Pergamon

Tetrahedron 58 (2002) 7681–7689

TETRAHEDRON

Allenyl(vinyl)methane photochemistry. Photochemistry of γ-allenyl-substituted α,β-unsaturated enone derivatives

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Received 7 June 2002; accepted 13 July 2002

Abstract—The photolyses of the γ-allenyl-substituted alkylidenecycloalkanones underwent mainly *E*–*Z* geometric isomerization; several enones gave pyrans by the photochemical intramolecular oxa-Diels–Alder reaction and bicyclo[2.1.0]pentanes by the intramolecular [2+2] cycloaddition. The photolyses of the γ-(3-methyl-1,2-butadienyl)-substituted 3-alkylidenepenta-2,4-diones led to bicyclo[2.1.0]pentane, while the γ-(1,2-propadienyl-substituted) 3-alkylidenepenta-2,4-diones underwent intramolecular [2+2] cycloaddition and intramolecular oxa-Diels–Alder reaction. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The photochemical intramolecular [2+2] cycloaddition of α,β-unsaturated enones linked to an alkene by hydrocarbon chains is well-known, has been extensively investigated, and has found widespread application in organic synthesis.[1] An allene is a good alkene that undergoes photochemical intramolecular [2+2] cycloaddition.[1–3] The syntheses of natural products by the intramolecular [2+2] cycloaddition of allenes with α,β-unsaturated enones has been reported.[1,3]

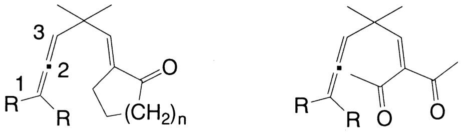
In the photochemistry of γ-allenyl-substituted α,β-unsaturated ketones, except for our communication,[4] there is only one report by Jeger et al., but its content is a mere note.[5] On the other hand, in the photochemistry of divinylmethane compounds, γ-vinyl-substituted α,β-unsaturated esters[6,7] and nitriles[6,8] underwent regioselective di-π-methane rearrangement by multiplicity control, while other photoreactions in addition to the di-π-methane rearrangement for the γ-vinyl-substituted α,β-unsaturated ketones took place.[9,10] Previously, we reported the photochemistry of allenyl(vinyl)methanes in which one vinyl is an α,β-unsaturated ester[11,12] or an α,β-unsaturated nitrile chromophore.[11] These compounds formed an intramolecular CT complex, and the excited state of each allenyl chromophore, vinyl chromophore, and CT complex, underwent different photoreactions. The energy levels and lifetimes of the n→π* and π→π* and the electron deficiency of the C=C moiety of the α,β-unsaturated ketones differ from those of the α,β-unsaturated esters. Thus we have considered that the newly prepared γ-allenyl-substituted α,β-unsaturated ketones undergo interesting photoreactions by an interaction between the allenyl and alkenoyl chromophores.

In this paper, we wish to report the photochemistry of the allenyl(alkenoyl)methanes **1**–**6** (Scheme 1).

2. Results

2.1. Preparation of the enones (1–6)

We first prepared the enones **1**–**4** by the aldol condensation of allenic aldehydes with cycloalkanones. Because the condensation with cyclopentanone using NaOMe as a base catalyst afforded a complex mixture, the isolation of **1** or **2** failed. On the other hand, **3** and **4** were obtained by purification using silica gel chromatography in 13 and 17% yields, respectively (Scheme 2). Kelleher et al.[13] have reported that α,β-unsaturated enones were prepared in good yields by the condensation using lithium iodide as a base catalyst. So we applied Kelleher's method for the condensation of allenic aldehydes with cyclopentanone. The enones **1** and **2** were obtained in satisfactory purity but in low yields (Scheme 3).



1: R=H, n=1
2: R=Me, n=1
3: R=H, n=2
4: R=Me, n=2

5: R=H
6: R=Me

Scheme 1.

Keywords: photochemistry; allenes; enones; Diels–Alder reactions; cycloadditions.

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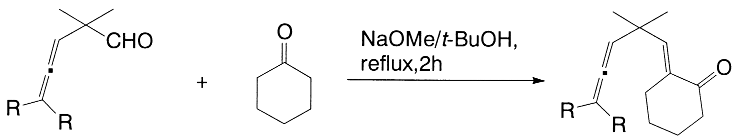
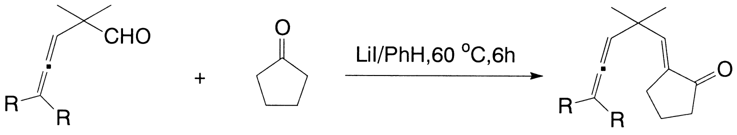
PII: S0040-4020(02)00856-6



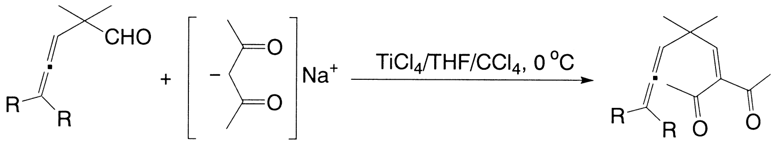
3: R=H
4: R=Me

Scheme 2.



1: R=H
2: R=Me

Scheme 3.



5: R=H
6: R=Me

Scheme 4.

Table 1. Photolyses of **1**–**6**

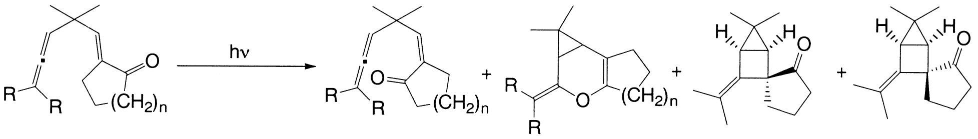
Enone	Time (h)	Products (isolated yields (%))			
1	6	**7** (8)	**8** (25)		
2	6	**9** (6)	**10** (5)	**11** (11)	**12** (17)
3	1	**13** (51)			
	18	(8)	**14** (6)		
4	1	**15** (51)			
5	9	**16** (7)	**17** (10)	**18** (2)	
6	4		**19** (22)		

The diketones **5** and **6** were prepared by Knoevenagel condensation of allenic aldehydes with sodium 2,4-pentanedionate using the procedure of Lehnert[14] (Scheme 4).

2.2. Photochemistry of the enones (1–4)

A solution of **1** in hexane was irradiated using a 100 W high-pressure mercury lamp with a pyrex jacket to give the (*Z*)-form **7** and pyran **8** (Table 1, Scheme 5), and considerable polymeric materials were further formed. A similar photolysis of **2** gave the pyran **10**, [2+2] cycloadducts **11** and **12**, and (*Z*)-form (**9**) (Table 1). It was found that the isolated *cis*-adduct **11** was readily isomerized to the *trans*-one **12** by observation of ^{1}H NMR. The photochemical isomerization of the (*E*) and (*Z*)-enones **1**, **2**, **7**, and **9** was analyzed by GLC. Each photolysis was found to form polymeric materials; hence, the total ratio of composition of the substrate and the intramolecular photoproducts decreased with prolongation of irradiation time. An induction period for the isomerization of the (*E*)-form **1** or **2** to the pyran **8** or **10** was found; whereas, in the direct photolyses of the (*Z*)-forms **7** and **9**, **8** and **10** were initially formed.

