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Allenyl(vinyl)methane photochemistry. Photochemistry of γ-(3-methyl-1-phenyl-1,2-butadienyl)-substituted α,β-unsaturated ester and nitrile derivatives

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Abstract—The direct photolyses of the γ-(3-methyl-1-phenyl-1,2-butadienyl)-substituted α,β-unsaturated esters and nitriles gave the bicyclo[2.1.0]pentanes, cross-conjugated trienes, and several intramolecular products, while the triplet-sensitization led to the former two compounds. It was found that the photochemoselectivity depended on the substituents on the vinyl group and would be controlled by the energy using the triplet sensitizers. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

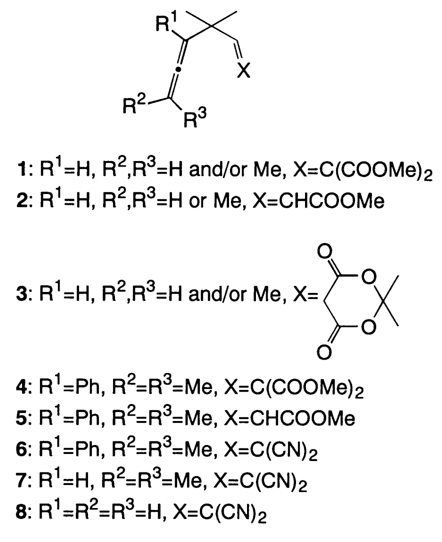
The photochemistry of the divinylmethanes[1] in which one vinyl is α,β-unsaturated esters[2,3] or ylidenemalononitrile[4] has been found to undergo regioselective di-π-methane rearrangement by multiplicity of the excited state. Such photochemoselectivity by multiplicity control is interesting. We then noted the photochemistry of allenyl(vinyl)methanes in which the vinyl is an electron-deficient alkene.[5–9] Previously, we reported the photochemistry of γ-allenyl-substituted alkylidenemalonates **1**,[6] α,β-unsaturated esters **2**,[6] and alkylidene Meldrum's acids **3** (Scheme 1).[7] In the photolyses of **1** and **2**, the intramolecular [2+2] cycloaddition predominantly occurred under the direct and sensitized photolyses to yield the bicyclo[2.1.0]pentanes.[6] On the other hand, the direct photolyses of **3** gave the alkenylidenecyclopropanes, while the sensitized photolyses afforded the bicyclo[2.1.0]pentanes. Further, the photochemistry of **3** presented the possibility of new multiplicity control of the photochemistry of the divinylmethanes.[7] Furthermore, for the triplet excited state, we confirmed that the activated chromophore was the vinyl chromophore based on the estimated triplet energy.[5–7]

We found that newly prepared allenyl(vinyl)methanes **4–6** (Scheme 1) each have a triplet excited state of the allene or vinyl moiety and their states produced different photoproducts: a cross-conjugated triene from the excited state of the allenyl chromophore and an intramolecular [2+2] cycloadduct from that of the vinyl chromophore.[8] In this paper, we report the photochemistry of **4–6** and also present the photochemistry of 1,1-dicyano-3,3-dimethyl-1,4,5-hexatriene **7** and 1,1-dicyano-3,3,6-trimethyl-1,4,5-heptatriene **8** in comparison with that of **6**.

2. Results and discussion

2.1. Preparation of esters and nitriles (4–8)

The phenyl-substituted allenic aldehyde **9** was initially prepared by the reaction of 2-methyl-4-phenyl-3-butyn-2-ol with isobutyraldehyde in the presence of a catalytic amount of *p*-toluenesulfonic acid (Scheme 2). The diester **4** was obtained by the condensation of **9** with dimethyl malonate using Lehnert's method.[10] The monoester **5** was



Scheme 1.

Keywords: allenes; cycloadditions; photochemistry; rearrangement.

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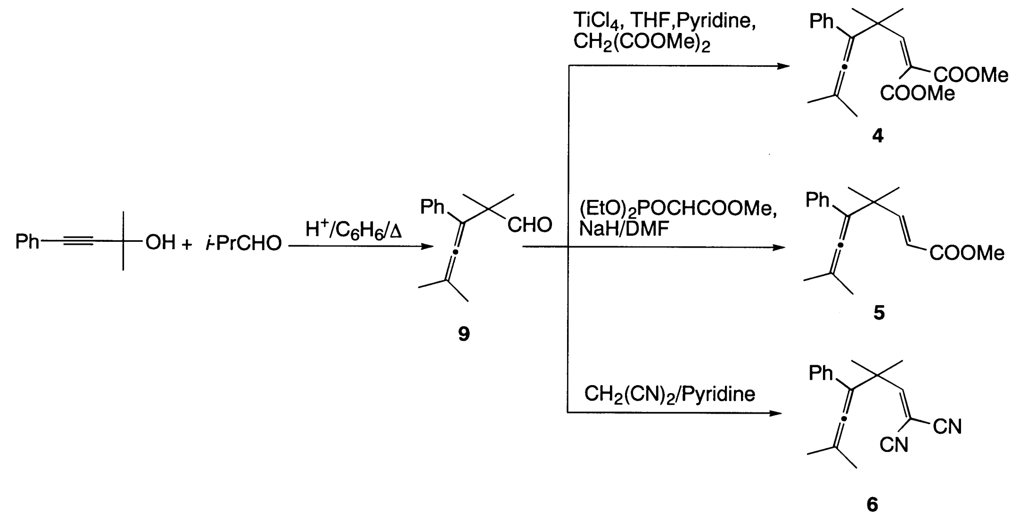
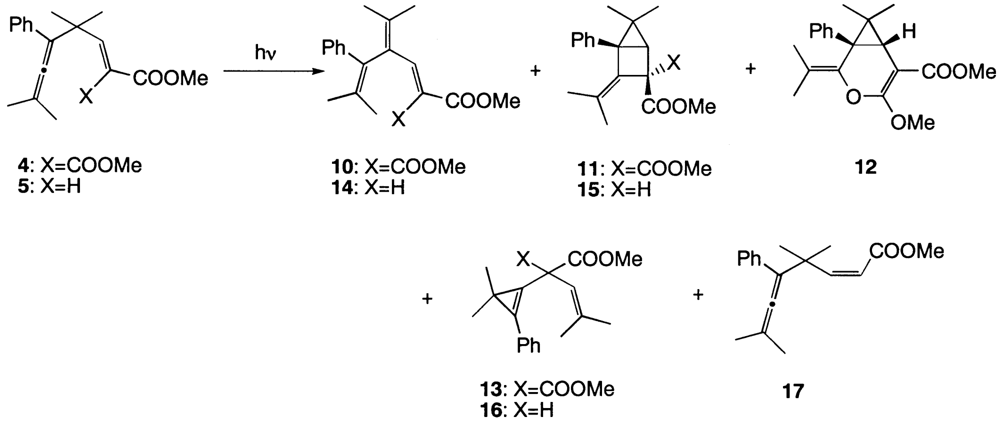


Scheme 2.

prepared by the reaction of **9** with methyl diethylphosphonoacetate in the presence of sodium hydride in DMF. The dinitriles **6**–**8** were prepared by the condensation of the allenic aldehydes with malononitrile in pyridine.

2.2. Photochemistry of esters (4 and 5)

The direct photolysis of the diester **4** in hexane gave a cross-conjugated triene **10**, bicyclo[2.1.0]pentane **11**, pyran **12**,



Scheme 3.

