields for the isomerization of **2a—c** or **3a,b** to the photoproducts were measured by GLC analyses and the photolyses were carried out by a merry-go-round method. A 6-W low pressure mercury lamp with a quartz-glass filter was used as a 254 nm radiation source. Argon or oxygen was bubbled into an acetonitrile or hexane solution (10 cm^3) of **2a—c** or **3a,b** (0.01 mol dm^{-3}) in a quartz tube. The solution was irradiated at room temperature. The light intensity was determined by tris(oxalato)ferrate(III) actinometry.[5]

For the quantum yields of the sensitized photolyses, 450-W high-pressure mercury lamp through a combination of a K_2CrO_4 solution and a Pyrex filter was used as a 313 nm irradiation source. A solution (10 cm^3) of **2a—c** or **3a,b** in hexane or acetonitrile were irradiated by a merry-go-round method. The light intensity was determined by stilbene actinometry.[5] These quantum yields are described in Tables 2 and 3.

Measurements of the *cis*- and *trans*-Stereoisomer Ratio of the

[2+2] Cycloadducts: In the case of direct photolyses, an acetonitrile-d_3 solution (1 cm^3) of the esters **3a**,**b**, or **8a** (ca. 10 mg) in a quartz NMR tube was degassed with argon and then irradiated for 1 h at room temperature using a 6-W low-pressure mercury lamp through a quartz jacket. On the other hand, an acetonitrile-d_3 solution (1 cm^3) of the mixture of the esters **3a**,**b**, or **8a** (ca. 10 mg) and xanthone (10 mg) in a Pyrex NMR tube was degassed with argon and then irradiated for 10 min at room temperature using a 100-W high-pressure mercury lamp through a Pyrex jacket. After irradiation, the ratio of the resulting [2+2] cycloadducts was immediately determined by ^{1}H NMR. The ratios of **6b-*c*** and **6b-*t*** are described in Table 4.

An acetonitrile-d_3 solution (1 cm^3) of **3b** (9.4 mg) in a quartz NMR tube was degassed with argon and then irradiated for 4 h at 0 °C using a 6-W low-pressure mercury lamp through a quartz filter. The ester **3b** was consumed to over 95%. A half portion was transferred to a Pyrex NMR tube in the presence of xanthone (4.8 mg). The mixture was degassed with argon and then irradiated for 10 min at 0 °C using a 100-W high-pressure mercury lamp through a Pyrex filter. The residual half portion was allowed to stand for 6 h at 0 °C and, further, for 7 d at room temperature. The changes in the ratio of **6b-*t*** and **6b-*c*** are described in Table 5.

Photolyses of 3b in the Presence of Hydrogen Selenide: Hydrogen selenide (**TOXIC**)$^{11)}$ prepared by the addition of water to aluminum selenide (27 mg) was introduced into toluene (0.5 cm^3). The hydrogen selenide–toluene solution (ca. 0.53 M) was added to a mixture of **3b** (5.2 mg) and heptadecane in quartz NMR tube at -78 °C. The solution was irradiated for 30 min at 0 °C using a 100-W high-pressure mercury lamp through a quartz filter. Selenium in this reaction was deposited around the inside of the quartz NMR tube containing the solution. The monoester **3b** was consumed to 30% by GLC analysis of the reaction mixture. The [2+2] cycloadduct **6b** was afforded in 4.4% yield, and several photoproducts were produced. The photoproducts, **9a** and **10a**, were elucidated by GLC and GCMS in comparison with authentic samples. The ratio of three main photoproducts having a molecular weight of *m*/*z* 196 is **9a** : **10a** : unidentified product = 1 : 2.7 : 5.3. The MS table of the unidentified photoproduct is as follows: MS *m*/*z* (rel intensity) 196 (M$^+$; 6), 182 (10), 181 (76), 149 (20), 123 (22), 137 (9), 122 (34), 121 (100), 107 (51), 105 (11), 93 (14), 91 (13), 81 (9), 78 (13), 40 (16).

Hydrogen selenide (**TOXIC**),$^{11)}$ prepared by the addition of water to aluminum selenide (54 mg), was introduced into toluene (1.0 cm^3). The hydrogen selenide–toluene (ca. 0.53 M) solution was added to a mixture of **3b** (9.4 mg), xanthone (4.3 mg) and heptadecane in a Pyrex NMR tube at -78 °C. The solution was irradiated for 30 min at 0 °C using a 100-W high-pressure mercury lamp through a quartz filter. The formation of the cyclopentenes **9a**, **10a**, and the unidentified photoproduct was confirmed by GLC and GCMS; the ratio of these photoproducts was 1 : 1.8 : 1.8.

Hydrogenation of the Bicyclo[2.1.0]pentane 6b: The adduct **6b** (335 mg, 1.72 mmol) and Pd/C (5%, 50 mg) was dissolved in methanol (25 cm^3). The mixture was vigorously stirred under a hydrogen atmosphere for 1 h and then filtered. The mother liquor was evaporated in vacuo. The residue oil was examined by medium-pressure silica-gel chromatography using 2% EtOAc/hexane as an eluent. From the first elution, 2-isopropyl-5-methoxycarbonyl-3,3-dimethyl-1-cyclopentene (**10a**) was obtained in 13% (44 mg) yield. The next elution gave 1-methoxycarbonyl-2-isopropylidene-4,4-dimethylcyclopentane (**9a**) in 31% (105 mg) yield. The spectroscopic data for **9a** were identical with those in the literature.$^{29)}$

10a: Colorless oil, IR (neat) 1740 cm^{-1} (COO); ^{1}H NMR (CDCl$_3$) δ = 0.98 (3H, d, J = 7.0 Hz), 1.02 (3H, s, 4-Me), 1.06 (3H, d, J = 7.0 Hz), 1.14 (3H, s, 4-Me), 1.95 (2H, d, J = 7.5 Hz, 5-CH$_2$), 2.10—2.50 (1H, m, CH), 3.50—3.80 (1H, m, 1-CH), 3.68 (3H, s, OMe), and 5.30 (1H, dd, J = 1.7 and 1.7 Hz, =CH); ^{13}C NMR (CDCl$_3$) δ = 21.1 (q), 21.8 (q), 28.0 (d, CH), 28.9 (q), 29.0 (q), 43.4 (t, 5-C), 44.2 (s, 4-C), 51.2 (d, 1-C), 51.7 (q, OMe), 135.9 (d, 3-C), 145.5 (s, 2-C), and 176.0 (s, C=O); MS *m*/*z* (rel intensity) 196 (M$^+$; 21), 181 (39), 137 (43), 136 (11), 122 (11), 121 (100), 107 (9), 95 (18), 93 (13), 91 (8), and 79 (10).

HRMS Found: *m*/*z* 196.1469. Calcd for $C_{12}H_{20}O_2$: M, 196.1462.

MO Calculation. MO calculation was performed using RHF PM3 method of Mac Spartan Plus of Wavefunction, Inc.

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