Bull. Chem. Soc. Jpn., ***68***, *3175—3188(1995)*

Allenyl(vinyl)methane Photochemistry. Photochemistry of 5-[2-(1,2-Propadienyl)-Substituted Alkylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones

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(Received May 29, 1995)

The Photochemistry of 5-[2-(1,2-propadienyl)-substituted alkylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones has been studied. These acylals formed an intramolecular charge-transfer (CT) complex between the 1, 2-propadienyl and vinyl moieties in acetonitrile and in hexane, the direct photolyses of which gave (1-alkenylidene)cyclopropanes as the main products, and the intramolecular [2+2] cycloadducts, 3-alkylidene-2′,2′,5,5-tetramethylspiro[bicyclo[2.1.0]pentane-2,5′-[1,3]dioxane]-4′,6′-diones as minor products. The (1-alkenylidene)cyclopropanes were produced from the enol intermediate via a preferred 1,5-hydrogen transfer of a diradical, which was formed via an intramolecular CT excited state. On the other hand, the acetone-sensitized photolyses afforded mainly the intramolecular [2+2] cycloadducts. It is considered that the lowest triplet energies of these acylals in acetonitrile were estimated to lie in the range of 250—290 kJ mol^{-1}, and that these energies were near to the values of the reported triplet energies of α,β-unsaturated esters, because the allene underwent a [2+2] cycloaddition to the triplet vinyl moiety, excited by triplet sensitization.

The photochemistry of bichromophoric molecules connected by a saturated paraffinic moiety has been extensively studied. In particular, the photochemistry of divinylmethane compounds is well-known to give vinylcyclopropanes by a di-π-methane rearrangement.[1)] A number of papers have been published with the intention of relating this photochemistry to substituent effects.[1)] As interesting examples in their reports, the direct and sensitized photolyses of divinylmethane compounds possessing electron-withdrawing group(s), such as cyano or alkoxycarbonyl at the geminal position to give different regioisomeric vinylcyclopropanes, have been reported.[1—4)] Zimmerman et al. elegantly explained this regioisomeric di-π-methane rearrangement by multiplicity control, and performed MO calculations of the divinylmethanes and the photochemical diradical intermediates.[2a,3,4c)]

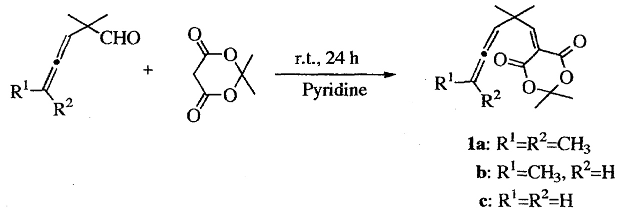
On the other hand, the irradiation of some terminal allenes linked to cycloalkenones[5,6)] or *endo*-α,β-unsaturated γ-lactones[7)] by hydrocarbon chains affords intramolecular [2+2] cycloadducts; parts of these reactions have been utilized for the syntheses of polycyclic compounds.[5,6)] Concerning the photochemistry of allenyl(vinyl)methanes, there have been few reports,[8—11)] except for our previous communications.[12—14)] These allenyl(vinyl)methanes undergo intramolecular [2+2] cycloaddition, mainly to afford bicyclo[2.1.0]pentanes.[8—10)]

We have noted the photochemistry of allenyl(vinyl)methanes possessing electron-withdrawing groups.[12—14)] It is known that methylene Meldrum's acids derived from Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione)[15)] bearing an electron-withdrawing group are strong electron-deficient alkenes.[15—17)] Leitich et al. have reported that several methylene Meldrum's acids underwent an intramolecular [2+2] cycloaddition to a terminal alkene or intermolecular [2+2] cycloaddition to cyclohexane to afford the cyclobutanes,[16d,18)] though the detailed mechanisms for these reactions have not been well clarified.

We have found that newly prepared allenyl(vinyl)methanes, isopropylidene 3,3,6-trimethyl-1,4,5-heptatriene-1,1-dicarboxylate (**1a**) and its derivatives (**1b** and **1c**), form an intramolecular CT complex between the allene moiety and the methylene Meldrum's acid. Therefore, **1a**—**c** are expected to undergo interesting photoreactions by such a CT interaction; we have thus studied their photochemistry.

Results and Discussion

Preparation of 1a—c. Allenic aldehydes were readily obtained by the reaction of alkynic alcohol with isobutylaldehyde in the presence of *p*-toluenesulfonic acid according to the published procedures.[19)] The starting materials **1a**—**c** were obtained by a Knoevenagel condensation of Meldrum's acid with the corresponding allenic aldehydes using pyridine as a base catalyst (Scheme 1).



Scheme 1.

UV-Absorption Spectra and Emission Spectra of 1a—c. The UV-absorption spectra of **1a**—**c** in acetonitrile and in hexane are shown in Figs. 1 and 2, respectively. The acylals **1a**—**c** in both solvents exhibit absorption maxima at ca. 220 nm, which are in agreement with that of 2,2-dimethylpropylidene Meldrum's acid (**2**); however, second shoulder absorptions are observed in a range of 250—320 nm and show bathochromic shifts in the order **1a**>**1b**>**1c**. Alkyl-substituted allenes show a shoulder absorption in a range of 200—250 nm and have an absorption maximum in a far-UV range;[20—22] therefore, the second absorptions of **1a**—**c** indicate the formation of an intramolecular CT complex between the allene moiety and the methylene Meldrum's acid. The ionization potential (IP) of 1,2-propadiene (allene) by molecular orbital (MO) calculations in several earlier reports lies in the range of 10.02 to 10.17 eV,[21,23] but alkyl-substituted allenes have lower IPs than 1,2-propadiene.[22,23] We then performed a RHF-PM3 MO calculation of 2,5,5-trimethyl-2,3-hexadiene (**3**), 5,5-dimethyl-2,3-hexadiene (**4**), and 4,4-dimethyl-1,2-pentadiene (**5**) as model constructions of the allene chromophores in **1a**—**c**. The IPs of **3**—**5** were obtained as 9.46, 9.74, and 9.81 eV, respectively. The calculated values are slightly higher than the IPs of alkenes, such as 2,3-dimethyl-2-butene (8.3 eV)[24] and cyclohexane (8.95 eV),[24,25] which are good electron donors.[26] Therefore, the formation of the CT complexes of the allenes **3**—**5** with methylene Meldrum's acids is expected. It is considered that, in the structure of **1a**—**c**, since the C=C bond at the δ- and ε-positions in the allene forms predominantly a CT complex with the methylene Meldrum's acid, a π_{alk}-orbital of the terminal methyl group(s) linked to the allene undergoes hyperconjugation to π-orbitals at the δ- and ε-positions.[20a] Therefore, the degree of bathochromic shifts observed corresponds to the number of electron-donating methyl groups linked to the allene. Moreover, the second absorptions of **1a**—**c** in hexane (Fig. 2) appear at a somewhat shorter wavelength region than those in acetonitrile. Generally, the distance for a single electron transfer (SET) from the donor to the acceptor molecules requires a geometry of ca. 7 Å, and the geometry of the resulting contact ion pair has a distance of 3—4 Å.[27] In **1a**, the distance between the β- and δ-carbons in the two chromophores linked by one methylene chain was calculated to be 2.472 Å by the PM3 MO method. This distance and the structure of **1a**—**c** enable the formation of a preferential intramolecular CT complex in the solvents.[28]

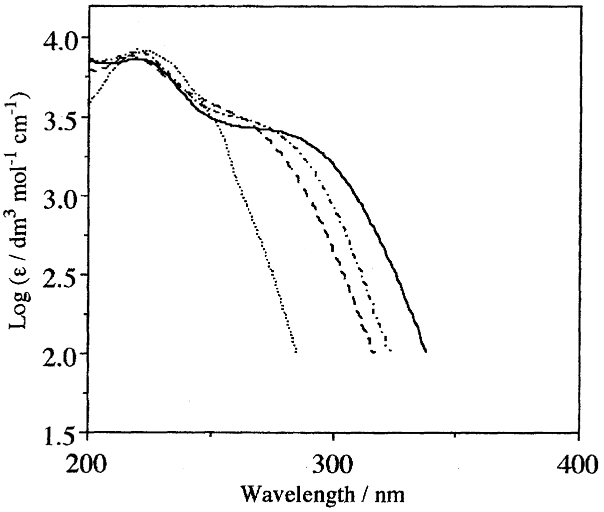


Fig. 1. UV-absorption spectra of **1a** (—), **1b** (–•–), **1c** (---), and **2** (••••) in acetonitrile.

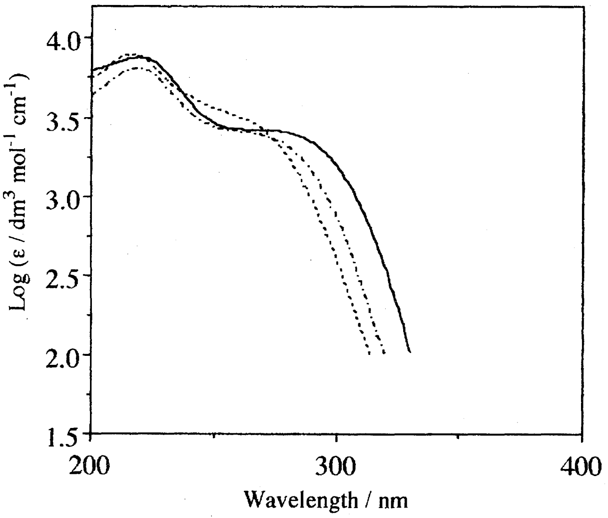


Fig. 2. UV-absorption spectra of **1a** (—), **1b** (–•–), and **1c** (---) in hexane.