Table 1. Direct and sensitized photolyses of **4**–**8**

Substrate	Solvent	Additive	Irradiation time/h	Products (isolated yield/%)			
4	Hexane		33^{a}	**10** (4)	**11** (15)	**12** (18)	**13** (4)
	Acetone		5^{b}	(12)	(3)		
	Benzene	Anthraquinone	6.5^{c}	(19)			
5	Hexane	None	25^{a}	**14** (1)	**15** (25)	**16** (15)	**17** (2)
	Acetone		15^{b}	(14)	(7)		
6	Acetonitrile	None	30^{a}	**18** (53)	**19** (26)	**20** (0.5)	
	Acetone		4.5^{b}	(38)			**21** (9)
	Acetonitrile	Michler's ketone	1^{c}		(64)		
7	Acetonitrile	None	5^{d}	**22** (11)	**23** (6)	**24** (0.7)	
	Acetone		1.2^{b}		(53)		
8	Acetonitrile		55^{a}	**25** (57)	**26** (8)		
	Acetone		13.5^{b}		(59)		

[a] The direct photolyses were performed using a 6-W low-pressure mercury lamp with a quartz jacket under argon atmosphere.
[b] The sensitized photolyses were performed using a 100-W high-pressure mercury lamp with a pyrex jacket under argon atmosphere.
[c] The solution of the substrate and sensitizer in a pyrex tube was irradiated using a 100-W high-pressure mercury lamp through a pyrex filter.
[d] The direct photolysis was performed using a 100-W high-pressure mercury lamp with a quartz jacket under argon atmosphere.

Table 2. Quantum yields for the isomerization of **4** and **5**

Substrate	λ/nm	Additive (E_T/kJ mol^{-1})[a]	Quantum yields			
4	254	None	Φ_{10}=0.013	Φ_{11}=0.043	Φ_{12}=0.030	Φ_{13}<0.0001
		2-Methyl-1,3-butadiene (251)[b,c]	0.0085	0.041	0.028	<0.0001
	313	Acetone (377–334)[b]	0.25	0.027		
	365	Acetophenone (310)[b]	0.37	0.016		
		Benzophenone (287)[b]	0.29	0.0018		
		2-Benzoylpyridine (279)[b]	0.16	<0.0001		
		Anthraquinone (259)[c]	0.082	<0.0001		
		4-Phenylacetophenone (254)[b]	0.012	<0.0001		
		1-Acenaphthone (236)[b]	0.0031	<0.0001		
5	254	None[b]	Φ_{14}=0.0065	Φ_{15}=0.14	Φ_{16}=0.0096	Φ_{17}<0.014
		2-Methyl-1,3-butadiene (251)[b,d]	0.0040	0.15	0.0095	0.012
	313	Acetone (377–334)[b]	0.026	0.054		
	365	Acetophenone (310)[b]	0.045	0.016		
		Benzophenone (287)[b]	0.040	0.0022		
		2-Benzoylpyridine (279)[b]	0.021	<0.0001		
		Anthraquinone (259)[e]	0.0066	<0.0001		
		4-Phenylacetophenone (254)[b]	0.0055	<0.0001		
		1-Acenaphthone (236)[b]	0.0028	<0.0001		

Total quantum yields for the formation of the photoproducts corresponding with the quantum yield for the disappearance of **4** or **5** below the conversion of 20%.

[a] Sensitizers absorb >95% of incident light.

[b] In hexane.

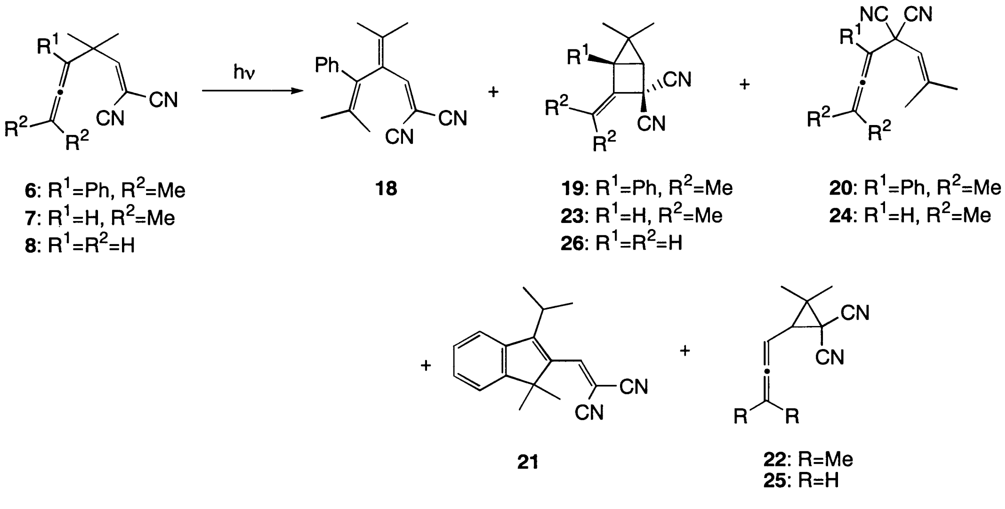
[c] Quencher concentration: 0.03 mol dm^{-3}.

[d] Quencher concn.: 0.07 mol dm^{-3}.

[e] In benzene.

and cyclopropene **13** (Scheme 3). On the other hand, the direct photolysis of the monoester **5** afforded **14–17** (Scheme 3). An induction period was found for the formation of the cyclopropenes **13** and **16**, and moreover, the isolated [2+2] cycloadducts **11** and **15** were irradiated to afford the cyclopropenes **13** and **16**. Though the acetone-sensitized photolyses of **4** or **5** afforded the triene **10** or **14** and the [2+2] cycloadduct **11** or **15**, polymeric materials were significantly produced. The yields from their photolyses are described in Table 1.

Table 2 shows the quantum yields for the isomerization of **4** and **5** under the direct and sensitized irradiation. In the direct photolyses, the isomerization of the cyclopropene **13** or **16** has very low quantum efficiency. For the direct photolyses in the presence of 2-methyl-1,3-butadiene (E_T=251 kJ mol^{-1}) as a quencher, the quantum yields for the formation of the bicyclo[2.1.0]pentanes, pyran, and *Z*-form are within experimental error in comparison with the non-additive conditions, whereas the quantum yields for the formation of the trienes **10** and **14** decrease by ca. 35% (**4**→**10**) and 38% (**5**→**14**) in the presence of the quencher. Acetone (E_T=377∼334 kJ mol^{-1}) and acetophenone (E_T=310 kJ mol^{-1}) are good sensitizers for the isomerization to the trienes **10** and **14** and to the [2+2] cycloadducts **11** and **15**. Benzophenone (E_T=287 kJ mol^{-1}) has an effect on their isomerization, though the quantum yields of the formation of the [2+2] cycloadducts **11** and **15** are smaller than those obtained with the use of acetone or acetophenone. 2-Benzoylpyridine (E_T=279 kJ mol^{-1}), anthraquinone (E_T=259 kJ mol^{-1}), 4-phenylacetophenone (E_T=254 kJ mol^{-1}) and 1-acetonaphthone (E_T=236 kJ mol^{-1}) having a triplet energy less than that of benzophenone show sensitizing effects for the formation of the trienes **10**



Scheme 4.

Table 3. Quantum yields for the isomerization of **6**

λ/nm	Additive (E_T/kJ mol^{-1})[a]	Quantum yields	
254	None	Φ_{18}=0.18	Φ_{19}=0.073
313	Acetone (377–334)	0.15	0.039
365	Acetophenone (310)	0.057	0.093
	Benzophenone (287)	0.14	0.29
	Thioxanthen-9-one (274)	0.051	0.14
	Michler's ketone (259)	<0.0001	0.11
	4-Phenylbenzophenone (249)	<0.0001	0.052

Total quantum yields for the formation of the photoproducts corresponded with the quantum yield for the disappearance of **6** below a conversion of 20%.

[a] Sensitizers absorb >95% of incident light.

and **14** only and the latter two sensitizers have a slight quantum efficiency. By these sensitized efficiencies, we considered that the trienes **10** and **14** would be prepared chemoselectively using sensitizers which have triplet energies in the range of 280 to 235 kJ mol^{-1}, and we then examined the anthraquinone-sensitization of **4**. As the result, the triene **10** was obtained only in 19% isolated yield.