For the direct photolyses of **3** and **4**, the *E*–*Z* geometric isomerization mainly occurred, and these geometric isomers were observed in an ca. *E*/*Z*=1:9 ratio as a steady state. Upon irradiation for 1 h, (*Z*)-isomers **13** and **15** were both obtained in 51% isolated yields (Table 1). During the prolonged irradiation of **3** or **4**, the composition of the (*E*) and (*Z*)-forms gradually decreased due to their polymerization and the formation of complicated photoproducts. In the case of **3** upon irradiation for 18 h, the (*Z*)-form **13** and pyran **14** were obtained (Table 1). Because the pyran **14** was an unstable product especially under acidic condition,



1: R=H, n=1
2: R=Me, n=1
3: R=H, n=2
4: R=Me, n=2

7: R=H, n=1
9: R=Me, n=1
13: R=H, n=2
15: R=Me, n=2

8: R=H, n=1
10: R=Me, n=1
14: R=H, n=2

11

12

Scheme 5.

Table 2. Quantum yields for the isomerization in the direct photolyses of the enones

Enone	Solvent	Quantum yields		
		Φ_{oxa}[a]	Φ_{cy}[b]	Φ_{ge}[c]
1	Hexane	<0.0001		0.24
	Acetonitrile	<0.0001		0.30
2	Hexane	<0.0001	0.011	0.19
	Acetonitrile	<0.0001	0.023	0.23
3	Hexane	<0.0001		0.29
	Acetonitrile	<0.0001		0.31
4	Hexane			0.34
	Acetonitrile			0.43
7	Hexane	0.049		0.18
	Acetonitrile	0.033		0.15
9	Hexane	0.0072	0.010	0.15
	Acetonitrile	0.011	0.021	0.13
13	Hexane	0.012		0.12
	Acetonitrile	0.0066		0.10
15	Hexane			0.10
	Acetonitrile			0.11
5	Hexane	0.0049	0.0049	
	Acetonitrile	0.0047	0.0045	
6	Hexane		0.11	
	Acetonitrile		0.12	

A 450 W high-pressure mercury lamp with a combination of K_2CrO_4 solution and a pyrex glass filter was used as a 313 nm radiation source, and the light intensity was determined by stilbene actinometry.

[a] Quantum yield for the intramolecular oxa-Diels–Alder reaction.

[b] Quantum yield for the intramolecular [2+2] cycloaddition.

[c] Quantum yield for the $E\rightarrow Z$ or $Z\rightarrow E$ geometric isomerization.

Table 3. Quantum yields for the isomerization in the acetophenone-sensitized photolyses of the enones

Enone	Quantum yields		
	Φ_{oxa}[a]	Φ_{cy}[b]	Φ_{ge}[c]
1	<0.0001		0.27
2	<0.0001	0.012	0.22
3	<0.0001		0.26
4			0.26
7	0.014		0.32
9	0.0084	0.038	0.22
13	0.017		0.080
15			0.053
5	<0.0001	0.017	
6		0.27	

A 450-W high-pressure mercury lamp with a combination of K_2CrO_4 solution and a pyrex glass filter was used as a 313 nm radiation source, and the light intensity was determined by stilbene actinometry. Acetophenone: conc. 1.20 mol dm^{-3}. A hexane solution of the enones (0.01 mol dm^{-3}) in a pyrex tube was irradiated under an argon atmosphere at room temperature.

[a] Quantum yield for the intramolecular oxa-Diels–Alder reaction.

[b] Quantum yield for the intramolecular [2+2] cycloaddition.

[c] Quantum yield for the $E\rightarrow Z$ or $Z\rightarrow E$ geometric isomerization.

isolation from the mixture of the photoproducts by silica gel chromatography failed. However, when activated aluminum oxide (neutral) chromatography was carried out, we accomplished the separation of **14** from the mixture of the photoproducts.

The quantum yields for the isomerization of the enones **1**–**4**, **7**, **9**, **13**, and **15** are described in Table 2. Quantum yields for the isomerization of the (*E*)-enones **1**, **2**, and **4** to the pyrans **8**, **10**, and **14** were only trace amounts, while those of the (*Z*)-forms **7**, **9** and **13** were measurable values. Table 3 shows the quantum yields for isomerization in the acetophenone-sensitization of the enones **1**–**4**, **7**, **9**, **13**, and **15**. Acetophenone (E_T=310 kJ mol^{-1}) affected the intramolecular isomerization. Though the compounds **1** and **2** were non phosphorescent, **7** and **9** were observed to show phosphorescent emissions in an EPA (ether/isopentane/ethanol=5:5:2) matrix at 77 K, and their triplet energies were both estimated to be 280 kJ mol^{-1} by 0–0 bands. However, when 2-methyl-1,3-butadiene was used as a quencher, quenching effects for each isomerization were not observed.

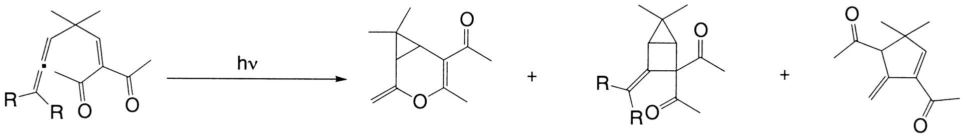
2.3. Photochemistry of the diketones (5 and 6)

The direct photolysis of **5** in hexane gave the pyran **16**, cycloadduct **17**, and cyclopentene **18** in 7, 10, and 2% isolated yields, respectively (Scheme 6). In a similar photolysis of **6**, intramolecular [2+2] cycloaddition preferentially proceeded to afford the intramolecular [2+2] cycloadduct **19** in 22% isolated yield. Quantum yields for the isomerization of the diketones **5** and **6** are described in Tables 2 and 3. Few solvent effects were found on the isomerization. Acetophenone (E_T=310 kJ mol^{-1}) sensitized the intramolecular [2+2] cycloaddition alone, and benzophenone (E_T=288 kJ mol^{-1}) also showed a sensitizing effect on the reaction. However, neither 4-phenylacetonaphthone (E_T=256 kJ mol^{-1}) nor 2-acetylnaphthalene (E_T=249 kJ mol^{-1}) had a sensitizing effect. Moreover, quenching effects by 2-methyl-1,3-butadiene on the isomerization of the enones were not observed. The quantum yield for the formation of **18** under the direct photolysis of **5** was only a trace amount. Although we considered that compound **18** was derived from the photolysis of the intramolecular [2+2] cycloadduct **17**, the direct photolysis of the isolated **17** did not lead to **18**.