The methylene Meldrum's acid, the acceptor chromophore, is nonfluorescent presumably because of an extremely rapid radiationless relaxation under concomitant rotation about the C=C bond, such as the *E*-*Z* geometrical isomerization, in the excited state reached upon local excitation (LE).[29,30] However, the CT absorption excitation (300 nm) of **1a**—**c** in acetonitrile leads to weak broad fluorescence emissions (Fig. 3). These emissions correspond to the CT absorption; their maxima show shifting in the order **1c**<**1b**<**1a**, while the excitation at shorter wavelengths (LE excitation) is less efficient. Consequently, the rapid radiationless deactivation in the LE excited state competes effectively with an internal conversion to the CT excited state.

Phosphorescence emissions of **1a**—**c** in EPA (ether–isopentane–ethanol, 5:2:2, v/v) at 77 K were not

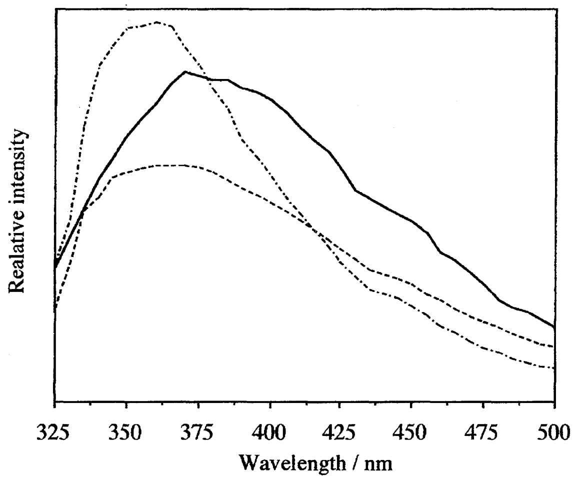
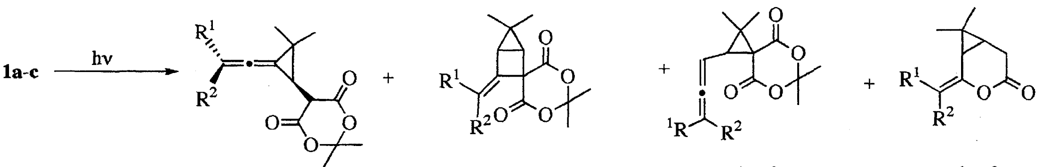


Fig. 3. Emission spectra of **1a** (0.48 mmol dm^{-3}, —), **1b** (1.05 mmol dm^{-3}, – • –), and **1c** (0.74 mmol dm^{-3}, - - -) in acetonitrile excited at 300 nm.

found.

Photochemistry of 1a—c. The direct photolyses of **1a**—**c** (0.01 mol dm^{-3}) in acetonitrile (400 cm^3) using a 6-W low-pressure mercury lamp with a quartz jacket under an argon atmosphere gave (1-alkenylidene)cyclopropane **6**—**9** as the main products and intramolecular [2+2] cycloadducts **10**—**13** as minor products (Scheme 2). Furthermore, in the direct photolysis of **1c**, the 1,2-propadienylcyclopropane **14** was obtained as another minor product. These photoproducts were separated by a medium-pressure silica-gel chromatograph equipped with an RI detector, except for the isolation of the (1-propenylidene)cyclopropanes **7** and **8**. The yields of these photoproducts are described in Table 1.

Because the low-pressure mercury lamp generates mainly 254 nm light, both the CT and local excitation (LE) absorption bands are initially excited by this light. We then examined the photolysis of **1a** by direct CT excitation. The combination of a 100-W high-pressure mercury lamp and a Pyrex filter is convenient for an examination of this CT excitation photochemistry, and generates light above 280 nm. The photolysis (> 280 nm) of **1a** (0.01 mol dm^{-3}) in acetonitrile (50 cm^3) gave **6** in better yield (Table 1) than in the 254 nm radiation condition. Furthermore, in the case of the photolysis (> 280 nm) of **1a** in hexane, it was found that **6** begins to deposit in the solution after about 10 min. After 8 h, the reaction mixture afforded **6** (27%) and **10** (7%); also, a δ-lactone **15** was further obtained (10%). In addition, the formation of several unidentified decomposed products in the reaction mixture was monitored by GLC.



6: $R^1=R^2=CH_3$
7: $R^1=CH_3$, $R^2=H$
8: $R^1=H$, $R^2=CH_3$
9: $R^1=R^2=H$

10: $R^1=R^2=CH_3$
11: $R^1=CH_3$, $R^2=H$
12: $R^1=H$, $R^2=CH_3$
13: $R^1=R^2=H$

14: $R^1=R^2=H$

15: $R^1=R^2=CH_3$

Scheme 2.

Table 1. Direct and Acetone-Sensitized Photolyses of **1a**—**c**$^{a)}$

Substrate	Solvent	Irradiation time/h	Products (Yield/%)$^{b)}$					
1a	Acetonitrile	48$^{c)}$	**6**	(28)	**10**	(17)		
	Acetonitrile	8$^{d)}$		(39)		(5)		
	Hexane	8$^{d)}$		(27)		(7)	**15**	(10)
	Acetone	1.3$^{e)}$		(3)		(53)		
1b	Acetonitrile	48$^{c)}$	**7+8**	(23)$^{f)}$	**11+12**	(3)$^{g)}$		
	Acetone	3$^{e)}$				(37)$^{h)}$		
1c	Acetonitrile	46$^{c)}$	**9**	(23)	**13**	(3)	**14**	(3)
	Acetone	7.5$^{e)}$				(46)		

a) All photolyses were carried out at room temperature under argon. b) Photoproducts were isolated by medium-pressure silica-gel chromatography equipped with an RI detector or by preparative TLC. c) An acetonitrile (400 cm^3) solution of **1a**—**c** (0.01 mol dm^{-3}) was irradiated using a 6-W low-pressure mercury lamp with a quartz jacket. d) A hexane or an acetonitrile solution (50 cm^3) of **1a** (0.01 mol dm^{-3}) in a Pyrex tube was irradiated using a 100-W high-pressure mercury lamp through a Pyrex jacket. e) An acetone solution (400 cm^3) of **1a**—**c** (0.01 mol dm^{-3}) was irradiated using a 100-W high-pressure mercury lamp with a Pyrex jacket. f) *cis*: *trans*=45 : 55. g) *E*-From : *Z*-from=1 : 1. h) *E*-From : *Z*-from=57 : 43.

Next, a solution of **1a**—**c** (0.01 mol cm^{-3}) in acetone (400 cm^3) was irradiated using a 100-W high-pressure mercury lamp with a Pyrex jacket under an argon atmosphere. The intramolecular [2+2] cycloaddition proceeded mainly in these photolyses to give **10**—**13** (Table 1). The isolation of **11** and **12** in the above direct photolysis of **1b** was carried out using medium-pressure silica-gel chromatography. However, because it was found that the *Z*-form **12** sublimated at 120 °C in a measurement of the melting point, the purification of **12** could be performed readily using a sublimation apparatus.

The quantum yields for the formation of (1-alkenylidene)cyclopropanes in direct photolyses are described in Table 2. For the quantum-yields determination, photolyses were performed up to 15% conversion of **1a**—**c**, and the reaction mixtures were analyzed by NMR; therefore, the quantum yields for the formation of minor products could not be determined. The quantum yields for the formation of [2+2] cycloadducts in the sensitized photolyses of **1a**—**c** are described in Table 3. Acetone and benzophenone are very effective in [2+2] cycloaddition. However, in the case of using 2-acetylnaphthalene, the sensitizing effect was hardly detectable ($\Phi<0.0001$).

Stereochemistry of Photoproducts. The structures of the photoproducts obtained in the reactions of **1a** and **1c** were readily established from spectroscopic data and microanalyses or HRMS.

The stereochemistry of the geometrical isomers in the photoproducts from **1b** was assigned based on the effects of adding a lanthanoid-induced shift (LIS) reagent [Yb(fod)$_3$] on the ^{1}H NMR spectra.

The relations between the chemical shift and mole ratio [Yb(fod)$_3$/adduct] of **11** and **12** are summarized in Figs. 4 and 5, respectively. The stereochemistry of **11** and **12** could be established unequivocally from the slope values of the methyl protons of the ethylidene moieties; i.e., **12** is the *Z*-form, the slope of which is much larger than that of *E*-from **11**.

Table 2. Quantum Yields for the Formation of Alkenylidenecyclopropanes on Direct Photolyses of **1a**—**c**$^{a,b)}$

Substrate	Solvent	Quantum yield
1		$\Phi_{alk}$$^{c)}$
1a	CH_3CN	0.12
	Hexane	0.11
1b	CH_3CN	0.10
	Hexane	0.13
1c	CH_3CN	0.056
	Hexane	0.071

a) A 6-W low-pressure mercury lamp with a quartz filter was used a 254 nm irradiation source and a solution (5 cm^3) of **1a**—**c** (0.01 mol dm^{-3}) in acetonitrile or hexane in quartz tube was irradiated. b) The light intensity was determined by tris(oxalato)ferrate(III) actinometry (Ref. 31). c) Quantum yields for the formation of (1-alkenylidene)cyclopropane **6**—**9**.