2.3. Photochemistry of nitriles (6–8)

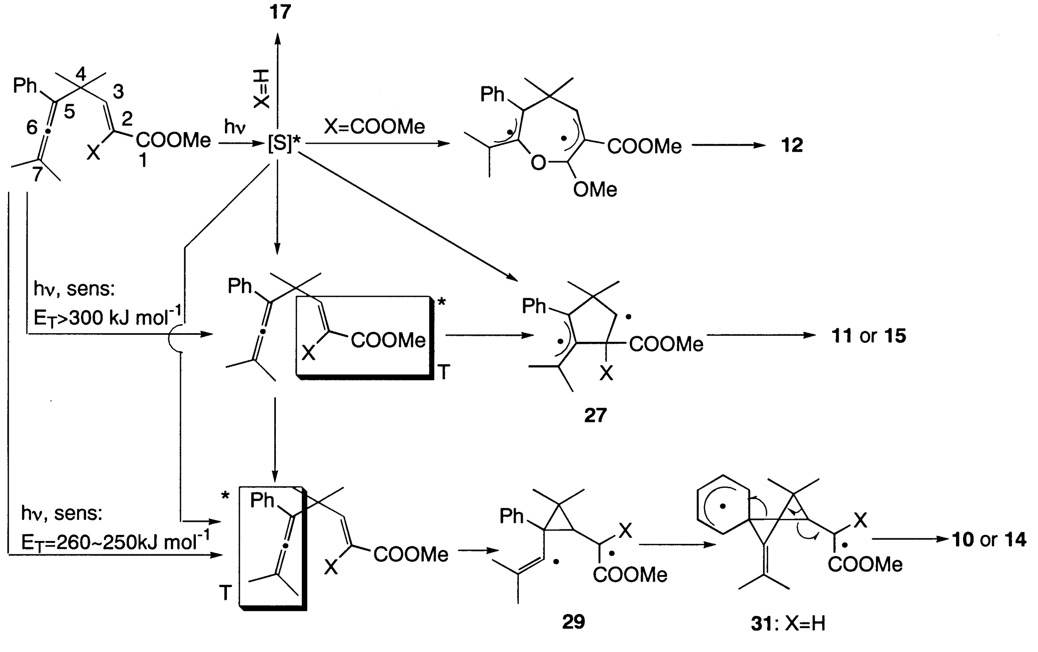
The direct photolysis of **6** in acetonitrile gave mainly cross-conjugated triene **18** and bicyclo[2.1.0]pentane **19**, and the by-product was obtained as 1,3-allyl rearrangement product **20** in a very low yield (Scheme 4). In the case of the acetone-sensitization of **6**, the bicyclo[2.1.0]pentane **19** and indene **21** were obtained. Although GLC analysis showed the formation of **18** and **19** during the acetone-sensitization of **6**, after prolonged irradiation, **18** decreased with increasing **21**. The yields from their photolyses are described in Table 1. The quantum yields for the isomerization of **6** are described in Table 3. Acetone, acetophenone, benzophenone, and thioxanthen-9-one (E_T=274 kJ mol^{-1}) show sensitizing effects for the formation of **18** or **19**, while Michler's ketone (E_T=259 kJ mol^{-1}) or 4-phenylbenzophenone (E_T=249 kJ mol^{-1}) scarcely affected the formation of **18**. We then carried out Michler's ketone-sensitization of **6** on the basis of their results, and compound **19** was obtained in 64% yield.

The direct photolysis of **7** in acetonitrile afforded an allenylcyclopropane **22**, bicyclo[2.1.0]pentane **23**, and 1,3-phenyl rearrangement compound **24** as intramolecular photoproducts (Scheme 4) and further led to considerably polymeric compounds and very small amounts of unidentified intramolecular compounds. On the other hand, the dinitrile **8** under direct photolysis underwent mainly a di-π-methane rearrangement to yield **25**, and further the intramolecular [2+2] cycloadduct **26** was obtained as a by-product (Scheme 4). The acetone-sensitization of **7** or **8** gave the intramolecular [2+2] cycloadduct **23** or **26** in good yields (Table 1).

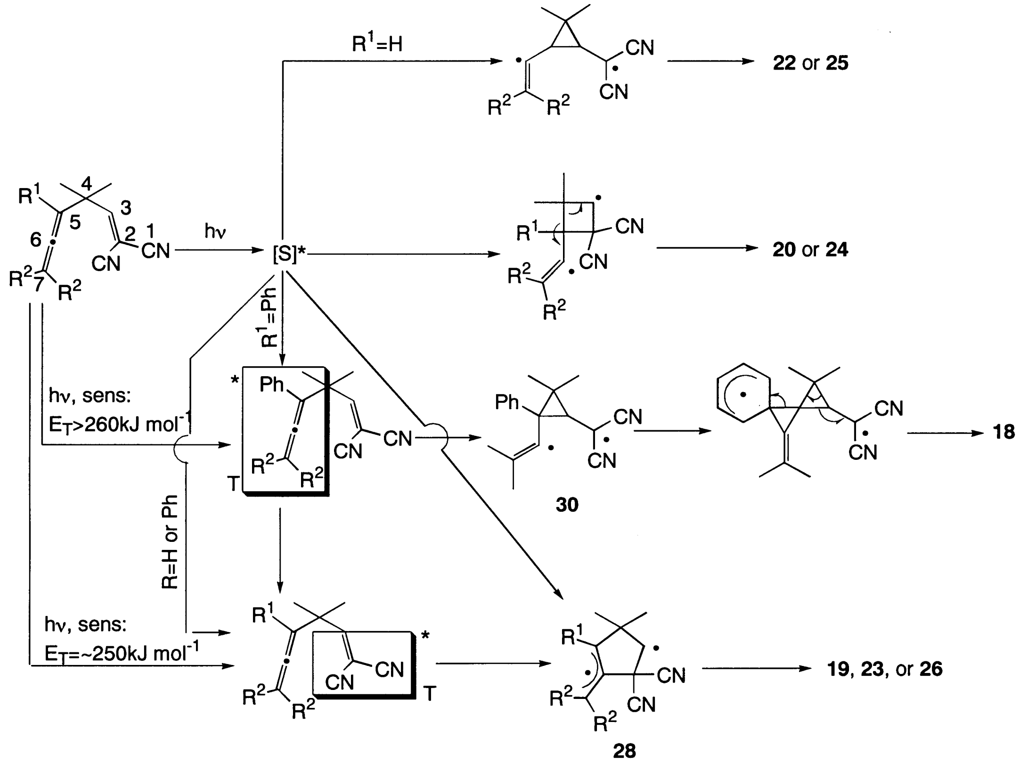
The structures of the photoproducts were established by spectroscopic data and microanalyses or HRMS.[11]

2.4. Reaction mechanisms of photochemistry of esters and nitriles

The sensitizing effects of esters **4** and **5** and nitrile **6** suggest that the trienes and [2+2] cycloadducts are derived from the triplet excited state of a different chromophore in the substrates. The triplet energy required for the formation of the [2+2] cycloadduct from ester **4** or **5** is estimated to be ca. 300 kJ mol^{-1}, while that from the nitrile **6** is ca. 250 kJ mol^{-1}. Based on our previous reports of the photochemistry on the γ-allenyl-substituted α,β-unsaturated esters,[5–8] the triplet energy required for the formation of the [2+2] cycloadduct is estimated to be ca. 300 kJ mol^{-1} and the activated chromophore is the vinyl moiety. The estimated triplet energies of esters **4** and **5** correspond with those of the reported α,β-unsaturated esters.[5–8]



Scheme 5.

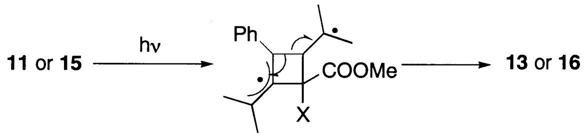


Scheme 6.