3. Discussion

3.1. Intramolecular [2+2] cycloaddition

On the basis of the photochemistry of γ-allenyl-substituted



5: R=H
6: R=Me

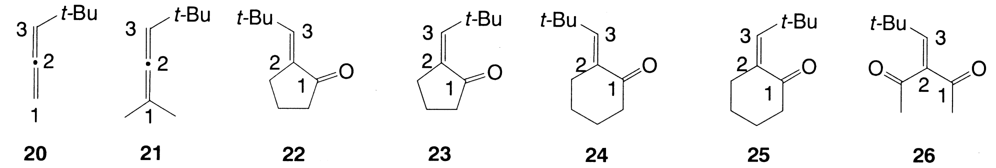
16

17: R=H
19: R=Me

18

Scheme 6.

Table 4. Calculated frontier orbital energies, HOMO and its coefficients of model compounds **20**–**26**



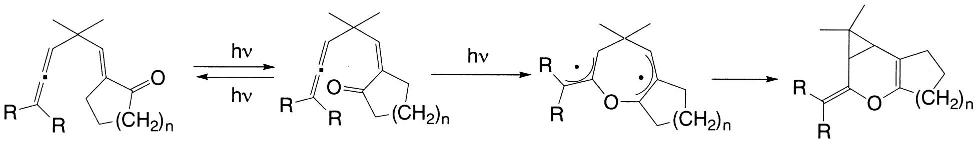
Compound	HOMO (eV)	MO coefficient			
		C_1	C_2	C_3	O
20	−9.82	−0.21	0.59	0.65	
21	−9.46	0.60	0.60	−0.18	
22	−10.03	0.01	−0.60	−0.60	0.23
23	−10.05	0.01	−0.56	−0.60	0.23
24	−9.94	0.04	−0.60	−0.61	0.22
25	−10.06	0.10	−0.61	−0.60	0.19
26	−10.60	0.19 (*E*)	−0.46	−0.31	0.28 (*E*)
		0.18 (*Z*)			0.46 (*Z*)

α,β-unsaturated esters and nitriles, we have obtained the following knowledge:[11,12]

1. Because the HOMO of a 1,2-propadienyl group lies at the C_2–C_3 moiety and the MO coefficients of C_3 is higher value than that of the C_2 (Table 4), the 1,2-propadienyl-substituted esters undergo more ineffective intramolecular [2+2] cycloaddition than the 3-methyl-1,2-propadienyl-substituted esters.
2. The allenyl(vinyl)methanes initially bond between the allene center carbon and the α-carbon of the α,β-unsaturated ester or the nitrile moiety to give cyclopentane-1,3-dienyl radicals.
3. The intramolecular [2+2] cycloaddition occurs via both singlet and triplet excited states.
4. The triplet intramolecular [2+2] cycloaddition occurs from the excited state of the α,β-unsaturated ester or the nitrile moiety.

Jeger et al.[5] reported that the 3-methyl-1,2-butadienyl-substituted alicyclic α,β-unsaturated enones readily underwent the intramolecular [2+2] cycloaddition. Judging by the quantum yields for the isomerization of the *exo*-cycloalkenones **1**–**4**, **7**, **9**, **13**, and **15**, the *E*–*Z* geometric isomerization mainly takes place, and the intramolecular [2+2] cycloaddition takes place as a side reaction in the photolyses of the enones **2** and **9**. On the other hand, the diketones **5** and **6** gave the intramolecular [2+2] cycloadducts **17** and **19**, but the quantum yield of **6**–**19** is a several tens of times greater than that of **5**–**17** (Tables 2 and 3). Such tendencies are analogous to the photochemistry of the γ-allenyl-substituted α,β-unsaturated esters;[11] hence, it is obvious that the HOMO in the allenyl moiety contributes greatly to the photochemical intramolecular [2+2] cycloaddition of these enones. The triplet energies of the enones **7** and **9** are ca. 280 kJ mol^{-1}, and further, those of the diketones **5** and **6** are estimated to be in range of 280–260 kJ mol^{-1}. These estimated triplet energies are close to the reported triplet energies of the α,β-unsaturated enones.[15] Therefore, the intramolecular [2+2] cycloaddition by the triplet sensitization occurs from the triplet-excited state of the enone moiety. Furthermore, due to the estimated triplet energies, it was expected that 2-methyl-1,3-butadiene could be efficient in the isomerization of the enones, though quenching effects were not found. Hence, it is considered that the isomerizations of these enones involve a singlet pathway.

Though we would have expected that the 3-methyl-1,2-butadienyl-substituted alkylidenecyclohexanones **4** and **15** undergoes intramolecular [2+2] cycloaddition, energy-wasting *E*–*Z* geometric isomerization mainly took place and prolonged irradiation produced polymers. A similar tendency for the preferential *E*–*Z* geometric isomerization was recognized in the photolyses of **3** except that pyran **14** was obtained under prolonged irradiation. We then performed PM3 MO calculations for the ground state of **20**–**26** as models of the chromophores of **1**–**7**, **9**, **13**, and **15** (Table 4). By the MO coefficients of the model compounds, it seems that the interaction between the α-carbon of the enone and the center carbon of the allene is possible. However, the intramolecular [2+2] cycloaddition of **1**–**4**, **7**, **9**, **13**, and **15** was hardly prohibited. This is considered that steric hindrance by the alkyl-substituent at the α-position of the enone moiety makes it hard for the intramolecular [2+2] cycloaddition to occur: i.e. overlapping between the MO's of the center carbon of the allene and of the α-carbon of these *exo*-cycloalkenones will be blocked. Especially, because the HOMO of the enones **1** and **3** lies at the 2,3-C=C moiety in the 1,2-propadienyl group and the MO at the 3-position has a larger coefficient than that at the 2-position (Table 4), no intramolecular [2+2] cycloaddition takes place. In the case of the photochemistry of the 1,2-propadienyl-substituted diketone **5**, the intramolecular [2+2] cycloadduct **17** was obtained. Because the HOMO of **26** lies at a lower level than that of the *exo*-cycloalkenones **22**–**25** due to two acetyl-substitutions at the geminal position on the vinyl moiety (Table 4), it is considered that some MO interaction between the α-carbon and the center carbon of the allene in **5** occurs. On the other hand, in the case of the photochemistry of the diketone **6**, because the HOMO of **21** lies at the 1,2-C=C moiety in the allenyl group, the intramolecular [2+2] cycloaddition progresses preferentially.



Scheme 7.