Table 3. Quantum Yields for the Formation of [2+2] Cycloadducts on the Sensitized Photolyses of **1a**—**c**$^{a)}$

Substrate	λ	Sensitizer	Quantum yield
1	nm		$\Phi_{add}$$^{b)}$
1a	313$^{c,d)}$	Acetone$^{e)}$	0.67
1b			0.33 (*E*), 0.32 (*Z*)
1c			0.24
1a	365$^{f,g)}$	Benzophenone$^{h)}$	0.57
1b			0.38 (*E*), 0.36 (*Z*)
1c			0.27

a) Quantum yields were determined by ^{1}H NMR analyses on the basis of a known amount of dimethyl malonate. b) Quantum yields for the formation of [2+2]-cycloadducts **10**—**13**. c) A 450-W high-pressure mercury lamp with a combination of a K_2CrO_4 solution and a Toshiba UV-D33S glass filter was used as a 313 nm irradiation source by a merry-go-round method. d) The light intensity was determined by stilbene actinometry (Ref. 31). e) A solution of **1a**—**c** (0.01 mol dm^{-3}) in acetone (10 cm^3) was fully degassed with argon and then irradiated. f) A 450-W high-pressure mercury lamp with a combination of a $CuSO_4$ solution and a Corning 7-37 glass filter was used as a 365 nm irradiation source. g) The light intensity was determined by potassium tris(oxalato)ferrate actinometry (Ref. 31). h) A solution of **1a**—**c** (0.01 mol dm^{-3}) and benzophenone (0.1 mol dm^{-3}) in acetonitrile was fully degassed with argon and then irradiated.

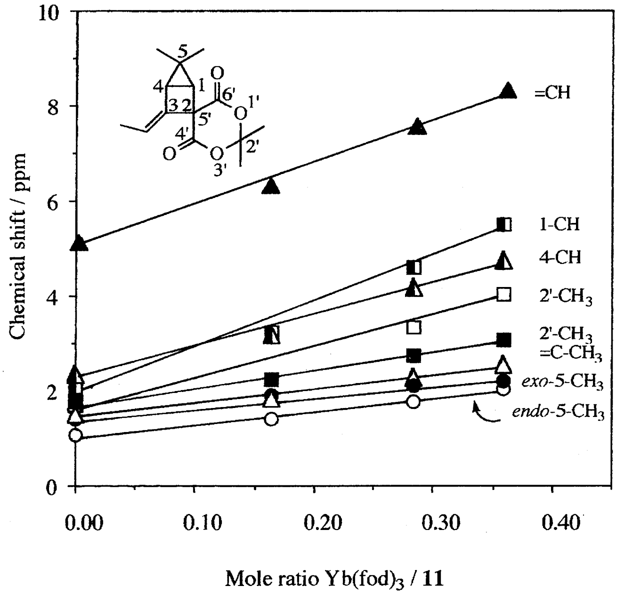


Fig. 4. Relationship between induced chemical shifts of the *E*-form **11** by Yb(fod)$_3$.

On the other hand, **7** and **8** could not be isolated; therefore, LIS measurements were performed in a mixture of these in $CDCl_3$. The shifts of the methine and methyl protons in **7** and **8**, except for the methyl protons in the 1-propadienylidene moiety, were not appreciably found. However, their stereochemistry could

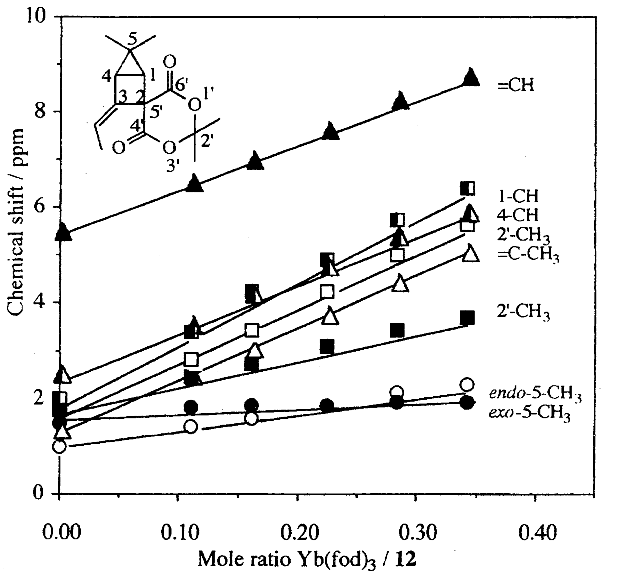


Fig. 5. Relationship between induced chemical shifts of the Z-form **12** by Yb(fod)$_3$.

be determined from the difference in the slopes of the methyl protons in the 1-propadienylidene moiety, i.e., the result of Fig. 6 suggests that the large value of the slope of methyl protons is the *cis*-form **8**, whereas the other is the *trans*-form **7**.

Photochemical Reaction Mechanisms. Reaction Pathway of (1-Alkenylidene)cyclopropane. It is well-known that the singlet excited state of carbonyl oxygen in α,β-unsaturated esters undergoes intramolecular hydrogen abstraction from the γ- or δ-alkyl hydrogen to produce β,γ-isomers or cyclopropylacetates.[32,33] The divinylmethanes, in which one vinyl is an α,β-unsaturated ester, also undergo intramolecular hydrogen abstraction to afford the cyclopropylacetates as minor products.[2b,2d,32j] Moreover, it has been reported that alkylidene Meldrum's acids also undergo a similar abstraction under direct photolyses.[16d,18] If the photochemical intramolecular hydrogen abstraction from the allenic δ-hydrogen in **1a**—**c** takes place, the formation of (1-alkenylidene)cyclopropanes **6**—**9** may be expected. Generally, because the *E–Z* geometrical isomerization of α,β-unsaturated esters occurs at a much faster rate than the hydrogen abstraction, the quantum yields for the isomerization of α,β-unsaturated esters to β,γ-isomers or cyclopropylacetates have been measured in the range of 0.005—0.031.[32h,32l] These quantum yields are too small compared with those for the formation of the (1-alkenylidene)cyclopropanes (Table 2). Although the intramolecular hydrogen abstraction from the olefinic γ-hydrogen by the excited carbonyl in several dienoic esters or acids is known,[33] in view of the relative bond energies of the C–H bonds, intramolecular hydrogen abstraction from the γ-methyl hydrogen (corresponds to δ-hydrogen) in **1a**—**c** seems to be preferable to that from the allenic δ-hydrogen. However, no formation of cyclopropyl acylals **16** via γ-methyl hydrogen abstraction was found in the direct photolyses of **1a**—**c**. Hence, the formation of (1-alkenylidene)cyclopropanes by allenic hydrogen abstraction is untenable. The results of excitation in both the CT and LE absorption bands by a low-pressure mercury lamp and excitation of the CT absorption band afford mainly the (1-alkenylidene)cyclopropanes. Hence, in addition to the emission spectra, there is the singlet CT excited state of **1a**—**c** at a lower level than the LE state. It is considered that the SET occurs from the HOMO of the allene moiety to the HOMO (SOMO) of the excited methylene Meldrum's acid. Furthermore, we calculated the 2,2-dimethylpropylidene Meldrum's acid (**2**) by the PM3 MO method. The relationships between the energy levels are summarized in Fig. 7. Because the HOMO level of **2** is lower than the HOMO levels of the allenes **3**—**5**, this indicates that the CT can be predominant. The proposed mechanism for the formation of (1-alkenylidene)cyclopropanes is shown in Scheme 3. The photoreaction is initiated by the intramolecular singlet CT excited state to yield the intramolecular contact ion pair (CIP), followed by produced 1,4-diradicals **17** and **18**. The *trans*-diradical **17** has a sterically preferential conformation which undergoes a 1,5-hydrogen shift, which affords the α-[2-(1-alkenylidene)]cyclopropyl enol **19** via an enol-type diradical, followed by a 1,3-hydrogen shift of **19**, which forms the (1-alkenylidene)cyclopropanes. The formation of **19** is expected to be deuterated at an α-position in the (1-alkenylidene)cyclopropanes, although the methine proton of alkyl-substituted Meldrum's acids acts as a Brønsted acid,[17b,17c] which can possibly exchange with deuterium, so that deuteration under irradiation in methanol-*d* was found; however, this result cannot