Furthermore, the triplet energy of the ylidenemalononitrile has been reported to be ca. 250 kJ mol^{-1}.[4a] The reported triplet energy corresponds with the estimated values for **6**. Hence, the intramolecular [2+2] cycloaddition of **4**–**6** under the sensitized photolyses occurs from the triplet of the vinyl chromophore. On the other hand, the triplet energy required for the formation of trienes **10**, **14** or **18** from **4**–**6** is estimated to be ca. 260 kJ mol^{-1}. It has been reported that the triplet of 3-phenyl-1,2-butadiene is quenched by 1,3-pentadiene (E_T=247 kJ mol^{-1}),[12] while the triplet of thioxanthen-9-one (E_T=274 kJ mol^{-1}) is quenched by 1-phenyl-1,2-propadiene.[13] Therefore, these reports suggest that the triplet energy of the monophenyl-substituted allene lies in the range of 250–270 kJ mol^{-1}. Because this range includes the estimated triplet energy of the phenyl-substituted allenyl chromophore in **4**–**6**, for esters **4** and **5**, acetone and acetophenone having higher triplet energy competitively affect both chromophores in **4** and **5**, although the sensitizers such as benzophenone, 2-benzoylpyridine and thioxanthen-9-one in the range of 260–290 kJ mol^{-1} can reach the excited state for the allenyl chromophore. Consequently, the anthraquinone would be sensitized selectively by the allenyl chromophore in **4** to yield the triene **10** (Scheme 5). For nitrile **6**, both of the allenyl and vinyl chromophores were excited by the sensitizers having a triplet energy of more than 260 kJ mol^{-1} to afford the triene **18** and bicyclo[2.1.0]pentane **19**. However, for the preparative scale of the acetone-sensitized photochemistry of **6**, the resulting triene **18** further undergoes the acetone-sensitized photoreaction to give the indene **21**. The triplet energy of the vinyl chromophore in esters **4** and **5** lies at a higher level than that of the allenyl chromophore, whereas the levels of the energy of the chromophores in **6** are the reverse (Scheme 6). Therefore, the vinyl chromophore of **6** is selectively excited by Michler's ketone, and the intramolecular [2+2] cycloaddition takes place. Thus, the photochemoselectivity for the formation of the trines and bicyclo[2.1.0]pentanes on the substituents on vinyl group would be controlled by the energy using triplet sensitizers.

Recently, we proved the reaction mechanism of the intramolecular [2+2] cycloaddition of the allenyl(vinyl)-methanes by trapping experiments of a biradical intermediate using hydrogen selenide.[5,6b] Accordingly, in the same pathway, the excited state of the vinyl chromophore in **4**–**6** initially bonds between 2-C and 6-C to afford a cyclopenta-1,3-diyl radical **27** or **28** from which ring closure yields the intramolecular [2+2] cycloadducts (Schemes 5 and 6). On the other hand, for the formation of the trienes, it is considered that the excited state of the allenyl chromophore bonds between 3-C and 5-C to yield **29** or **30**, which undergoes a 1,2-phenyl migration to yield the trienes. This reaction pathway was supported by a PM3 MO calculation; the optimal structure of biradical **31** corresponded to the structure of **14**. 2-Methyl-1,3-butadiene under direct photolyses was recognized to have a quenching effect on the formation of the trienes but not on the formation of the [2+2] cycloadducts. Because we have proposed that the intramolecular [2+2] cycloaddition of the allenyl(vinyl)-methanes occurs via both the singlet and triplet pathways, in the cases of the photochemistry of **4** and **5**, the intramolecular [2+2] cycloadducts **11** and **15** are produced not only from the triplet pathway but also the singlet one, and further, due to the quenching effects, the trienes are derived via the triplet excited state.

The direct photolysis of **4** gave pyran **12**. Pyran **12** was not obtained from sensitized photolyses, and its formation did



Scheme 7.

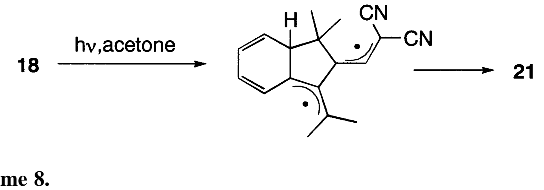
not show the quenching effect by 2-methyl-1,3-butadiene. Therefore, **12** is derived from the photochemical intramolecular *oxa*-Diels–Alder reaction via the singlet-excited state of a *Z*-carbonyl in **4** (Scheme 5). Such an intramolecular *oxa*-Diels–Alder reaction has been found in the photochemistry of several allenyl(vinyl)methanes[5,7a,9] and 3,6-heptadien-2-ones.[14]

The direct photolyses of **7** and **8** gave the allenylcyclopropanes **22** and **25**, i.e. di-π-methane rearrangement compounds, while the diesters which have the same allenyl chromophore in **7** or **8** led mainly to the [2+2] cycloadducts.[5,6] Such a difference is explainable by the MO coefficients of the vinyl chromophore. In our previous report,[6b] the MO coefficient for the α-carbon of 2,2-dimethylpropylidenemalonate is larger than that of the β-one. Hence, γ-allenyl-substituted α,β-unsaturated esters undergo preferential interaction between the allene center and the α-carbon. However, the PM3 MO calculation for 2,2-dimethylpropylidenemalononitrile as a model of the vinyl moiety in **6–8** indicates that the MO coefficient (0.68) of the β-carbon is larger than that (0.50) of the α-carbon. In the photochemistry of **7** and **8**, therefore, the di-π-methane rearrangement occurred by preferential MO interaction between the 5-C and 3-C (Scheme 6). On the other hand, it seems that the minor compounds **20** and **24** were produced by the MO interaction between 5-C and 2-C in the nitriles **6** and **7** (Scheme 6).

It is apparent that the cyclopropenes **13** and **16** were derived via the photochemical pathway of the [2+2] cycloadducts **11** and **15** by the GLC analyses. Moreover, the indene **21** is also the photoproduct from the triene **18**. Because these compounds are secondary photoproducts, a detailed reaction mechanism has not been fully examined, but we consider the following. The resulting bicyclo[2.1.0]pentane **11** or **15** was further excited to undergo cleavage of the cyclopropane ring, and subsequently a cyclobutane ring opening gave the cyclopropene **13** or **16** (Scheme 7). On the other hand, the indene **21** is derived from the interaction between the π-orbitals of the phenyl and vinyl moieties in the triplet excited state of **18** (Scheme 8).

3. Conclusions

Generally, the photochemistry via the triplet excited state of bichromophoric compounds takes place with the lower triplet of either chromophore by an intramolecular energy transfer. Previously, we reported that the compounds **1** and **2** underwent a photoreaction via the excited state of the vinyl chromophore.[6] However, the triene and [2+2] cycloadducts are derived from the triplet excited state of the different chromophores of the reported allenyl(vinyl)methanes **4–6**, and the control of the photochemoselectivity can be subject to the use of triplet sensitizers and the substituents on the vinyl group.



Scheme 8.

4. Experimental

4.1. General

The melting points were determined on a micro hot stage (Yazawa) and are uncorrected. The NMR spectra were measured in a $CDCl_3$ solution using JEOL JNM-EX 90, Bruker Avance-400, and JEOL Lamda-400 spectrometers. The IR spectra were obtained with a BIO-RAD FTS-60A spectrophotometer. The MS and HRMS spectra were obtained with a JEOL JMS AX-500 spectrometer using 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). The UV-absorption spectra were measured on a Shimadzu UV-160A spectrophotometer. Spectroscopic-grade acetonitrile, hexane, and commercial acetone were stored over molecular sieve 4A. The sensitizers used were recrystallized or distilled.

4.2. Preparation of the esters and nitriles

4.2.1. 2,2,5-Trimethyl-3-phenyl-3,4-hexadienal (9). 2-Methyl-4-phenyl-3-butyn-2-ol (8.0 g, 50 mmol), isobutyraldehyde (30 cm^3, 0.33 mol), and TsOH (12 mg) were dissolved in benzene (30 cm^3) in a round glass vessel. The vessel was joined to a water separator with a condenser, and the mixture was refluxed for 120 h under an argon atmosphere. The reaction mixture was washed with sodium acetate solution (1 mol dm^{-3}, 50 cm^3), dried over $MgSO_4$, and evaporated in vacuo. The residual oil was distilled under reduced pressure to give the aldehyde **9** in 41% (4.4 g) yield: bp 90–110°C (2.0 Torr); IR (neat) 1951 (C=C=C), 1731 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.23 (s, 6H, CH_3-2×2), 1.81 (s, 6H, CH_3-6×2), 7.20–7.35 (m, 5H, ArH), 9.56 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.6 (q, 2C), 21.9 (q, 2C), 49.7 (s, C-2), 98.9 (s), 106.6 (s), 126.7 (d), 128.0 (d, 2C), 128.2 (d, 2C), 136.9 (s), 203.5 (s), 203.7 (d); MS *m/z* (rel. intensity) 214 (M^+, 9), 200 (17), 199 (100), 143 (19), 129 (12). HRMS Found: *m/z* 214.1337. Calcd for $C_{15}H_{18}O$: M, 214.1358.