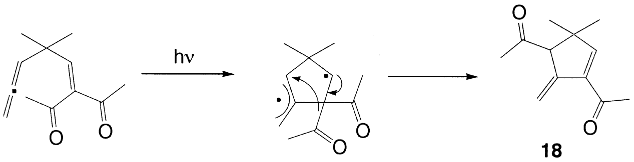
3.2. Intramolecular oxa-Diels–Alder reaction

In the photochemistry of these enones, except for **4** and **15**, the formation of pyrans by an intramolecular oxa-Diels–Alder reaction was found. It is obvious that the pyrans **8**, **10**, and **14** were derived from the photoreaction of the *Z*-enones by GLC analyses and the quantum yields. These results also suggest that an excited state of a *Z*-acetyl moiety in the diketone **5** afforded the pyran **16**. We have found the formation of the pyran-type compounds as by-products in some allenyl(vinyl)methane photochemistry,[11a–d,12] and further, it has been reported that the photochemistry of several alkenyl(alkenoyl)methane compounds (3,6-heptadien-2-ones) afforded pyran compounds via the intramolecular oxa-Diels–Alder reaction.[10] Such a photochemical oxa-Diels–Alder reaction initially causes bonding between the excited oxygen of the carbonyl group and the center carbon of the allene or the C_7 of the 3,6-heptadien-2-ones to afford oxacycloheptane biradical intermediates, followed by a ring closure to give the pyrans (Scheme 7). The *exo*-cycloalkenones have a reasonable *s-cis* conformation. In addition, the IR spectrum of the diketone **5** shows two types of carbonyl bands at 1712 and 1665 cm^{-1}. The former band suggests that either of the two acetyl groups of **5** has an *s-cis* conformation with the C=C bond. The five-membered enones undergo the oxa-Diels–Alder reaction more efficiently than the six-membered enones. By a PM3 molecular orbital calculation, the torsion angle about the *s-cis* C=C–C=O single bond in the *Z*-forms of the six-membered enones is ca. 70°, while the five-membered enones are nearly coplanar. These calculations were supported by UV-absorption spectra of the (*Z*)-enones: i.e. $n-\pi^*$ transitions of the (*Z*)-forms of the five-membered enones showed more bathchromic shifts (ca. 30 nm) than those of the six-membered enones.[16] Therefore, because a kink in the torsion angle in the C=C–C=O causes differences in the overlapping between the MO's of the center carbon of the allene and of the excited oxygen of the carbonyl group, we consider that ring-size effects on the photochemical intramolecular oxa-Diels–Alder reaction were found. Acetophenone sensitized the *exo*-cycloenones to undergo the oxa-Diels–Alder reaction but did not affect the diketone **5**. Furthermore, the quenching effects for the oxa-Diels–Alder reaction of the *exo*-cycloenones were not found. In the photochemistry of the γ-allenyl-substituted α,β-unsaturated esters in our previous reports, each pyran-type compound was obtained from direct photolysis only. However, it is considered that the pyrans **8**, **10**, and **14** are produced not only via a singlet pathway but also by a triplet pathway.

Although the allenes have been employed as useful dienophiles for dienes in the thermal Diels–Alder reaction[17] or for heterodienes in the photochemical intermolecular cycloaddition, namely the Schöenberg reaction,[18] such a photochemical intramolecular oxa-Diels–Alder reaction of the enone with the allene is the first example.

3.3. Formation of 18

Although we had considered that the cyclopentene **18** in the direct photolysis of **5** was produced from a photoreaction of the resulting bicyclo[2.1.0]pentane **17**, the isolated **17** upon direct irradiation did not afford **18**. This result suggests that the cyclopentene **18** was derived from the direct photolysis of **5**. Because the cyclopentene **18** is a by-product, the detailed mechanism has not been fully clarified, but we consider the following. The resulting cyclopentane-1,3-diyl radical undergoes a 1,3-acyl rearrangement to give **18** (Scheme 8).



Scheme 8.

4. Conclusion

Although the photolyses of the γ-allenyl-substituted alkylidenecycloalkanones mainly undergo *E*–*Z* geometric isomerization, the intramolecular oxa-Diels–Alder reaction and intramolecular [2+2] cycloaddition take place in the photolyses of several enones. The differences in these reactivities cause the configuration of the C=C–C=O moiety and the location of the HOMO in the allene moiety. Because the vinyl moiety of the γ-allenyl-substituted 3-alkylidene-2,4-pentadione is more electron-deficient than the γ-allenyl-substituted 3-alkylidenecycloalkanones, the intramolecular [2+2] cycloaddition occurs to give the bicyclo[2.1.0]pentanes.

5. Experimental

5.1. General

The melting points were determined on a micro hot stage (Yazawa) and are uncorrected. The NMR spectra were measured in a $CDCl_3$ or C_6D_6 solution using Bruker Avance-400 and JEOL JNM-EX 90 spectrometers. The IR spectra were obtained with a BIO-RAD FTS-60A spectrophotometer. The MS and HRMS were obtained with a JEOL JMS AX-500 and JEOL JMS-600H spectrometers. The UV-absorption spectra were measured on a Shimadzu UV-160A spectrophotometer. The phosphorescence spectra were measured on a Hitachi F-3010 spectrofluorometer attached to a phosphorescence-measurement apparatus.

Spectroscopic-grade hexane was washed with conc. H_2SO_4, distilled, and stored over 4Å molecular sieves. Spectroscopic-grade acetonitrile, benzene, and commercial acetone were stored over 4Å molecular sieves. The sensitizers used were recrystallized or distilled.

5.2. Preparation of 1–6

5.2.1. (*E*)-2-(2,2-Dimethyl-3,4-pentadienylidene)cyclopentanone (1) and (*E*)-2-(2,2,5-trimethyl-3,4-hexadienylidene)cyclopentanone (2). The aldol condensation using lithium iodide described by Kelleher et al. was used.[13] A benzene solution (100 cm^3) of cyclopentanone (8.6 g, 0.10 mol), the allenic aldehyde (0.10 mol), and lithium iodide (13.7 g, 0.10 mol) was stirred for 6 h at 60°C under an argon atmosphere. The reaction mixture was washed with water (100 cm^3), dried with $MgSO_4$ and evaporated in vacuo. The residual oil was chromatographed on silica gel using 3% ether–hexane as an eluent to give **1** and **2**.

*Data for **1***. Yield 9.1%; IR (neat) 1954 (C=C=C), 1721, (C=O), 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.24 (6H, s, 2-Me×2), 1.91 (2H, pentaplet, J=7.6 Hz, $CH_2CH_2CH_2$), 2.28 (2H, t, J=7.8 Hz, $COCH_2$), 2.74 (2H, dt, J=2.6, 7.3 Hz, =CCH_2), 4.81 (2H, d, J=6.6 Hz, C=C=CH_2), 5.19 (1H, t, J=6.6 Hz, CH=C=C), 6.55 (1H, t, J=2.6 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.9 (t), 27.3 (t), 28.0 (2C, q, 2-Me), 36.2 (s, 2-C), 37.6 (t), 77.5 (t, 5-C), 98.7 (d, 3-C), 135.3 (s, >C=), 143.3 (d, 1-C), 206.6 (s, 4-C), 208.5 (s, C=O); MS m/z (rel. intensity) 176 (M^+, 18), 161 (100), 148 (24), 137 (32), 133 (19), 120 (25), 119 (32), 105 (85), 95 (82), 91 (42), 79 (31), 77 (29), 67 (27), 53 (23), 41 (54), 32 (39), 26 (21). HRMS Found: m/z 176.1215. Calcd for $C_{12}H_{16}O$; M, 176.1202.