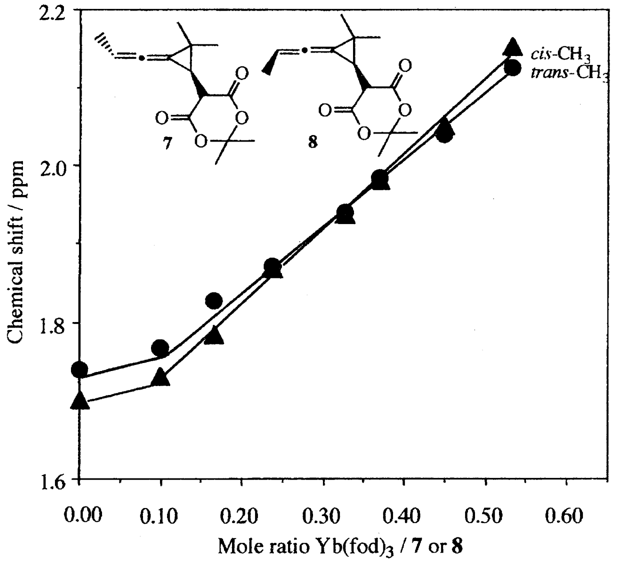
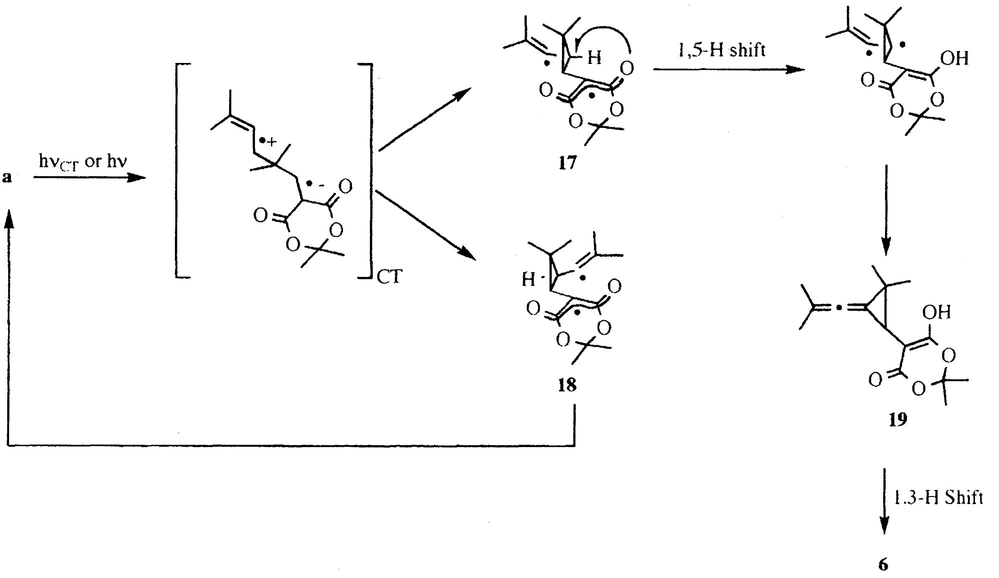


Fig. 6. Relationship between induced chemical shifts of methyl protons of 1-propadienyl moieties of **7** and **8** by Yb(fod)$_3$.



Scheme 3.

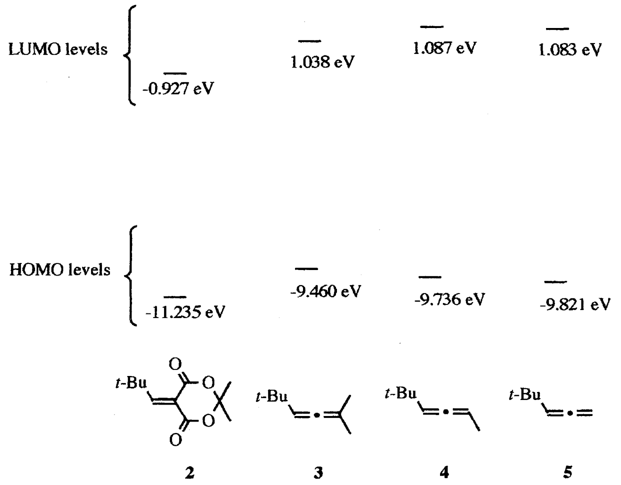


Fig. 7. Molecular orbital correlation diagrams of 2,2-dimethylpropylidene Meldrum's acid (**2**), 2,5,5-trimethyl-2,3-hexadiene (**3**), 5,5-dimethyl-2,3-hexadiene (**4**), and 4,4-dimethyl-1,2-pentadiene(**5**).

prove the presence of the enol intermediate.[34)] We then calculated the optimal structures of **17**, **18**, and **19** by the PM3 MO method, which are summarized in Fig. 8. Interestingly, the optimal structure of *trans*-diradical **17** is similar to that of the enol **19**. In addition, the heat of formation ($\Delta H = -480.3$ kJ mol^{-1}) of the optimal *trans*-diradical **17** is also similar to that of **19** ($\Delta H = -480.2$ kJ mol^{-1}). These results support the above hydrogen-transfer mechanism. On the other hand, the structural calculations of the *cis*-diradical **18** are in analogy with those of **1a**; hence, this indicates that **18** undergoes a reversible cleavage at the C_3–C_5 bond to **1a** (Scheme 3).

Intramolecular [2+2] Cycloaddition. It has been reported that several divinylmethanes underwent intramolecular [2+2] cycloaddition to afford the bicyclo[2.1.0]pentanes,[8—10,35)] but that the multiplicities occurring in these cycloadditions differ based on the compounds: i.e., singlet pathway and triplet pathway.[35)] The intramolecular [2+2] cycloaddition of **1a**—**c** takes place apparently from the triplet excited state by sensitization effects. In the acetone-sensitized photolysis of **1a**, although **6** was produced (Table 1), **1a** is considered to have a larger absorption coefficient above 280 nm than **1b** and **1c**, whose direct excitation partly occurred above the 280 nm radiation conditions.

Based on the photochemistry of the allenyl(styryl)-methane(s), Lankin et al.[9a)] have considered that their intramolecular [2+2] cycloaddition involves either a pathway through a 1,4-diradical, such as **17** and **18**, or a cyclopentane diradical, such as **20**.[36)] According to the photochemical [2+2] cycloaddition of cycloalkenone to alkenes,[5,37,38)] the lowest triplet of the enone reacts with the ground-state alkene to afford a triplet 1,4-diradical. A spin inversion of the resulting triplet diradical to the singlet diradical is followed by ring closure to produce the cyclobutane. The photochemical intermolecular [2+2] cycloaddition of allene to triplet cycloalkenones is well-known.[5b,39,40)]

On the other hand, it has been reported that the thermolyses of allenyl(vinyl)methane gave rearrangement compounds via the diradical intermediate **20** (Scheme 4).[41,42)] Moreover, the thermolyses or photolyses of diazene also give similar intermediates (Scheme 4).[43)] In the case of R=H, the main products are *exo*-methylenecyclopentenes, whereas the 2-methylenebicyclo[2.1.0]pentanes are formed mainly because of a lower activation energy and the presence of methyl substituents, where the substituents are two methyl groups.[43a)]

Therefore, it seems reasonable to assume that the [2+2] cycloadducts were produced via a diradical **21** (Scheme 5). The formation of the bicyclo[2.1.0]pentanes via the photochemical process of 1,4-diene has been sup-

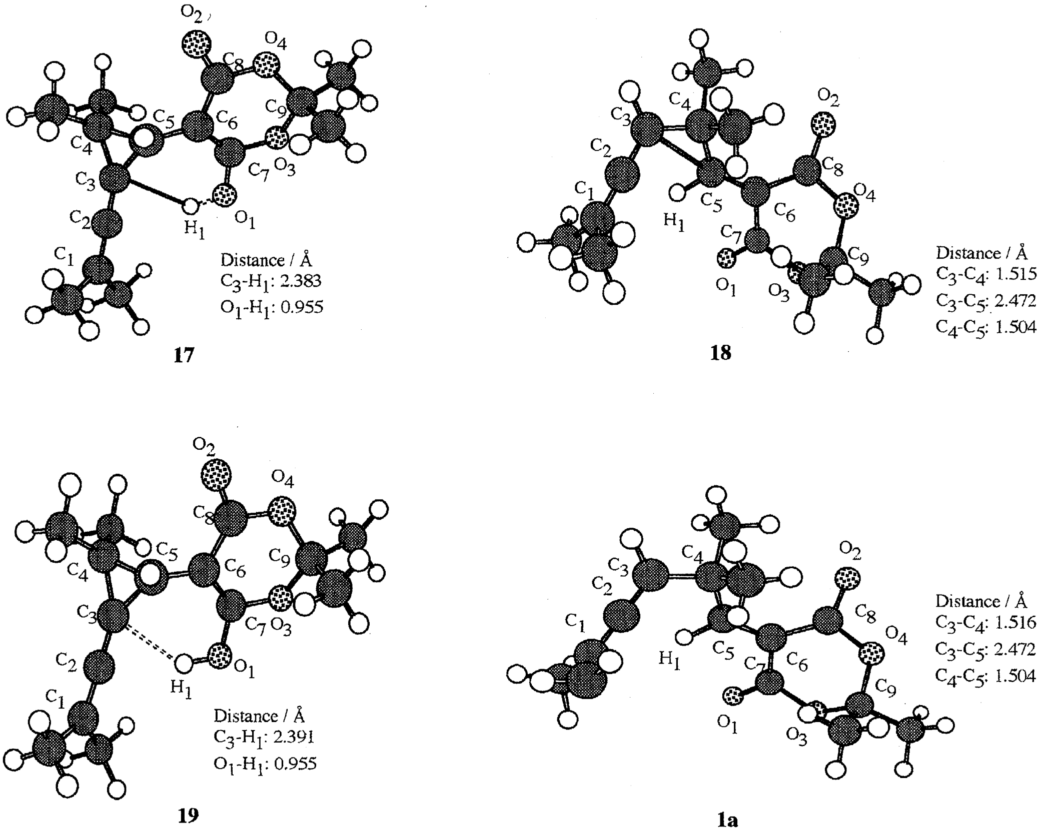
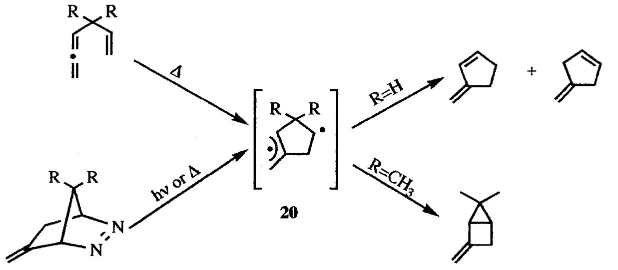
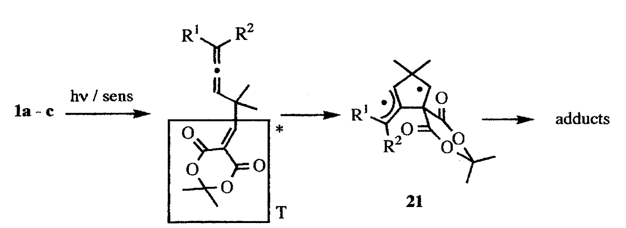