4.2.2. 1,1-Bismethoxycarbonyl-3,3,6-trimethyl-4-phenyl-1,4,5-heptatriene (4). The $TiCl_4$ method described by Lehnert was used.[10] A mixture of $TiCl_4$ (5.0 cm^3, 0.05 mol) and CCl_4 (30 cm^3) was slowly added to THF (50 cm^3) at −5°C under argon. To the THF–$TiCl_4$ suspension was added a mixture of aldehyde (2.1 g, 98 mmol), dimethyl malonate (1.3 g, 98 mmol) in THF (30 cm^3) and then a solution of pyridine (5.0 cm^3) in THF (30 cm^3) was added slowly dropwise over 1 h at 0°C. The mixture was stirred for 24 h at room temperature and then quenched with water (50 cm^3) and ether (50 cm^3). The solution was separated and the aqueous layer was extracted with ether (50 cm^3×2). The combined organic fractions were dried over MgSO$_4$ and evaporated in vacuo. The residue was chromatographed on silica gel (150 g) using hexane/EtOAc (98:2, v/v) to give the ester **4** in 65% (2.1 g) yield: IR (neat) 1965 (C=C=C), 1734 (C=O), 1638 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.31 (s, 6H, CH$_3$-3×2), 1.81 (s, 6H, CH$_3$-6×2), 3.68 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 7.20 (s, 1H, =CH), 7.25–7.28 (m, 5H, ArH); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 20.4 (q, 2C), 27.5 (q, 2C), 40.5 (s), 52.5 (q), 54.6 (q), 98.9 (s), 110.8 (s), 125.0 (s), 126.4 (d), 127.9 (s), 128.3 (d, 2C), 136.9 (s), 154.7 (d), 166.9 (s, 2C), 201.5 (s); MS m/z (rel. intensity) 328 (M$^+$, 6), 296 (10), 196 (12), 144 (12), 143 (100), 128 (24). HRMS Found: m/z 328.1650. Calcd for $C_{20}H_{24}O_4$: M, 328.1675.

4.2.3. Methyl (*E*)-4,4,7-trimethyl-5-phenyl-2,5,6-octatrienoate (5). Methyl diethylphosphonoacetate (6.31 g, 30 mmol) was dissolved in DMF (30 cm^3). To the mixture was added sodium hydride (0.72 g, 30 mmol) which was washed with pentane. The solution was stirred for 10 min at room temperature under argon and then the aldehyde (**9**: 5.36 g, 25 mmol) was added. The mixture was stirred for 24 h at room temperature and then quenched with water (50 cm^3). The solution was extracted with ether (50 cm^3× 2). The combined organic fractions were dried over MgSO$_4$ and evaporated in vacuo. The residue was chromatographed on silica gel (150 g) using hexane/ether (99:1, v/v) to give the ester in 59% (4.0 g) yield as a colorless oil: IR (neat) 1972 (C=C=C), 1725 (C=O), 1649 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.23 (s, 6H, CH$_3$-3×2), 1.82 (s, 6H, CH$_3$-6×2), 3.71 (s, 3H, OCH$_3$), 5.83 (d, 1H, J15.8 Hz, =CH), 7.18 (d, 1H, J=15.8 Hz, =CH), 7.20 (s, 5H, ArH); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 20.6 (q, 2C), 27.4 (q, 2C), 40.5 (s), 51.4 (q), 97.7 (s), 110.4 (s), 118.0 (d), 126.4 (d), 127.8 (d, 2C), 128.8 (d, 2C), 137.7 (s), 157.9 (d), 167.4 (s), 201.8 (s); MS m/z (rel. intensity) 270 (M$^+$, 7), 211 (15), 195 (10), 144 (13), 143 (100), 128 (29). HRMS Found: m/z 270.1584. Calcd for $C_{18}H_{22}O_2$: M, 270.1621.

4.2.4. 1,1-Dicyano-4-phenyl-3,3,6-trimethyl-1,4,5-heptatriene (6). Malononitrile (2.0 g, 30 mmol) and **9** (6.4 g, 30 mmol) were dissolved with pyridine (5 cm^3). The mixture was stirred for 24 h at room temperature and then acidified with HCl (6 mol dm^{-3}). The mixture was extracted with ether (50 cm^3). The ethereal solution was dried over MgSO$_4$ and evaporated in vacuo. The residue was chromatographed on silica gel with EtOAc/Hexane (5:95, v/v) as an eluent to give **6** in 46% (3.5 g) yield as yellow crystals: mp 95°C (ether/hexane); IR (KBr) 2237 (CN) 1961 (C=C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.48 (s, 6H, CH$_3$-3×2), 1.83 (s, 6H, CH$_3$-6×2), 7.11–7.40 (s, 5H, ArH), 7.43 (s, 1H, CH-2); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 20.1 (q, 2C), 28.0 (q, 2C), 43.0 (s, C-3), 87.8 (s), 100.7 (s, C-1), 109.1 (s), 110.7 (s, CN), 113.8 (s, CN), 127.1 (d, C-2), 128.3 (ds, 3C), 128.4 (d, 2C), 176.4 (d, C-2), 201.7 (s, C-5); MS m/z (rel. intensity) 262 (M$^+$, 8), 248 (21), 247 (100), 232 (46), 231 (18). Anal. calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.20; H, 7.06; N, 10.57.

4.2.5. 1,1-Dicyano-3,3,6-trimethyl-1,4,5-heptatriene (7) and 1,1-dicyano-3,3-dimethyl-1,4,5-hexatriene (8). In a manner similar to that described above for the preparation of **6**, a condensation of 2,2,5-trimethyl-3,4-hexadienal[7a]or 2,2-dimethyl-3,4-pentadienal[7a] with malononitrile gave the nitrile **7** or **8**.

Data for 7. A yellow oil, bp 90–95°C (2 Torr); IR (neat) 2250 (CN), 1970 (C=C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.37 (s, 6H, CH$_3$-3×2), 1.74 (d, 6H, J=1.3 Hz, CH$_3$-6×2), 5.04 (septet, 1H, J=1.3 Hz, CH-4), 7.21 (s, 1H, CH-2); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 20.2 (q, 2C), 27.2 (q, 2C), 40.7 (s, C-3), 86.9 (s, C-1), 94.9 (d, C-4), 100.5 (s, C-6), 111.1 (s, CN), 113.3 (s, CN), 175.9 (d, C-2), 201.0 (s, C-5); MS m/z (rel. intensity) 186 (M$^+$, 2), 171 (35), 67 (100), 41 (45). HRMS Found: m/z 186.1155. Calcd for $C_{12}H_{14}N_2$: M, 186.1158.

Data for 8. A yellow oil, 85–90°C (3 Torr); IR (neat) 2245 (CN), 1960 (C=C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$, 90 MHz) δ 1.38 (s, 6H, CH$_3$-3×2), 4.94 (d, 2H, J=7.0 Hz, C=C=CH$_2$), 5.24 (dd, 1H, J=6.2, 7.0 Hz, CH=C=C), 7.26 (s, 1H, CH-2); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 27.4 (q, 2C), 39.4 (s, C-3), 79.2 (t, C-6), 87.6 (s, C-1), 96.2 (d, C-4), 110.9 (s, CN), 113.2 (s, CN), 175.1 (d, C-2), 207.5 (s, C-5); MS m/z (rel. intensity) 158 (M$^+$, 16), 157 (35), 143 (91), 116 (100), 93 (40), 92 (90), 65 (45), 39 (69). HRMS Found: m/z 158.0836. Calcd for $C_{10}H_{10}N_2$: M, 158.0845.