*Data for **2***. Yield 5.4%; IR (neat) 1968 (C=C=C), 1722, (C=O), 1639 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (6H, s, 2-Me×2), 1.71 (6H, d, J=2.9 Hz, C=C=CMe_2), 1.90 (2H, pentaplet, J=7.6 Hz, CH_2CH_2-CH_2), 2.27 (2H, t, J=7.6 Hz, $COCH_2$), 2.76 (2H, dt, J=2.7, 7.3 Hz, =CCH_2), 5.01 (1H, septet, J=2.9 Hz, CH=C=C), 6.56 (1H, t, J=2.7 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 19.9 (t), 20.6 (2C, q, 6-C), 27.6 (t), 28.1 (2C, q, 2-Me), 37.2 (s, 2-C), 37.6 (t), 97.5 (d, 3-C), 98.0 (s, 5-C), 134.9 (s, >C=), 144.1 (d, 1-C), 199.6 (s, 4-C), 208.5 (s, C=O); MS m/z (rel. intensity) 204 (M^+, 14), 189 (48), 161 (23), 148 (20), 138 (26), 137 (32), 134 (33), 95 (100), 67 (28), 55 (21), 41 (38). HRMS Found: m/z 204.1489. Calcd for $C_{14}H_{20}O$; M, 204.1515.

5.2.2. (*E*)-2-(2,2-Dimethyl-3,4-pentadienylidene)cyclohexanone (3) and (*E*)-2-(2,2,5-trimethyl-3,4-hexadienylidene)cyclohexanone (4). A solution of cyclohexanone (9.81 g, 0.10 mol), the allenic aldehyde (0.10 mol), and NaOMe (2.0 g, 0.05 mol) in *t*-butyl alcohol (100 cm^3) was refluxed for 2 h under an argon atmosphere in a water bath. The reaction mixture was evaporated under reduced pressure, and the residual oil was acidified with 1.0 mol dm^{-3} HCl solution and then extracted with CH_2Cl_2 (100 cm^3). The organic fraction was dried with $MgSO_4$ and evaporated in vacuo. The residue was chromatographed on silica gel eluting with 3% EtOAc–hexane to give **3** and **4**.

*Data for **3***. Yield 13%; IR (neat) 1954 (C=C=C), 1689, (C=O), 1612 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.24 (6H, s, 2-Me×2), 1.64–1.78 (2H, m, CH_2), 1.80–1.91 (2H, m, CH_2), 2.44 (2H, t, J=6.7 Hz, $COCH_2$), 2.65 (2H, dt, J=1.9, 6.9 Hz, =CCH_2), 4.80 (2H, d, J=6.6 Hz, C=C=CH_2), 5.21 (1H, t, J=6.6 Hz, CH=C=C), 6.53 (1H, t, J=1.9 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) 23.4 (t), 23.7 (t), 27.6 (t), 28.9 (2C, q, 2-Me), 35.6 (s, 2-C), 40.4 (t), 77.5 (t, 5-C), 99.2 (d, 3-C), 137.6 (s, >C=), 145.2 (d, 1-C), 202.2 (s), 206.5 (s); MS m/z (rel. intensity) 190 (M^+, 0.7), 175 (98), 162 (21), 151 (100), 148 (23), 133 (22), 119 (36), 105 (50), 91 (45), 81 (30), 79 (38), 77 (30), 67 (28), 55 (36), 53 (28), 43 (32), 41 (60), 39 (34), 26 (21). HRMS Found: m/z 190.1344. Calcd for $C_{13}H_{18}O$; M, 190.1358.

*Data for **4***. Yield 17%; IR (neat) 1950 (C=C=C), 1689, (C=O), 1611 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.20 (6H, s, 2-Me×2), 1.68–1.75 (2H, m, CH_2), 1.70 (6H, d, J=2.9 Hz, C=C=CMe_2), 1.81–1.88 (2H, m, CH_2), 2.43 (2H, t, J=6.7 Hz, $COCH_2$), 2.69 (2H, dt, J=2.0, 6.8 Hz, =CCH_2), 5.03 (1H, septet, J=2.6 Hz, CH=C=C), 6.55 (1H, t, J=2.0 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 (2C, q, 6-C), 23.4 (t), 23.6 (t), 27.6 (t), 29.1 (2C, q, 2-Me), 36.6 (s, 2-C), 40.4 (t), 98.3 (s, 5-C), 98.4 (d, 3-C), 137.2 (s, >C=), 146.1 (d, 1-C), 199.3 (s), 202.4 (s); MS m/z (rel. intensity) 218 (M^+, 15), 203 (91), 175 (22), 151 (100), 148 (49), 133 (34), 105 (26), 91 (29), 81 (38), 79 (28), 77 (21), 69 (27), 67 (44), 55 (40), 53 (21), 43 (40), 41 (70), 39 (22). HRMS Found: m/z 218.1651. Calcd for $C_{15}H_{22}O$; M, 218.1671.

5.2.3. 3-Acetyl-5,5-dimethyl-3,6,7-octatrien-2-one (5) and 3-acetyl-5,5,8-trimethyl-3,6,7-nonatrien-2-one (6). The $TiCl_4$ method described by Lehnert was used.[14] A solution of $TiCl_4$ (11 cm^3, 0.1 mol) in carbon tetrachloride (25 cm^3) was slowly added dropwise under argon to dry THF (200 cm^3) with stirring and cooling at 0°C. To the THF–$TiCl_4$ suspension was added a mixture of the allenic aldehyde (0.05 mol) and pyridine (8.0 cm^3, 0.10 mol) in THF (25 cm^3) and further, sodium 1,3-pentanedionate prepared by the reaction of sodium hydride (0.24 g, 0.10 mol) with 1,3-pentanedione (10.0 g, 0.10 mol) in DMF (50 cm^3) was added dropwise over 1 h. The mixture was stirred for 24 h at room temperature and then quenched with water (50 cm^3). The layers were separated. The organic layer was washed with sat. $NaHCO_3$ solution and sat. NaCl solution and then diluted with ether (50 cm^3). The separated aqueous layer was extracted with ether (50 cm^3×2). The combined ethereal layers were dried over $MgSO_4$ and evaporated in vacuo. The residue oil was distilled under reduced pressure, and a collective fraction in the range of 80–90°C (0.9 Torr, 1 Torr=133.322 Pa) was chromatographed on silica gel eluting with 10% EtOAc–hexane to give **5** and **6**.

*Data for **5***. Yield 23%; IR (neat) 1955 (C=C=C), 1712 (C=O), 1665 (C=O), 1626 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.26 (6H, s, 5-Me×2), 2.31 (3H, s, MeCO), 2.32 (3H, s, MeCO), 4.83 (1H, d, J=6.6 Hz, C=C=CH), 4.84 (1H, d, J=8.4 Hz, C=C=CH), 5.17 (1H, dd, J=6.6, 8.4 Hz, CH=C=C), 6.54 (1H, s, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.0 (q, 1-C), 28.3 (2C, q, 5-Me×2), 32.8 (q, 1-C), 37.0 (s, 5-C), 78.0 (t, 8-C), 98.2 (d, 6-C), 143.2 (s, 3-C), 151.2 (d, 4-C), 198.0 (s, C=O), 205.3 (s, C=O), 207.2 (s, 7-C); MS *m/z* (rel. intensity) 192 (M^+, 4), 178 (10), 177 (69), 159 (10), 150 (12), 149 (31), 137 (11), 135 (21), 134 (15), 107 (11), 91 (16), 43 (100). HRMS Found: *m/z* 192.1095. Calcd for $C_{12}H_{16}O_2$; M^+, 192.1151.