Fig. 8. Optimal structures of **1a** and **17**—**19** by PM3 MO calculation.



Scheme 4.

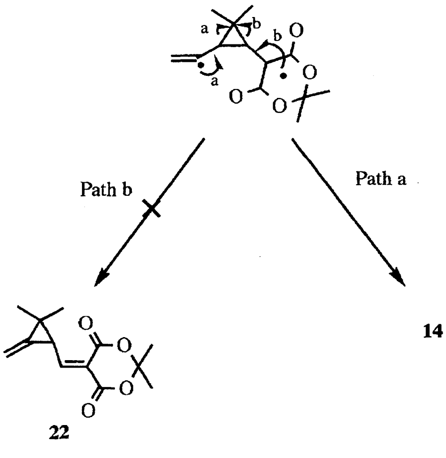


Scheme 5.

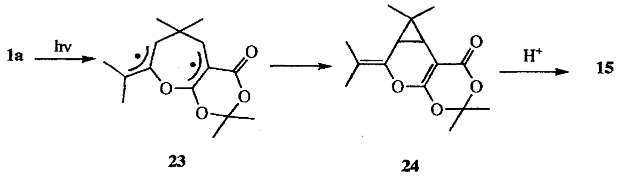
ported on the basis of the "rule of five".[5a,35k,41)]

The cycloaddition of **1a**—**c** was affected by benzophenone (E_T=288 kJ mol^{-1}) and acetone (E_T=334—377 kJ mol^{-1}) sensitization, but 2-acetylnaphthalene (E_T= 247 kJ mol^{-1}) was less effective. The acylals **1a**—**c** do not show phosphorescence emissions, though the lowest triplet energies of **1a**—**c** are estimated to lie in the range of 250—290 kJ mol^{-1}. The energy of the vertical triplet excited state for linear allene has been estimated to be ca. 413 kJ mol^{-1}.[44,45)] However, from the excited-state chemistry of allene, it is necessary to take into account the presence of a planar triplet and a bent triplet of allene and a cyclopropylidene so that a nonvertical triplet energy transfer is allowable to their phantom states.[44,45)] Moreover, the Paterno–Büchi reaction of triplet ketones to allenes is known,[46)] although in the acetone-sensitized photolyses of **1a**—**c** oxetane compounds were not obtained. Hence, the [2+2] cycloaddition of **1a**—**c** occurs through an effective triplet–triplet energy transfer of the sensitizer to either chromophore. The planer and bent triplet energies were calculated to be 230 and 198 kJ mol^{-1}, respectively[44,45)] and, further, cyclopropylidene has 328 kJ mol^{-1} of a triplet.[45b)] The triplet energies of alkylidene Meldrum's acid has been estimated to have values similar to those of α,β-unsaturated esters. For simple α,β-unsaturated esters, the values have been reported as follows: dimethyl fumarate; 255—280 kJ mol^{-1},[47)] dimethyl maleate; 293—323 kJ mol^{-1},[47)] maleic anhydride; 302 kJ mol^{-1},[47)] methyl (E)-2-methyl-2-butenoate; ca. 300 kJ mol^{-1}.[32l)] Therefore, the energy transfer from the triplet sensitizer can afford either the planer, bent allene, or methylene Meldrum's acid triplet. The estimated triplet energies of **1a**—**c** are near to the reported triplet energy of dimethyl fumarate, and somewhat less than the triplet energies of the above-mentioned α,β-unsaturated esters.[3l,47] Therefore, it seems that the excitation sensitizers cause a triplet–triplet energy transfer to the methylene Meldrum's acid moiety in **1a**—**c**. A similar result was obtained in the photochemistry of [2-(1,2-propadienyl)-substituted alkylidene]malonates.[13] The α-carbon of the Meldrum's acid chromophore in the resulting triplet excited state added to the allene center carbon to afford the diradical **21**, followed by yielding the [2+2] cycloadducts (Scheme 6). Becker et al. have studied the photochemistry of a substituted allene linked to cyclohexenone by hydrocarbon chains, and reported that the rate of [2+2] cycloaddition increases in the other 1,2-propadiene > 3-substituted 1,2-propadiene > 3,3-disubstituted 1,2-propadiene, since the substituted allenes and these cycloadditions were affected by a steric hindrance.[6k] However, in the photochemistry of **1a**—**c**, the quantum yields of sensitized [2+2] cycloaddition were in the order 3,3-dimethyl-1,2-propadiene, 1,2-butadiene > 1,2-propadiene. Because this order corresponds to that of the allene IPs, the sensitized [2+2] cycloaddition of **1a**—**c** may proceed involving a triplet exciplex mechanism.

Di-π-Methane Rearrangement. In these photolyses, the expected di-π-methane rearrangement compound was obtained only as a minor product in the direct photolysis of **1c**. It seems that the regioselective di-π-methane rearrangement compound **14** is a reasonable product via path a in Scheme 7 based on the earlier reports by Zimmerman et al.[2a,3a,3b] and considering the structure of methylenecyclopropane **22**. The formation of **14** also indicates the presence of diradical intermediates, such as **17** and **18**. From a MO calculation, it is considered that the hydrogen transfer of a diradical occurs at a much faster rate than the di-π-methane rearrangement. In the case of the direct photolysis of **1c**, because the vinyl radical in the resulting diradicals is less stable than the radicals from **1a** and **1b**, it is considered that the di-π-methane rearrangement took place partly with a competitive hydrogen transfer and a reversible reaction to **1a**—**c**.



Scheme 6.



Scheme 7.

Reaction Pathway of the δ-Lactone. In the photolysis of **1a** in hexane, the δ-lactone **8** was obtained. It is well-known that methylene Meldrum's acids are heterodienes in an *oxa*-Diels–Alder reaction to form dihydropyrans.[48] In these reactions, part of the resulting dihydropyrans would be transformed to δ-lactones. When a solution of **1a** in hexane was allowed to stand at room temperature in the dark, no intramolecular *oxa*-Diels–Alder reaction took place. Consequently, it has become apparent that the δ-lactone **15** was derived via the photochemical pathway. Previously, we communicated[14] that the *Z*-form of 2-(3,4-pentadienylidene-substituted) cycloalkanone underwent a photochemical intramolecular *oxa*-Diels–Alder reaction to afford the dihydropyran. It is well-known that an excited carbonyl acts as an effective electron acceptor to alkenes to produce oxetanes, and increasing solvent polarity results in decreasing yields of oxetane due to an increase in the dissociation of an intermediate exciplex to radical ions. Such a tendency is similar to the formation of **15**. Furthermore, the intra-[10,49] and intermolecular[46] formations of oxetane are also found from the photolyses of alkanones with several allenes; those reactions appear to be greatly preferable for the carbonyl oxygen of alkanone to bond to the center carbon of allene. Hence, it seems that in nonpolar solvents the direct photolyses of **1a** gave the dihydropyran **24** via a diradical **23**, followed by degradation leading to the δ-lactone **15** (Scheme 7). The methylene moiety in the δ-lactone **15** in this reaction should supply hydrogens by a hydrogen donor. From GCMS analyses of the resulting **15** from the photolyses of **1a** in deuterated solvents, such as cyclohexane-d_{12} and benzene-d_6, it became apparent that for the formation of **15** a solvent is not a hydrogen donor. Therefore, it is considered that **15** was derived from the addition reaction of **24** with hydrogen of 5-methine of **6**.

Conclusion

The main conclusions of this paper are summarized as follows: the (1-alkenylidene)cyclopropanes were produced from the enol intermediate via the preferred 1,5-hydrogen transfer of the *trans*-diradical, which was formed through the intramolecular CT singlet excited state between the 1,2-propadienyl and methylene Meldrum's moieties in **1a**—**c**. The sensitized photolyses of **1a**—**c** gave the intramolecular [2+2] cycloadducts. The triplet–triplet energy transfer process was from the sensitizer to the methylene Meldrum's acid chromophore in **1a**—**c**.