4.3. Photolyses of 4

4.3.1. Direct photolysis of 4. A solution of **4** (657 mg, 2.00 mmol) in hexane (400 cm^3) was irradiated under argon at room temperature for 33 h using a 6-W low-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the residual oil was subjected to medium-pressure silica gel chromatography using 2% ether–hexane as an eluent to give 3-isopropylidene-1,1-bismethoxycarbonyl-5-methyl-4-phenyl-1,4-hexadiene (**10**: 26 mg, 4%), 3-isopropylidene-2,2-bismethoxycarbonyl-5,5-dimethyl-4-phenylbicyclo[2.1.0]pentane (**11**: 99 mg, 15%), 2-isopropylidene-3-oxa-4-methoxy-5-methoxycarbonyl-7,7-dimethyl-1-phenylbicyclo[4.1.0]hept-4-ene (**12**: 118 mg, 18%), and methyl 2-methoxycarbonyl-3-methyl-1-(3,3-dimethyl-2-phenylcyclopropen-1-yl)-2-pentenoate (**13**: 25 mg, 4%).

Data for 10. An oil; IR (neat) 1737 (C=O), 1597 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.66 (s, 3H, CH$_3$), 1.69 (s, 3H, CH$_3$), 1.85 (s, 3H, CH$_3$), 2.02 (s, 3H, CH$_3$), 3.51 (s, 3H, OCH$_3$), 3.75 (s, 3H, OCH$_3$), 7.24 (s, 5H, ArH), 7.85 (s, 1H, CH-2); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 21.2 (q), 22.0 (q), 23.1 (q), 23.3 (q), 51.9 (q, OCH$_3$), 52.5 (q, OCH$_3$), 122.6 (s), 126.0 (d), 127.3 (d, 2C), 129.3 (s), 129.8 (d, 2C), 131.9 (s), 133.2 (s), 135.0 (s) 140.5 (d), 147.6 (s), 165.9 (s, CO), 166.5 (s, CO); MS m/z (rel. intensity) 328 (M$^+$, 63), 296 (100). HRMS Found: m/z 328.1725. Calcd for $C_{20}H_{24}O_4$: 328.1675.

Data for 11. Colorless crystalline solid: mp 102–105°C (hexane); IR (neat) 1733 (C=O), 1602 (C=C) cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (s, 3H, CH$_3$), 1.27 (s, 3H, CH$_3$), 1.57 (s, 3H, CH$_3$), 1.73 (s, 3H, CH$_3$), 2.29 (s, 1H, 1-CH), 3.77 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 7.22–7.50 (m, 5H, aromatic H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 18.0 (q), 19.1 (q), 20.1 (q), 23.7 (q), 29.2 (s, C-5), 36.4 (d, C-1), 48.1 (s, C-4), 52.1 (q, OCH_3), 52.6 (q, OCH_3), 57.4 (s, C-2), 126.7 (d), 127.9 (d, 2C), 129.0 (s), 130.2 (s), 131.2 (d, 2C), 137.7 (s), 170.9 (s, CO), 171.3 (s, CO); MS *m*/*z* (rel. intensity) 328 (M^+, 67), 193 (100). HRMS Found: *m*/*z* 328.1731. Calcd for $C_{20}H_{24}O_4$: 328.1675.

Data for 12. An oil: IR (neat) 1720 ($C{=}O$), 1682 ($C{=}C$) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 3H, CH_3-7), 1.27 (s, 3H, CH_3-7), 1.68 (s, 3H, CH_3), 1,73 (3H, s, CH_3), 1.78 (s, 1H, CH-6), 3.70 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 7.21–7.36 (m, 5H, ArH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 17.5 (q), 19.9 (q), 24.4 (q), 29.4 (q), 29.7 (s, C-7), 32.1 (d, C-6), 50.9 (q, OCH_3), 55.6 (q, CH_3), 79.4 (s, C-1), 118.2 (s), 126.1 (d), 128.3 (d and s, 3C), 130.2 (s), 142.4 (d, 2C), 144.6 (s), 163.5 (s, CO), 167.8 (s); MS *m*/*z* (rel. intensity) 328 (M^+, 10), 143 (100). HRMS Found: *m*/*z* 328.1693. Calcd for $C_{20}H_{24}O_4$: 328.1675.

Data for 13. An oil: IR (neat) 1824 (cyclopropene), 1741 ($C{=}O$) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 6H, CH_3), 1.54 (d, *J*=0.8 Hz, 3H, CH_3), 1.82 (d, *J*=1.1 Hz, 3H, CH_3), 3.78 (s, 6H, OCH_3), 6.08 (septet, 1H, *J*=1.1 Hz, 1H, $=$CH), 7.26–7.49 (m, 5H, ArH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 19.0 (q), 23.1 (s), 24.7 (q, 2C), 26.5 (q), 53.0 (q, 2C, OCH_3), 58.3 (s), 120.3 (s), 123.4 (s), 125.1 (s), 128.3 (d), 128.5 (d, 2C), 129.1 (s), 129.6 (d, 2C), 138.6 (s) 169.3 (s, 2C, CO); MS *m*/*z* (rel. intensity) 328 (M^+, 17), 143 (100). HRMS Found: *m*/*z* 328.1670. Calcd for $C_{20}H_{24}O_4$: 328.1675.

4.3.2. Acetone-sensitized photolysis of 4. A solution of **4** (657 mg, 2.00 mmol) in acetone (400 cm^3) was irradiated under argon at room temperature for 5 h using a 100-W high-pressure mercury lamp with a pyrex jacket. After evaporation of the solvent, the residual oil was subjected to medium-pressure silica gel chromatography using 2% ether–hexane as an eluent to give **10** (79 mg, 12%) and **11** (20 mg, 3%).

4.3.3. Anthraquinone-sensitized photolysis of 4. A benzene solution (50 cm^3) of **4** (155 mg, 0.472 mmol) and anthraquinone (43 mg) in a pyrex tube was degassed with argon and then irradiated for 6.5 h using a 100-W high-pressure mercury lamp through a pyrex glass filter. The ester **4** was consumed by 12% according to GLC analysis. After evaporating solvent, the residue was subjected to preparative TLC to give **11** in 19% (26 mg) yield.

4.4. Photolyses of methyl (*E*)-4,4,7-trimethyl-5-phenyl-2,5,6-octatrienoate (5)

4.4.1. Direct photolysis of 5. A solution of **5** (543 mg, 2.00 mmol) in hexane (400 cm^3) was irradiated under argon at room temperature for 25 h using a 6-W low-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the residual oil was subjected to medium-pressure silica gel chromatography using 2% ether–hexane as an eluent to yield methyl (*E*)-4-isopropylidene-6-methyl-5-phenyl-2,5-heptadienoate (**14**: 5 mg, 1%), *trans*-2-isopropylidene-3-methoxycarbonyl-5,5-dimethyl-1-phenylbicyclo-[2.1.0]pentane (**15**: 136 mg, 25%), methyl 4-methyl-2-[(3,3-dimethyl-2-phenylcyclopropen-1-yl)-3-pentenoate (**16**: 81 mg, 15%), and methyl (*Z*)-4,4,7-trimethyl-5-phenyl-2,5,6-octatrienoate (**17**: 10 mg, 2%).

Data for 14. A colorless oil; IR (neat) 1720 ($C{=}O$), 1612 ($C{=}C$) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.62 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 3.71 (s, 3H, OCH_3), 5.79 (d, 1H, *J*=15.4 Hz, 2-CH), 7.20 (s, 5H, ArH), 7.82 (d, 1H, *J*=15.4 Hz, CH-3); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 20.2 (q), 21.4 (q), 22.1 (q), 23.4 (q), 51.4 (q, OCH_3), 117.7 (d, C-2), 126.1 (d), 127.7 (d, 2C), 129.4 (d, 2C), 132.3 (s), 132.9 (s), 135.1 (s), 141.1 (s) 142.0 (d, C-3), 142.9 (s), 168.4 (s, CO); MS *m*/*z* (rel. intensity) 270 (M^+, 64), 195 (56), 32 (100). HRMS Found: *m*/*z* 270.1565. Calcd for $C_{18}H_{22}O_2$: 270.1621.