Data for ***6***. Yield 21%; IR (neat) 1967 (C=C=C), 1712 (C=O), 1665 (C=O), 1626 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.21 (6H, s, 5-Me×2), 1.71 (6H, d, *J*=2.9 Hz, C=C=CMe_2), 2.31 (3H, s, MeC=O), 2.34 (3H, s, MeC=O), 4.98 (1H, septet, *J*=2.9 Hz, C=C=CH), 6.56 (1H, s, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.3 (2C, q, 9-C), 25.9 (q, 1-C), 28.4 (2C, q, 5-Me), 33.0 (q, 1-C), 38.0 (s, 5-C), 96.9 (d, 6-C), 98.7 (s, 8-C), 143.0 (s, 3-C), 151.9 (d, 4-C), 198.1 (s, C=O), 200.1 (s, 7-C), 205.2 (s, C=O); MS *m/z* (rel. intensity) 220 (M^+, 5), 205 (18), 111 (10), 43 (100), 41 (13). HRMS Found: *m/z* 220.1432. Calcd for $C_{14}H_{20}O_2$; M, 220.1464.

5.3. Photochemistry of 1–6

5.3.1. Photochemistry of 1. A solution of **1** (800 mg, 4.55 mmol) in hexane (400 cm^3) was degassed with argon and then irradiated for 6 h using a 100 W high-pressure mercury lamp with a pyrex jacket. After evaporation of the solvent, the photoproducts were separated by medium-pressure silica gel chromatography using 2.5% ether–hexane as an eluent to give (*Z*)-2-(2,2-dimethyl-3,4-pentadienylidene)cyclopentanone (**7**: 64 mg, 8%) and 10,10-diemthyl-2-methylene-3-oxatricyclo[7.1.0.$0^{4,8}$]deca-4(8)-ene (**8**: 201 mg, 25%).

Data for ***7***. IR (neat) 1953 (C=C=C), 1715, (C=O), 1623 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.31 (6H, s, 5-Me×2), 1.71–2.05 (2H, m, CH_2), 2.34 (2H, t, *J*=7.1 Hz, $COCH_2$), 2.62 (2H, dt, *J*=1.6, 7.1 Hz, =CCH_2), 4.77 (2H, d, *J*=6.6 Hz, C=C=CH_2), 5.71 (1H, t, *J*=6.6 Hz, CH=C=C), 5.99 (1H, t, *J*=1.6 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.5 (t), 28.3 (2C, q, 2-Me), 34.0 (t), 35.9 (s, 2-C), 41.1 (t), 77.1 (t, 5-C), 99.4 (d, 3-C), 136.0 (s, =C), 147.2 (d, 1-C), 206.2 (s), 206.4 (s); MS *m/z* (rel. intensity) 176 (M^+, 25), 175 (21), 161 (100), 119 (23), 105 (51), 91 (29), 55 (25), 41 (28), 38 (24). HRMS Found: *m/z* 176.1230. Calcd for $C_{12}H_{16}O$; M, 176.1202.

Data for ***8***. IR (neat) 1702 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.86 (3H, s, 10-Me), 1.16 (3H, s, 10-Me), 1.29 (1H, d, *J*=8.5 Hz), 1.66 (d, *J*=8.5 Hz), 1.71–2.47 (6H, m, $CH_2CH_2CH_2$), 4.21 (1H, d, *J*=0.9 Hz, =CH), 4.52 (1H, d, *J*=0.9 Hz, =CH); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.9 (q), 19.6 (t), 24.0 (d), 25.5 (s, 10-C), 26.7 (q), 27.1 (d), 30.2 (t), 31.7 (t), 88.9 (t, =CH_2), 106.2 (s, =C), 146.8 (s, O–C=), 154.0 (s, O–C=); MS *m/z* (rel. intensity) 176 (M^+, 78), 175 (42), 161 (100), 135 (30), 121 (20), 119 (21), 105 (31), 91 (26), 55 (24), 43 (26), 41 (20). HRMS Found: *m/z* 176.1198. Calcd for $C_{12}H_{16}O$; M, 176.1202.

5.3.2. Photochemistry of 2. A solution of **2** (830 mg, 4.07 mmol) in hexane (400 cm^3) was degassed with argon and then irradiated for 6 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 2.5% ether–hexane as an eluent to give (*Z*)-2-(2,2,5-trimethyl-3,4-hexadienylidene)-cyclopentanone (**9**: 50 mg, 6%), 2-isopropylidene-10,10-dimethyl-3-oxatricyclo[7.1.0.$0^{4,8}$]deca-4(8)-ene (**10**: 42 mg, 5%), *cis*-3-isopropylidene-5,5-dimethylspiro[bicyclo[2.1.0]-pentane-2,2′-cyclopentanone (**11**: 91 mg, 11%), and its *trans*-isomer (**12**: 140 mg, 17%).

Data for ***9***. IR (neat) 2962, 2933, 2908, 2870, 1969 (C=C=C), 1717, (C=O), 1624 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 1.27 (6H, s, 2-Me×2), 1.68 (6H, d, *J*=2.6 Hz, C=C=CMe_2), 1.69–2.04 (2H, m, CH_2), 2.32 (2H, t, *J*=7.5 Hz, $COCH_2$), 2.61 (2H, dt, *J*=2.2, 9.2 Hz, =CCH_2), 5.38 (1H, septet, *J*=2.6 Hz, CH=C=C), 5.99 (1H, t, *J*=2.2 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.5 (t), 20.8 (2C, q, 6-C), 28.3 (2C, q, 2-Me), 34.0 (t), 37.2 (s), 41.0 (t), 97.3 (s, 5-C), 98.8 (d, 3-C), 135.5 (s, >C=), 148.0 (d, 1-C), 199.2 (s, 4-C), 206.0 (s, C=O); MS *m/z* (rel. intensity) 204 (M^+, 25), 189 (100), 186 (22), 171 (48), 161 (35), 148 (31), 137 (27), 134 (67), 133 (45), 119 (27), 105 (27), 95 (45), 91 (31), 79 (23), 77 (24), 67 (32), 55 (33), 43 (20), 41 (55), 38 (23). HRMS Found: *m/z* 204.1506. Calcd for $C_{14}H_{20}O$; M, 204.1515.