Experimental

General. The melting points were determined on a micro hot stage (Yazawa) and are uncorrected. The IR spectra were taken with KBr disks or a $CHCl_3$ liquid film inserted between NaCl plates using a BIO-RAD FTS-60A or JASCO A-3 spectrophotometer. The ^1H and ^{13}C NMR spectra were measured in a $CDCl_3$ solution with a JEOL JNM-EX90 (89.45 MHz for ^1H and 22.40 MHz for ^{13}C) spectrometer using tetramethylsilane as an internal standard. The MS and HRMS spectra were obtained with a JEOL JNM-AX-500 spectrometer using a direct-insertion probe or GCMS at an ionization voltage of 70 eV; the gas chromatograph connected to the MS spectrometer was a Hewlett–Packard 5890 equipped with a capillary column (OV-1, 0.24 ϕmm×25 m). GLC was performed with a Shimadzu GC-14A equipped with a capillary column (OV-1, 0.24 ϕmm×25 m). The UV-absorption spectra were measured on a Shimadzu UV-160A spectrophotometer. The fluorescence and phosphorescence spectra were measured on a Hitachi F-3010 spectrofluorometer attached to a phosphorescence-measurement apparatus. Microanalyses were performed on a Perkin–Elmer 240C elemental analyzer. The silica-gel used was Wako gel C-200. The purification and isolation of the photoproducts were performed using a Kusano C.I.G prepacked-column (silica-gel: grain size 10 μm, 22 mm×100 mm glass column) equipped with an RI detector (Shimadzu RID-2). Preparative TLC was performed on Merck Kiselgel $60F_{254}$ (13792) glass-backed plates.

Spectroscopic-grade acetonitrile and commercial acetone were stored over molecular sieve 4A. Commercial sensitizers were recrystallized or distilled. Commercial $Yb(fod)_3$ was dried under reduced pressure at 60 °C. 2,2-Dimethylpropylidene Meldrum's acid was obtained by the condensation of pivalaldehyde with Meldrum's acid according to a reported method.[50]

General Procedure of Preparation of 1a—c by the Condensation of Meldrum's Acid with the Allenyl Aldehydes. A mixture of Meldrum's acid (0.1 mol) and the corresponding allenyl aldehydes[19] (0.1 mol) in pyridine (20 cm^3) was stirred for 24 h at room temperature. After removing pyridine in vacuo below 40 °C, the residual oil was chromatographed on silica-gel using hexane/acetone (95/5) as an eluent to give **1a**—**c**.

1a: Yield 18%, colorless crystals, mp 45—46 °C (from benzene/hexane); IR ($CHCl_3$) 1960 ($C{=}C{=}C$), 1770 (ester CO), 1740 (ester CO), and 1620 cm^{-1} ($C{=}C$); ^1H NMR ($CDCl_3$) $\delta=1.41$ [6H, s, $>\!C(CH_3)_2$], 1.70 [6H, d, $J=3.1$ Hz, $CH{=}C{=}C(C\mathit{H}_3)_2$], 1.74 [6H, s, $=C(COO)_2C(CH_3)_2$], 5.37 [1H, septet, $J=3.1$ Hz, $C\mathit{H}{=}C{=}C(CH_3)_2$], and 7.80 (1H, s, $=CH$); ^{13}C NMR ($CDCl_3$) $\delta=20.2$ (q), 20.4 (q), 26.6 (q), 26.7 (q), 28.4 (q), 38.9 (s, $>\!C\!<$) 96.2 (d, $\underline{C}H{=}C{=}C$), 99.0 [s, $CH{=}C{=}\underline{C}(CH_3)_2$], 104.4 [s, $=C(COO)_2\underline{C}\!<$], 118.4 (s, $CH{=}\underline{C}$), 158.7 (s, COO), 162.8 (s, COO), 172.2 (d, $\underline{C}H{=}C$), and 203.5 (s, $C{=}\underline{C}{=}C$); MS m/z (rel intensity) 206 (M^+-acetone; 100).

Found: C, 68.31; H, 7.61%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

Isopropylidene 3,3-Dimethyl-1,4,5-heptatriene-1,1-dicarboxylate (1b): Yield 23%, colorless crystals, mp 55 °C (from benzene/hexane); IR ($CHCl_3$) 1965 ($C{=}C{=}C$), 1770 (ester CO), 1740 (ester CO), and 1620 cm^{-1} ($C{=}C$); ^1H NMR ($CDCl_3$) $\delta=1.43$ [6H, s, $>\!C(CH_3)_2$], 1.67 (3H, dd, $J=3.5$ and 7.1 Hz, $CH{=}C{=}CHC\mathit{H}_3$), 1.74 [6H, s, $=C(COO)_2C(CH_3)_2$], 5.22 (1H, dq, $J=7.1$ and 7.1 Hz, $CH{=}C{=}C\mathit{H}CH_3$), 5.46 (1H, dq, $J=3.5$ and 7.1 Hz, $C\mathit{H}{=}C{=}CHCH_3$), and 7.81 (1H, s, $=CH$); ^{13}C NMR ($CDCl_3$) $\delta=14.4$ (q, $CH{=}C{=}CH\underline{C}H_3$), 27.5 (q), 27.6 (q), 28.1 (q, 2C), 38.4 (s, $>\!C\!<$), 89.3 (d, $\underline{C}H{=}C{=}CHCH_3$), 97.8 (d, $CH{=}C{=}\underline{C}HCH_3$), 104.5 [s, $=C(COO)_2\underline{C}\!<$], 118.6 (s, $CH{=}\underline{C}$), 158.8 (s, COO), 162.8 (s, COO), 172.2 (d, $\underline{C}H{=}C$), and 203.5 (s, $CH{=}\underline{C}{=}CH$); MS m/z (rel intensity) 192 (M^+-acetone; 100).

Found: C, 67.25; H, 7.16%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

Isopropylidene 3,3-Dimethyl-1,4,5-hexatriene-1,1-dicarboxylate (1c): Yield 34%, colorless crystals, mp 50—51 °C (from benzene/hexane); IR ($CHCl_3$) 1955 ($C{=}C{=}C$), 1770 (ester CO), 1740 (ester CO), and 1620 cm^{-1} ($C{=}C$); ^1H NMR ($CDCl_3$) $\delta=1.46$ [6H, s, $>\!C(CH_3)_2$], 1.75 [6H, s, $=C(COO)_2C(CH_3)_2$], 4.83 (2H, d, $J=6.7$ Hz, $CH{=}C{=}C\mathit{H}_2$), 5.62 [1H, t, $J=6.7$ Hz, $C\mathit{H}{=}C{=}CH_2$], and 7.78 (1H, s, $=CH$); ^{13}C NMR ($CDCl_3$) $\delta=27.4$ (q, 2C), 27.7 (q, 2C), 37.6 (s, $>\!C\!<$), 78.3 (t, $CH{=}C{=}\underline{C}H_2$), 97.7 (d, $\underline{C}H{=}C{=}CH_2$), 104.5 [s, $=C(COO)_2\underline{C}\!<$], 118.9 (s, $CH{=}\underline{C}$), 158.8 (s, COO), 162.6 (s, COO), 171.5 (d, $\underline{C}H{=}C$), and 207.1 (s, $CH{=}\underline{C}{=}CH_2$); MS m/z (rel intensity) 178 (M^+-acetone; 100).

Found: C, 65.87; H, 6.81%. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%.

Direct Photolysis of 1a. Method A: A Solution of **1a** (1.05 g, 3.98 mmol) in acetonitrile (400 cm^3) was irradiated for 48 h under argon at room temperature by a 6-W low-pressure mercury lamp with a quartz jacket. The reaction mixture was evaporated in vacuo, and the photoproducts were isolated by medium-pressure silica-gel chromatography using hexane/EtOAc (85 : 15, v/v) as an eluent. A first elution gave 3-isopropylidene-2′,2′,5,5-tetramethylspiro[bicyclo[2.1.0]pentane-2,5′-[1,3]dioxane]-4′,6′-dione (**10**) in 17% (178 mg) yield as colorless crystals: mp 115—116 °C (from benzene/hexane); IR ($CHCl_3$) 1780 (ester CO), and 1745 cm^{-1} (ester CO); ^1H NMR ($CDCl_3$) $\delta=0.96$ (3H, s), 1.43 (3H, s), 1.46 (3H, s), 1.71 (3H, s), 1.75 (3H, s), 1.93 (3H, s), 1.94 (1H, d, $J=5.7$ Hz, 1-CH), and 2.94 (1H, br d, $J=5.7$ Hz, 4-CH);[51] ^{13}C NMR ($CDCl_3$) $\delta=17.8$ (q), 18.5 (q), 19.1 (q), 25.0 (q), 28.5 (q), 28.7 (q), 29.3 (s), 33.2 (d, 1-C), 36.6 (d, 4-C), 52.8 (s, 2-C), 104.5 (s, 2′-C), 124.3 (s), 128.1 (s), 165.1 (s, COO), and 167.0 (s, COO); MS m/z (rel intensity) 206 (M^+-acetone; 100).