Data for 15. A colorless oil; IR (neat) 1733 ($C{=}O$), 1602 ($C{=}C$) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.92 (s, 3H, CH_3-5), 1.23 (s, 3H, CH_3-5), 1.27 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.94 (s, 1H, CH-4), 3.16 (br s, 1H, CH-3), 3.78(s, 3H, OCH_3), 7.21–7.56 (m, 5H, ArH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.8 (q), 18.1 (q), 19.4 (q), 23.2 (q), 28.7 (s, C-5), 32.4 (d, C-4), 43.5 (d, C-3), 49.0 (s, C-1), 51.6 (q, OCH_3), 125.5 (s, $>C=$), 126.5 (d), 127.9 (d, 2C), 130.7 (s, $>C=$), 131.3 (d, 2C), 138.3 (s), 174.3 (s, CO); MS *m*/*z* (rel. intensity) 270 (M^+, 28), 211 (100), 195 (63). HRMS Found: *m*/*z* 270.1565. Calcd for $C_{18}H_{22}O_2$: 270.1621.

Data for 16. A colorless oil; IR (neat) 1824 (cyclopropene), 1735 ($C{=}O$) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.29 (s, 6H, $CH_3{\times}2$), 1.73 (d, 3H, *J*=1.3 Hz, CH_3), 1.80 (d, 3H, *J*= 1.3 Hz, CH_3), 3.74 (s, 3H, OCH_3), 4.52 (d, 1H, *J*=8.8 Hz, CH-2), 5.52 (d septet, 1H, *J*=8.8, 1.3 Hz, CH-3), 7.17–7.56 (m, 5H, ArH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 18.2 (q), 21.7 (q), 25.0 (s), 25.1 (q), 25.7 (q), 42.9 (d), 52.2 (q, CH_3O), 119.2 (d, $CH=$), 123.6 (s, C-1), 127.8 (d), 128.5 (d, 2C), 129.1 (d, 2C), 129.6 (s), 129.8 (s), 135.6 (s), 172.2 (s, CO); MS *m*/*z* (rel. intensity) 270 (M^+, 26), 211 (100). HRMS Found: *m*/*z* 270.1574. Calcd for $C_{18}H_{22}O_2$: 270.1621.

Data for 17. A colorless oil; IR (neat) 1983 ($C{=}C{=}C$), 1732 ($C{=}O$), 1639 ($C{=}C$) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.41 (s, 6H), 1.79 (s, 6H), 3.64 (s, 3H, OCH_3), 5.72 (d, 1H, *J*=13.2 Hz, $=$CH), 6.22 (d, 1H, *J*=13.2 Hz, $=$CH), 7.25–7.29 (m, 5H, ArH); MS *m*/*z* (rel. intensity) 270 (M^+, 9), 143 (100). HRMS Found: *m*/*z* 270.1569. Calcd for $C_{18}H_{22}O_2$: 270.1621.

4.4.2. Acetone-sensitized photolysis of 5. A solution of **5** (543 mg, 2.00 mmol) in acetone (400 cm^3) was irradiated under argon at room temperature for 15 h using a 100-W high-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using ether/hexane (2/98, v/v) as an eluent to give **14** (76 mg, 14%) and **15** (38 mg, 7%).

4.5. Photolyses of 6

4.5.1. Direct photolysis of 6. A solution of **6** (996 mg, 3.8 mmol) in acetonitrile (400 cm^3) was irradiated under an argon atmosphere using a 6-W low-pressure mercury lamp with a quartz jacket. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using EtOAc/hexane (5:95, v/v). The first fraction gave 5,5-dicyano-2,7-dimethyl-4-phenyl-2,3,6-octatriene (**20**) in 0.5% (5 mg) yield: IR (neat) 2200 (CN) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.45 (s, 6H, CH_3×2), 1.88 (d, 3H, J=1.4 Hz, =CCH_3), 2.00 (d, 3H, J=1.4 Hz, =CCH_3), 5.38 (septet, 1H,J=1.4 Hz, =CH), 7.20–7.66 (m, 5H, ArH); MS *m/z* (rel. intensity) 262 (M$^+$, 7), 248 (11), 247 (55), 232 (19), 144 (13), 143 (100), 128 (49), 127 (15), 115 (16), 103 (11) 91 (10), 77 (15). HRMS Found: *m/z* 262.1491. Calcd for $C_{18}H_{18}N_2$: 262.1471. The next fraction gave 2,2-dicyano-3-isopropylidene-5,5-dimethyl-4-phenylbicyclo[2.1.0]pentane (**19**) in 26% (255 mg) yield: colorless crystals (ether/hexane), mp 85–86°C; IR (KBr) 2242 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.03 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.60 (s, 3H, =CCH_3), 1.84 (s, 3H, =CCH_3), 2.37 (s, 1H, CH-1), 7.36 (s, 5H, ArH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 17.5 (q), 18.2 (q), 18.9 (q), 22.6 (q), 29.3 (s), 29.8 (s), 34.2 (d), 50.2 (s), 113.8 (s), 115.1 (s), 125.6 (s), 127.9 (d), 128.5 (d, 2C), 130.4 (d, 2C), 132.8 (s), 134.3 (s); MS *m/z* (rel. intensity) 262 (M$^+$, 30), 248 (20), 247 (100), 233 (12), 232 (44), 231 (10), 220 (22), 219 (16), 206 (11), 205 (19), 190 (10), 143 (10), 128 (19), 115 (13), 91 (11), 77 (14), 41 (11). Anal. calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.58; H, 7.05; N, 10.69. The third fraction gave 1,1-dicyano-3-isopropylidene-5-methyl-4-phenyl-1,4-hexadiene (**18**) in 53% (524 mg) yield; yellow crystals (ether/hexane); mp 82–86°C; IR (KBr) 2224 (CN), 1583, 1560 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.54 (s, 3H, CH_3), 1.70 (s, 3H, CH_3), 1.98 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 7.10–7.45 (m, 5H, ArH), 7.83 (s, 1H, =CH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 21.3 (q, 2C), 22.7 (q), 24.2 (q), 80.3 (s), 112.4 (s), 115.5 (s), 126.6 (d), 127.8 (d, 2C), 128.6 (s), 129.2 (d, 2C), 134.9 (s), 138.0 (s), 139.4 (s), 159.2 (d), 158.4 (s); MS *m/z* (rel. intensity) 263 (M$^+$+1, 16), 262 (M$^+$, 74), 248 (21), 247 (100), 233 (10), 232 (40), 231 (12), 230 (13), 220 (23), 219 (32), 218 (11), 207 (10), 106 (16), 205 (22), 190 (10), 185 (48), 165 (13), 143 (16), 129 (10), 128 (17), 119 (14), 116 (13), 115 (27), 103 (10), 91 (34), 77 (19), 51 (11), 41 (19), 39 (14). Anal. calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.50; H, 7.08; N, 10.60.

4.5.2. Acetone-sensitized photolysis of 6. The acetone solution (400 cm^3) of **6** (996 mg, 3.8 mmol) was irradiated under an argon atmosphere at room temperature for 4.5 h using a 100-W high-pressure mercury lamp with a pyrex jacket. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using 5% EtOAc–hexane as an eluent. The first fraction gave **19** in 38% (380 mg) yield. Next fraction gave 2-(1,1-dicyanoethen-2-yl)-3-isopropyl-1,1-dimethylindene (**21**) in 9% (87 mg) yield: yellow crystals (ether); mp 91–92°C; IR (KBr) 2218 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.39 (s, 6H, CH_3-1×2), 1.42 (d, 6H, J=8.5 Hz, CH_3×2), 3.27 (septet, 1H, J=8.5 Hz, CH), 7.26–7.44 (m, 3H, aromatic H, and =CH), 7.66–7.78 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.1 (q, 2C), 24.5 (q, 2C), 28.6 (d), 49.8 (s), 82.1 (s), 114.1 (s), 114.9 (s), 122.0 (d), 124.3 (d), 127.0 (d), 129.3 (d), 138.6 (s), 142.3 (s), 153.1 (d), 156.7 (s), 161.0 (s); MS *m/z* (rel. intensity) 262 (M$^+$, 42), 247 (18), 232 (15), 231 (10), 221 (12), 220 (67), 219 (35), 206 (20), 205 (100), 204 (10), 203 (10), 194 (24), 190 (18), 165 (12), 43 (21), 28 (26). Anal. calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.29; H, 7.09; N, 10.61.