Data for ***10***. IR (neat) 2953, 2943, 2916, 2855, 1703 (C=C), 1680 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.76 (3H, s, 10-Me), 1.19 (3H, s 10-Me), 1.20 (1H, d, *J*=8.8 Hz, CH), 1.57 (1H, d, *J*=8.8 Hz, CH), 1.70 (6H, s, =CMe_2), 1.70–1.96 (2H, m, CH_2), 2.23–2.47 (4H, m, CH_2CH_2); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 15.5 (q), 16.6 (q), 18.8 (q), 19.5 (t), 22.8 (d), 23.4 (d), 25.1 (s, 10-C), 26.6 (q), 30.4 (t), 31.8 (t), 104.8 (s, =C), 108.7 (s, =C), 141.0 (s, O–C=), 147.9 (s, O–C=); MS *m/z* (rel. intensity) 204 (M^+, 90), 203 (28), 189 (100), 161 (37), 148 (27), 134 (58), 133 (36), 119 (27), 105 (27), 91 (25), 55 (21), 41 (32). HRMS Found: *m/z* 204.1492. Calcd for $C_{14}H_{20}O$; M, 204.1515.

Data for ***11***. IR (neat) 1734 (C=O), 1640 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.97 (3H, s, 5-Me), 1.20 (3H, s, 5-Me), 1.45 (3H, s, =CMe), 1.49 (1H, d, *J*=5.3 Hz, CH), 1.67 (3H, s, =CMe), 1.67–2.43 (7H, m, including CH as a doublet of *J*=5.3 Hz at 2.21 ppm); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 18.6 (q), 18.8 (q), 19.0 (q), 19.2 (t), 24.1 (q), 26.7 (s, 5-C), 31.8 (d, 1-C), 31.9 (t), 34.6 (d, 4-C), 38.4 (t), 56.5 (s, 2-C), 121.1 (s, =C), 133.7 (s, =C), 221.0 (s, C=O); MS *m/z* (rel. intensity) 204 (M^+, 11), 161 (47), 148 (45), 133 (100), 105 (21), 91 (22), 41 (24). HRMS Found: *m/z* 204.1506. Calcd for $C_{14}H_{20}O$; M, 204.1515.

Data for ***12***. IR (neat) 1736 (C=O), 1628 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.91 (3H, s, 5-Me), 1.28 (3H, s, 5-Me), 1.45 (3H, s, =CMe), 1.60 (3H, s, =CMe), 1.68 (1H, d, *J*=5.4 Hz, CH), 1.92–2.55 (7H, m, including CH as a doublet of *J*=5.4 Hz at 1.99 ppm); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 17.9 (t), 18.2 (q), 18.6 (t), 19.4 (t), 24.9 (q), 28.8 (s, 5-C), 32.6 (d, 1-C), 36.2 (t), 36.5 (d, 4-C), 36.8 (t), 55.6 (s, 2-C), 123.8 (s, =C), 130.7 (s, =C), 217.2 (s, C=O); MS *m/z* (rel. intensity) 204 (M^+, 10), 161 (50), 148 (41), 133 (100), 105 (23), 43 (57), 39 (24), 36 (29). HRMS Found: *m/z* 204.1475. Calcd for $C_{14}H_{20}O$; M, 204.1515.

5.3.3. Photochemistry of 3. A solution of **3** (760 mg, 4.00 mmol) in hexane (400 cm^3) was irradiated for 1 h using a 100 W high-pressure mercury lamp with a pyrex jacket under an argon atmosphere. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using 2.5% ether–hexane as an eluent to give (*Z*)-2-(2,2-dimethyl-3,4-pentadienylidene)-cyclohexanone (**13**) in 51% (390 mg) yield: IR (neat) 1953 (C=C=C), 1696 (C=O), 1636 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (6H, s, 2-Me×2), 1.70–1.81 (2H, m, CH_2), 1.88–1.94 (2H, m, CH_2), 2.39 (2H, br t, *J*=6.1 Hz, =CCH_2), 2.44 (2H, t, *J*=6.6 Hz, $COCH_2$), 4.74 (2H, d, *J*=6.6 Hz, C=C=CH_2), 5.27 (1H, t, *J*=6.6 Hz, CH=C=C), 5.41 (1H, t, *J*=1.3 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.1 (t), 27.4 (t), 29.2 (2C, q, 2-Me), 35.9 (s, 2-C), 39.2 (t), 44.8 (t), 77.0 (t, 5-C), 100.0 (d, 3-C), 139.0 (d, 1-C), 139.6 (s, =C), 206.6 (s, 4-C), 208.2 (s, C=O); MS *m*/*z* (rel. intensity) 190 (M$^+$, 10), 189 (25), 175 (100), 151 (35), 119 (20), 105 (31), 91 (28), 79 (21), 43 (23), 41 (31). HRMS Found: *m*/*z* 190.1344. Calcd for $C_{13}H_{18}O$; M, 190.1358.

5.3.4. 11,11-Dimethyl-2-methylene-3-oxatricyclo-[8.1.0.0^{4,9}]undeca-4(9)-ene (14). A hexane solution (170 cm^3) of **3** (324 mg) was irradiated for 18 h using a 100 W high-pressure mercury lamp with a pyrex jacket under an argon atmosphere. After evaporation of the solvent, the residue was chromatographed on neutral activated aluminum oxide to give **13** and **14** in 8% (29 mg) and 6% (20 mg) yields, respectively.

*Data for **14***. IR ($CHCl_3$) 1714 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89 (3H, s, 11-Me), 1.16 (3H, s, 11-Me), 1.60–2.42 (8H, m, $CH_2CH_2CH_2$ and 2×CH), 4.10 (1H, s, =CH), 4.42 (1H, s, =CH); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2 (q), 23.3 (t), 23.4 (t), 24.9 (s), 26.7 (t), 27.1 (d), 27.3 (d), 28.4 (q), 29.1 (t), 88.4 (t, =CH_2), 104.2 (s), 143.0 (s), 153.6 (s); MS *m*/*z* (rel. intensity) 190 (M$^+$, 51),189 (29), 176 (15), 175 (100), 162 (18), 148 (17), 133 (6), 119 (6), 105 (9). HRMS: *m*/*z* 190.1332. Calcd for $C_{13}H_{18}O$; M, 190.1358.

5.3.5. Photochemistry of 4. A solution of **4** (870 mg, 3.99 mmol) in hexane (400 cm^3) was irradiated for 1 h using a high-pressure mercury lamp with a pyrex jacket under argon atmosphere. After evaporation of the solvent, the residue was subjected to medium-pressure silica gel chromatography using 2.5% ether–hexane as an eluent to give (*Z*)-2-(2,2,5-trimethyl-3,4-hexadienylidene)cyclohexanone (**15**) in 51% (440 mg) yield. IR (neat) 1950 (C=C=C), 1689 (C=O), 1638 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.14 (6H, s, 2-Me×2), 1.69 (6H, s, C=C=CMe_2), 1.75–2.10 (4H, m), 2.30–2.55 (4H, m), 5.03 (1H, septet, *J*=2.6 Hz, CH=C=C), 5.39 (1H, t, *J*=2.6 Hz, CH=C); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 20.7 (2C, q, 6-C), 27.2 (t), 27.5 (t), 29.2 (2C, q, 2-Me), 37.0 (s, 2-C), 39.4 (t), 44.9 (t), 97.3 (s, 5-C), 99.0 (d, 3-C), 139.4 (2C, sd, 1-C and =C<), 199.4 (s, 4-C), 207.9 (s, C=O); MS *m*/*z* (rel. intensity) 218 (M$^+$, 12), 203 (100), 185 (55), 175 (20), 151 (34), 148 (63), 133 (29), 105 (25), 91 (25), 81 (20), 67 (24), 55 (30), 43 (31), 41 (50). HRMS Found: *m*/*z* 218.1651. Calcd for $C_{15}H_{22}O$; M, 218.1671.