Found: C, 68.08; H, 7.44%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

A second elution gave [2,2-dimethyl-3-(2-methyl-1-propenylidene)cyclopropyl]-2,2-dimethyl-1,3-dioxan-4,6-dione (**6**) in 28% (297 mg) yield as colorless crystals. The IR spectrum of this compound showed a characteristic allenic band (2030 cm^{-1})[52] and, in the ^{13}C NMR spectrum, the three carbons of allene appeared at $\delta=89.1$, 99.9, and 187.1, respectively, the chemical shifts of which are adequately close to those of reported (2-methyl-1-propenylidene)cyclopropane.[53] The physical and other spectroscopic data of **6** are as follows: mp 113—115 °C (from benzene/hexane); IR ($CHCl_3$) 1780 (ester CO) and 1740 cm^{-1} (ester CO); ^1H NMR ($CDCl_3$) $\delta=1.26$ (3H, s, cyclopropyl-Me), 1.35 (3H, s, cyclopropyl-Me), 1.76 (3H, s, 2-Me), 1.78 (9H, s, 2-Me and $Me_2C{=}C{=}C$), 1.7—1.9 (1H, m, cyclopropane-CH), and 3.25 (1H, d, J=9.7 Hz, 5-CH); ^{13}C NMR (CDCl$_3$) δ=20.3 (q), 21.2 (q), 21.5 (q), 24.2 (s, cyclopropane $>$C$<$), 25.8 (q), 26.9 (q), 28.3 (d, cyclopropane CH), 28.8 (q), 47.4 (d, 5-C), 105.1 (s, 2-C), 164.3 (s, COO), and 164.9 (s, COO); MS m/z (rel intensity) 206 (M$^+$ − acetone; 100).

Found: C, 67.86; H, 7.66%. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%.

Method B. An acetonitrile solution (50 cm^3) of **1a** (133 mg, 0.50 mmol) in a Pyrex tube was degassed with argon and irradiated for 8 h at room temperature with stirring by using a 100-W high-pressure mercury lamp (> 280 nm) through a Pyrex filter. The reaction mixture was evaporated in vacuo, and the products were subjected to preparative TLC using hexane/EtOAc (9 : 1, v/v) to give **6** (51 mg, 39%) and **10** (7.7 mg, 5%).

Method C. In a manner similar to Method B, a hexane solution (50 cm^3) of **1a** (135 mg, 0.51 mmol) was irradiated for 8 h. Purification by preparative TLC gave **6** (37 mg, 27%), **10** (9.3 mg, 7%), and **15** (9 mg, 10%).

2-Isopropylidene-7,7-dimethyl-3-oxabicyclo[4.1.0]heptan-4-one (15): Oil; IR (CHCl$_3$) 1756 (CO) and 1690 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ=0.98 (3H, s), 1.17 (3H, s), 1.1—1.4 (1H, m, 6-CH) 1.5—1.7 (1H, m, 1-CH), 1.69 (3H, s), 1.74 (3H, s), 2.27 (1H, dd, J=4.4 and 18.1 Hz, 5-CH), and 2.77 (1H, dd, J=7.9 and 18.1 Hz, 5-CH); ^{13}C NMR (CDCl$_3$) δ=15.2 (q), 16.5 (q), 18.5 (q), 20.6 (d), 20.9 (d), 22.0 (s, 7-C), 26.7 (t and q), 115.0 (s, $\underline{\mathrm{C}}$=C–O), 140.9 (s, C=$\underline{\mathrm{C}}$–O), and 169.1 (s, COO); MS m/z (rel intensity) 180 (M$^+$; 96), 165 (25), 152 (14), 138 (21), 137 (100), 123 (21), 119 (12), 110 (47), 109 (47), 95 (51), 81 (21), 79 (11), 70 (31), 69 (16), 67 (34), 55 (14), and 53 (11).

HRMS Found: m/z 180.1126. Calcd for $C_{11}H_{16}O_2$: M, 180.1151.

Direct Photolysis of 1a in Deuterated Solvents. In Cyclohexane-*d*$_{12}$ or Benzene-*d*$_6$. A cyclohexane-d_{12} or benzene-d_6 (1 cm^3) solution of **1a** (5 mg, 0.02 mmol) in a Pyrex NMR tube was degassed with dry argon, and then irradiated for 5 h using a 100-W high-pressure mercury lamp throughout a Pyrex jacket. The reaction mixture was subjected to a GCMS analysis, from which the element table for **15** was identical with that of the above corresponding product.

Direct Photolysis of 1b in Acetonitrile. A solution of **1b** (1.00 g, 4.00 mmol) in acetonitrile (400 cm^3) was irradiated according to above Method A. The reaction mixture was evaporated in vacuo, and the photoproducts were isolated by medium-pressure silica-gel chromatography using hexane/EtOAc (85 : 15, v/v) as an eluent. The starting material **1b** (5 mg) was recovered from a first elution. A second elution afforded **11** (9 mg), and third elution gave a mixture (15 mg) of **11** and **12** in a 1 : 1 ratio by ^{1}H NMR. A fourth elution gave **12** (8 mg). The total yield of adducts **11** and **12** was 3%. Further elution gave a mixture of *trans*- and *cis*-5-[2,2-dimethyl-3-(1-propenylidene)cyclopropyl]-2,2-dimethyl-1,3-dioxane-4,6-dione, **7** and **8**, (230 mg, 23%) whose ratio was 55 : 45 based on ^{1}H NMR analysis.

7 and 8: Colorless crystals, mp 116—120 °C (from benzene/hexane); IR (KBr) 2015 (C=C=C), 1775 (ester CO), 1735 (ester CO), 1390, and 1385 cm^{-1} ; ^{1}H NMR (CDCl$_3$) δ=1.28 (1.71H, s, *trans*-cyclopropane Me), 1.32 (1.29H, s, *cis*-cyclopropane Me), 1.39 (1.71H, s, *trans*-cyclopropane Me), 1.41 (1.29H, s, *cis*-cyclopropane Me), 1.75 (1.71H, d, J=7.0 Hz, *trans*-CH_3CH=C=C), 1.78 (1.29H, d, J=7.0 Hz, *cis*-CH_3CH=C=C), 1.82 [6H, s, (COO)$_2$CMe$_2$], 1.8—2.1 (1H, m, *cis*- and *trans*-cyclopropane-CH), 3.25 (0.57H, d, J=10.6 Hz, *trans*-5-CH), 3.27 (0.43H, d, J=9.7 Hz, *cis*-5-CH), and 5.1—5.6 (1H, m, *cis*- and *trans*-CH$_3$CH=C=C); ^{13}C NMR (CDCl$_3$) δ=15.1 (q), 15.2 (q), 20.1 (q), 20.4 (q), 24.9 (s), 25.0 (s), 25.6 (q), 25.9 (q), 26.7 (q), 26.8 (q), 28.6 (d), 28.7 (q, 2C), 28.9 (d), 47.4 (d, 2C, 5-CH), 89.7 (d), 89.8 (d), 105.1 (s, 2C, 2-C), 164.3 (s, COO), 164.5 (s, COO), 164.6 (s, COO), and 190.0 (s, C=$\underline{\mathrm{C}}$=C); MS m/z (rel intensity) 250 (M$^+$; 4), 192 (M$^+$ − acetone; 100), 174 (69), 149 (22), 147 (17), 146 (38), and 133 (65).

Found: C, 66.97; H, 7.36%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

(*E*)-3-Ethylidene-2′,2′,5,5-tetramethylspiro[bicyclo[2.1.0]pentane-2,5′-[1,3]dioxane]-4′,6′-dione (11): Colorless crystals, mp 131—133 °C (from benzene/hexane); IR (KBr) 1775 (ester CO), 1740 (ester CO), 1395, and 1380 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.07 (3H, s, 5-Me), 1.39 (3H, s, 5-Me), 1.67 (3H, d, J=6.7 Hz, =CMe), 1.76 (3H, s, 2′-Me), 1.80 (3H, s, 2′-Me), 2.01 (1H, d, J=5.7 Hz, 1-CH), 2.56 (1H, br d, J=5.7 Hz, 4-CH), and 5.47 (1H, dq, J=0.9 and 6.7 Hz); ^{13}C NMR (CDCl$_3$) δ=12.9 (q), 18.3 (q), 24.7 (q), 28.6 (q), 29.2 (s and q, 2C), 32.1 (d), 35.7 (d), 54.9 (s), 104.9 (s), 120.4 (d), 133.3 (s), 164.7 (s), and 167.4 (s); MS m/z (rel intensity) 164 (M$^+$ − acetone; 29) and 133 (100).

Found: C, 67.07; H, 7.23%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

(*Z*)-3-Ethylidene-2′,2′,5,5-tetramethylspiro[bicyclo[2.1.0]pentane-2,5′-[1,3]dioxane]-4′,6′-dione (12): Colorless needles, mp 121—123 °C (from benzene/hexane); IR (KBr) 1778 (ester CO), 1743 (ester CO), 1396, and 1381 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.05 (3H, s, 5-Me), 1.43 (3H, d, J=7.0 Hz, =CMe), 1.47 (3H, s, 5-Me), 1.76 (3H, s, 2′-Me), 1.90 (3H, s, 2′-Me), 2.00 (1H, d, J=5.8 Hz, 1-CH), 2.53 (1H, br d, J=5.8 Hz, 4-CH), and 5.47 (1H, q, J=7.0 Hz); ^{13}C NMR (CDCl$_3$) δ=13.6 (q), 17.9 (q), 25.0 (q), 28.5 (q), 28.7 (q), 29.6 (s), 34.6 (d), 37.8 (d), 52.7 (s), 104.6 (s), 120.0 (d), 131.4 (s), 164.7 (s), and 166.6 (s); MS m/z (rel intensity) 164 (M$^+$ − acetone; 20) and 133 (100).