4.5.3. Michler's ketone-sensitized photolysis of 6. An acetonitrile solution (50 cm^3) of **6** (134 mg, 0.52 mmol) and Michler's ketone (30 mg) in a pyrex tube was degassed with argon and then irradiated for 1 h using a 100-W high-pressure mercury lamp through a pyrex glass filter. After evaporated of the solvent, the residue was subjected to preparative TLC using EtOAc/hexane (5:95, v/v) to give **19** in 64% (86 mg) yield.

4.6. Photolyses of 7 and 8

4.6.1. Direct photolysis of 7. A solution of **7** (761 mg, 4.1 mmol) in acetonitrile (400 cm^3) was irradiated under an argon atmosphere at room temperature for 5 h with a 100-W high-pressure mercury lamp with a quartz jacket. After solvent removal, the residual oil was separated by medium-pressure silica gel chromatography using EtOAc/hexane (10:90, v/v). The first fraction gave 3,3-dicyano-2,7-dimethyl-2,5,6-octatriene (**24**: 5 mg, 0.7%); a yellow oil, IR (neat) 2250 (CN) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.83 [d, 6H, J=2.7 Hz, C=C=C(CH_3)$_2$], 1.84 (d, 3H, J=1.3 Hz, C=CCH_3), 1.98 (d, 3H, J=1.3 Hz, C=CCH_3), 5.23 (m, 2H, CH=C and CH=C=C); MS *m/z* (rel. intensity) 186 (M$^+$, 1), 185 (6), 171 (13), 120 (13), 119 (20), 105 (6), 67 (100), 65 (15), 41 (30). HRMS Found: *m/z* 186.1153. Calcd for $C_{12}H_{14}N_2$: 186.1158. The second fraction gave 2,2-dicyano-3-isopropylidene-5,5-dimethylbicyclo[2.1.0]pentane (**23**: 47 mg, 6%): a yellow oil, IR (neat) 2243 (CN) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.06 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.69 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.17 (d, 1H, J=5.3 Hz, CH-1), 2.51 (d, 1H, J=5.3 Hz, CH-4); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.1 (q), 18.1 (q), 18.5 (q), 23.2 (q), 26.5 (d), 27.8 (d), 29.4 (s, 2-C), 36.4 (s, C-5), 113.7 (s, CN), 114.9 (s, CN), 121.8 (s), 131.5 (s); MS *m/z* (rel. intensity) 186 (M$^+$, 7), 172 (11), 171 (97), 169 (10), 156 (32), 155 (11), 145 (16), 144 (100), 143 (20), 130 (13), 117 (25), 116 (18), 91 (13), 77 (14), 67 (23), 65 (12), 51 (13), 43 (17), 41 (43), 38 (37). HRMS Found: *m/z* 186.1176. Calcd for $C_{12}H_{14}N_2$: 186.1158. The final fraction gave 1,1-dicyano-3-(3-methyl-1,2-butadienyl)-2,2-dimethylcyclopropane (**22**: 84 mg, 11%): a yellow oil, IR (neat) 2250 (CN) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.39 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.74 (d, 3H, J=2.6 Hz, C=C=CCH_3), 1.75 (d, 3H, J=2.6 Hz, C=C=CCH_3), 2.35 (d, 1H, J=7.6 Hz, CH-3), 4.88 (dqq, 1H, J=7.6, 2.6, and 2.6 Hz, CH=C=C); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.0 (s, C-1), 17.3 (q), 20.1 (q), 20.2 (q), 23.8 (q), 35.1 (s, C-2), 41.3 (d, C-3), 80.4 (d, *C*H=C=C), 99.2 (s, CH=C=*C*), 113.0 (s, CN), 114.6 (s, CN), 205.9 (s, CH=*C*=C); MS *m/z* (rel. intensity) 186 (M$^+$, 8), 171 (99), 156 (35), 144 (41), 80 (34), 79 (36), 67 (100), 41 (61), 38 (45). HRMS Found: *m/z* 186.1176. Calcd for $C_{12}H_{14}N_2$: 186.1158.

4.6.2. Direct Photolysis of 8. A solution of **8** (633 mg, 4.0 mmol) in acetonitrile (400 cm^3) was irradiated under an argon atmosphere at room temperature for 55 h with a 6-W low-pressure mercury lamp with a quartz jacket. After solvent removal, the residual oil was separated by medium-pressure silica gel chromatography using EtOAc/hexane

(10:90, v/v) to yield 2,2-dicyano-5,5-dimethyl-3-methylenebicyclo[2.1.0]pentane (**26**: 50 mg, 8%) and 1,1-dicyano-2,2-dimethyl-3-(1,2-propadienyl)cyclopropane (**25**: 363 mg, 57%).

Data for 25. A yellow oil, IR 2242 (CN), 1954 (C=C=C) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.40 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.43 (ddd, 1H, J=1.8, 4.2, 6.2 Hz, CH-3), 5.20 (m, 3H, $CH=C=CH_2$); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.2 (s, C-1), 17.4 (q), 23.7 (q), 34.9 (s, C-2), 40.2 (d, C-3), 78.3 (t, $CH=C=\mathit{C}H_2$), 82.4 (d, $\mathit{C}H=C=CH_2$), 112.7 (s, CN), 114.3 (s, CN), 211.9 (s, $CH=\mathit{C}=CH_2$),; MS m/z (rel. intensity) 158 (M^+, 16), 157 (38), 143 (100), 116 (95), 93 (36), 92 (57), 65 (32), 51 (38), 39 (61). HRMS Found: m/z 158.0836. Calcd for $C_{10}H_{10}N_2$: 158.0845.

Data for 26. A yellow oil, IR 2245 (CN) cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.41 (s, 3H), 2.37 (d, 1H, J=4.9 Hz, CH-1), 2.63 (br d, 1H, J=4.9 Hz, CH-4), 5.22 (d, 1H, J=2.6 Hz, =CH), 5.34 (dd, 1H, J=1.4, 2.6 Hz, =CH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 16.1 (q), 23.2 (q), 27.2 (s), 30.5 (sd, 2C), 38.5 (d), 111.1 (t, $=CH_2$), 113.3 (s, CN), 115.1 (s, CN), 138.8 (s, C-3); MS m/z (rel. intensity) 158 (M^+, 4), 143 (87), 116 (100), 93 (30), 38 (32). HRMS Found: m/z 158.0858. Calcd for $C_{10}H_{10}N_2$: 158.0845.

4.6.3. Acetone-sensitized photolysis of 7 and 8. The acetone solution (400 cm^3) of **7** or **8** (0.01 mol dm^{-3}) was irradiated under an argon atmosphere at room temperature using a 100-W high-pressure mercury lamp with a pyrex jacket. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography to yield **23** or **26**. The yields of the products are described in Table 1.

4.7. MO calculation

MO calculation was performed using the UHF method for the biradical intermediate **31** and the RHF method for **14** and 2,2-dimethylpropylidenemalononitrile of Mac Spartan Plus of Wavefunction, Inc.

4.8. Measurements of quantum yields

The quantum yields for the isomerization of **4**–**6** to the photoproducts were measured by GCL or NMR 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 irradiation source. On the other hand, a 450-W high-pressure mercury lamp with a combination of a K_2CrO_4 solution and a pyrex glass filter was used as a 313-nm irradiation 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 irradiation source. Argon was bubbled into a solution (10 cm^3) of **4**–**6** (0.01 mol dm^{-3}) in a quartz or pyrex tube. The solution was irradiated at room temperature using each of the above lamps. The light intensity of the 254- and 365-nm irradiation sources was determined by tris(oxalato)ferrate(III) actinometry,[15] while that of the 313-nm radiation source was determined by stilbene actinometry.[15] The photolyses were performed at conversions of less than 20% of **4**–**6**. The data are described in Tables 2 and 3.

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