Found: C, 67.17; H, 7.21%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25%.

Direct Photolysis of 1c in Acetonitrile. A solution of **1c** (940 mg, 3.98 mmol) in acetonitrile (400 cm^3) was irradiated similarly to the above method. After 46 h, the reaction mixture was evaporated in vacuo, and the photoproducts were isolated by medium-pressure silica-gel chromatography using hexane/EtOAc (9 : 1, v/v) as an eluent. A first elution gave 1,1,6,6-tetramethyl-2-(1,2-propadienyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (**14**; 29 mg, 3%). The second elution afforded 3-methylene-2′,2′,5,5-tetramethylspiro[bicyclo[2.1.0]pentane-2,5′-[1,3]dioxane]-4′,6′-dione (**13**; 31 mg, 3%). A third elution afforded 5-(2,2-dimethyl-2-vinylidenecyclopropyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (**9**; 220 mg, 23%).

9: Colorless crystals, mp 100—104 °C (from benzene/hexane); IR (KBr) 2020 (C=C=C), 1780 (ester CO), 1745 (ester CO), 1395, and 1385 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.30 (3H, s, cyclopropane-Me), 1.41 (3H, cyclopropane-Me), 1.86 (6H, s, 5-Me×2), 1.98 (1H, ddd, J=4.0, 4.0, and 10.2 Hz), 3.28 (1H, d, J=10.2 Hz), 4.92 (1H, d, J=4.0 Hz), and 4.93 (1H, d, J=4.0 Hz); ^{13}C NMR ($CDCl_3$) δ=20.1 (q), 25.5 (q), 26.2 (q), 28.7 (q), 29.6 (d, cyclopropane-CH), 47.4 (d, 2-CH), 78.2 (t, $\underline{C}H_2=C=C$), 88.3 (s, $CH_2=C=\underline{C}$), 105.2 (s, 5-C), 164.3 (s, 2C, COO×2), and 194.0 (s, $CH_2=\underline{C}=C$); MS m/z (rel intensity) 178 (M^+ − acetone; 20) and 147 (100).

Found: C, 65.73; H, 6.74%. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%.

13: Colorless crystals, mp 96—97 °C (from benzene/hexane); IR ($CHCl_3$) 1780 (ester CO), 1740 (ester CO), 1685 (C=C), 1395, and 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (3H, s, 5-Me), 1.42 (3H, s, 5-Me), 1.76 (3H, s, 2′-Me), 1.74 (3H, s, 2′-Me), 2.10 (1H, d, J=5.3 Hz, 1-CH), 2.61 (1H, d, 4-CH), 5.03 (1H, dd, J=1.7 and 1.8 Hz, vinyl-H), and 5.13 (1H, dd, J=0.8 and 1.8 Hz, vinyl-H); ^{13}C NMR ($CDCl_3$) δ=18.5 (q, 5-Me), 24.7 (q, 5-Me), 28.6 (q, 2′-Me), 29.0 (q, 2′-Me), 32.8 (d, 1-C), 38.0 (d, 4-C), 52.8 (s, 2-C), 105.0 (s, 2′-C), 109.4 (t, $=CH_2$), 142.1 (s, 3-C), and 164.2 (s, COO); MS m/z (rel intensity) 178 (M^+ − acetone; 20) and 147 (100).

Found: C, 65.93; H, 6.78%. Calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%.

14: Colorless crystals, mp 69—72 °C (from hexane); IR ($CHCl_3$) 1955 (C=C=C), 1760 (ester CO), and 1730 cm^{-1} (ester CO); ^{1}H NMR ($CDCl_3$) δ=1.40 (3H, s, 2-Me), 1.44 (3H, s, 2-Me), 1.70 (3H, s, 6-Me), 1.74 (3H, s, 6-Me), 3.18 (1H, br d, J=9.3 Hz, 1-CH), 4.7—4.9 (2H, m, $CH=C=C\mathit{H}_2$), and 5.71 (1H, ddd, J=6.6, 6.6, and 9.3 Hz, $C\mathit{H}=C=CH_2$); ^{13}C NMR ($CDCl_3$) δ=17.6 (q), 21.4 (q), 26.8 (q), 27.7 (q), 29.7 (s), 41.7 (d), 55.7 (s), 76.3 (t), 84.0 (d), 105.0 (s), 163.6 (s, COO), 164.6 (s, COO), and 211.3 (s); MS m/z (rel intensity) 236 (M^+, 2), 221 (M^+ − Me; 4), 178 (91), 134 (46), and 120 (100).

HRHS Found: m/z 236.1069. Calcd for $C_{13}H_{16}O_4$: M, 236.1048.

Acetone-Sensitized Photolysis of 1a. A solution of **1a** (1.05 g, 4.00 mmol) in acetone (400 cm^3) was irradiated for 1.3 h at room temperature under an argon atmosphere using a 100-W high-pressure mercury lamp with a Pyrex jacket. The pressure in the reaction mixture was reduced in order to remove the solvent. Medium-pressure silica-gel chromatographic purification of the residue eluted with hexane/EtOAc (85 : 15, v/v) gave two products **6** (50 mg, 5%) and **10** (559 mg, 53%). The analytical data of **6** and **10** were identical with those measured from direct photolysis of **1a** in acetonitrile.

Acetone-Sensitized Photolysis of 1b. A solution of **1b** (1.01 g, 4.00 mmol) in acetone (400 cm^3) was irradiated for 3 h similarly to the above-mentioned method. After solvent removal, the residue was observed as a mixture in a ratio of **11** : **12**=57 : 43 by ^{1}H NMR analysis based on the methyl protons on the cyclopropane ring of the adducts and was meticulously separated by medium-pressure silica-gel chromatography with hexane/EtOAc (85 : 15, v/v). A first elution gave **11** (168 mg). A second elution afforded a mixture of **11** and **12** (165 mg) by ^{1}H NMR analysis. Further elution afforded **12** (47 mg). The total yield of the adducts was 37%. The analytical data of **11** and **12** were identical with those measured from direct photolysis of **1b** in acetonitrile. Part of the mixture of **11** and **12** was heated in a sublimation apparatus using a Shibata glass-tube-oven to give the pure adduct **12** as colorless needles.

Acetone-Sensitized Photolysis of 1c. A solution of **1c** (940 mg, 4.07 mmol) in acetone (400 cm^3) was irradiated for 7.5 h in a manner similar to the above-mentioned method. Medium-pressure silica-gel chromatographic purification of the residue eluted with hexane/EtOAc (85 : 15, v/v) gave **13** (434 mg, 46%). The analytical data of **13** were identical with those measured from a direct photolysis of **1c** in acetonitrile.

Measurement of Quantum Yields. The quantum yields were measured by NMR analyses on the basis of the generation of photoproducts. A 6-W low-pressure mercury lamp with a quartz-glass filter was used as a 254 nm radiation source. An acetonitrile or hexane solution (5 cm^3) of **1a**—**c** (0.01 mol dm^{-3}) in a quartz tube was fully degassed with argon, and irradiated under an argon atmosphere at 30 °C. On the other hand, a 450-W high-pressure mercury lamp with the combination of a K_2CrO_4 solution and a Pyrex glass filter was used as a 313 nm radiation source; the same lamp with a combination of a $CuSO_4$ solution and a Corning 7-37 glass filter was used as a 365 nm radiation source. An acetonitrile solution (5 cm^3) of **1a**—**c** (0.01 mol dm^{-3}) and the sensitizers (see Table 3) in a Pyrex tube was fully degassed with argon. The light intensity of the 254 and 365 nm radiation source was determined by potassium tris(oxalato)ferrate(III) actinometry,[31] while that of the 313 nm radiation source was determined by stilbene actinometry.[31] The photolyses were performed at conversions of less than 15% of **1a**—**c**. After the reaction mixture was evaporated under reduced pressure, a photolystate was analyzed by ^{1}H NMR based on a known amount of dimethyl malonate. The data are described in Tables 2 and 3.

LIS Experiments. In the cases of **7** and **8**, the LIS was determined by a stepwise addition of $Yb(fod)_3$ to a solution of the mixture of 1-propenylidenecyclopropanes (*cis* : *trans*= 45 : 55, 26 mg) in $CDCl_3$ (0.3 cm^3). On the other hand, in the cases of **11** and **12**, the LIS experiments were assayed by measuring the respective adduct.

MO Calculation. MO calculations were performed using RHF (for **1a**, **2**—**5**, and **19**) and UHF (for **17** and **18**) PM3 methods of Hyper Chem of Auto Disk, Inc.

The authors are grateful to Miss Sachiko Kimura of Analysis Center, Institute of Science and Technology, College of Science and Technology, Nihon University for microanalytical measurements. The present work was supported by a Joint Research Grant, a Research Grant for Assistants, and a General Individual Research Grant from Nihon University.

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