5.3.6. Photochemistry of 5. A solution of **5** (768 mg, 4.00 mmol) in hexane (400 cm^3) was irradiated using a 100 W high pressure mercury lamp with a pyrex jacket under an argon atmosphere at room temperature. The reaction was monitored by GLC. Irradiation was stopped (9 h), when **5** had disappeared by 65%. After evaporation of the solvent, the residual oil was subjected to medium-pressure silica gel chromatography using 10% ether–hexane as an eluent to give 5-acetyl-4,7,7-trimethyl-2-methylene-3-oxabicyclo[4.1.0]hepta-4-ene (**16**: 55 mg, 7%), 2,2-diacetyl-5,5-dimethyl-3-methylenebicyclo[2.1.0]-pentane (**17**: 77 mg, 10%), and 1,4-diacetyl-3,3-dimethyl-5-methylenecyclopenta-1-ene (**18**: 13 mg, 2%).

*Data for **16***. IR (neat) 1699 (C=O), 1680 (C=C), 1590 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 0.73 (3H, s, 7-Me), 0.89 (3H, s, 7-Me), 1.19 (1H, d, *J*=8.8 Hz, 1-CH), 1.46 (1H, d, *J*=8.8 Hz, 6-CH), 1.98 (3H, s, COMe), 2.26 (3H, s, 4-Me), 4.21 (1H, d, *J*=0.9 Hz, =CH), 4.75 (1H, d, *J*=0.9 Hz); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 14.9 (q), 19.1 (q), 24.2 (d, 6-C), 25.1 (s, 7-C), 25.4 (d, 1-C), 26.4 (q), 29.7 (q), 92.5 (t, =CH_2), 108.8 (s, 5-C), 151.1 (s), 157.6 (s), 198.7 (s, CO); MS *m*/*z* (rel. intensity) 192 (M$^+$, 43), 177 (29), 149 (14), 135 (16), 91 (12), 43 (100). HRMS Found: *m*/*z* 192.1120. Calcd for $C_{12}H_{16}O_2$; M, 192.1151.

*Data for **17***. IR (neat) 1720 (C=O), 1699 (C=O), 1672 (C=C) cm^{-1}; ^{1}H NMR (C_6D_6, 90 MHz) δ 0.68 (3H, s, 5-Me), 0.94 (3H, s, 5-Me), 1.82 (1H, d, *J*=4.8 Hz, 4-CH), 1.98 (3H, s, COMe), 2.15 (1H, d, *J*=4.8 Hz, 1-CH), 2.29 (3H, s, COMe), 4.78 (1H, s, =CH), 5.17 (1H, d, *J*=0.9 Hz); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 17.9 (q), 24.1 (q), 25.4 (q), 27.2 (q), 27.6 (s, 5-C), 31.7 (d, 4-C), 35.6 (d, 1-C), 73.6 (s, 2-C), 108.3 (t, =CH_2), 143.7 (s, 3-C), 202.2 (s, CO), 206.3 (s, CO); MS *m*/*z* (rel. intensity) 192 (M$^+$, 0.1), 150 (12), 149 (15), 135 (15), 108 (20), 107 (17), 93 (10), 91 (13), 43 (100). HRMS Found: *m*/*z* 192.1120. Calcd for $C_{12}H_{16}O_2$; M, 192.1151.

*Data for **18***. IR (neat) 1720 (C=O), 1699 (C=O), 1672 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.13 (3H, s, 3-Me), 1.28 (3H, s, 3-Me), 2.11 (3H, s, COMe), 2.39 (3H, s, COMe), 3.50 (1H, dd, *J*=1.7, 1.8 Hz, 4-CH), 5.07 (1H, dd, *J*=1.3, 1.7 Hz), 5.07 (1H, d, *J*=1.8 Hz), 6.71 (1H, d, *J*=1.3 Hz); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 22.8 (q), 28.3 (q), 29.7 (q), 30.7 (q), 46.0 (s, 3-C), 68.4 (d, 4-C), 112.6 (t, =CH_2), 139.4 (s, =C), 146.1 (s, =C), 157.5 (d, =CH), 196.2 (s, CO), 207.8 (s, CO); MS *m*/*z* (rel. intensity) 192 (M$^+$, 54), 150 (44), 149 (73), 135 (70), 119 (10), 109 (11), 108 (100), 107 (66), 93 (33), 91 (29), 79 (15), 77 (12), 65 (14). HRMS Found: *m*/*z* 192.1088. Calcd for $C_{12}H_{16}O_2$; M, 192.1151.

5.3.7. Photochemistry of 6. A solution of **6** (880 mg, 4.00 mmol) in hexane (400 cm^3) was irradiated using a 100-W high-pressure mercury lamp with a pyrex jacket under an argon atmosphere at room temperature. The reaction was monitored by GLC. Irradiation was stopped for 9 h, when **6** had disappeared by 5%. After evaporation of the solvent, the residual oil was subjected to medium-pressure silica gel chromatography using 10% ether–hexane as an eluent to give 2,2-diacetyl-3-isopropylidene-5,5-dimethylbicyclo-[2.1.0]pentane (**19**) in 22% (193 mg): IR (neat) 1719

(C═O), 1691 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz) δ 1.05 (3H, s, 5-Me), 1.06 (3H, s, 5-Me), 1.62 (3H, s, ═CMe), 1.66 (3H, s, ═CMe), 1.97 (1H, d, J=5.1 Hz, 4-CH), 2.11 (3H, s, COMe), 2.29 (3H, s, COMe), 2.34 (1H, d, J=5.1 Hz, 1-CH); ^{13}C NMR (CDCl$_3$, 22.5 MHz) δ 17.2 (q), 19.3 (q), 19.5 (q), 24.2 (q), 25.1 (q), 26.8 (s, 5-C), 27.4 (q), 29.7 (d, 1-C), 35.4 (d, 4-C), 71.9 (s, 2-C), 126.5 (s), 128.1 (s), 205.1 (s, CO), 207.1 (s, CO); MS m/z (rel. intensity) 220 (M$^+$, 1), 177 (43), 135 (69), 121 (14), 119 (21), 43 (100). HRMS Found: m/z 220.1408. Calcd for $C_{14}H_{20}O_2$; M, 220.1464.

5.4. Measurements of quantum yields

The quantum yields of the isomerization of **1–6** to the photoproducts were measured by GLC analyses, and the photolyses were carried out by a merry-go-round method. A 450 W high-pressure mercury lamp through a combination of a K_2CrO_4 solution and a pyrex filter was used as a 313 nm irradiation source. Argon was bubbled into a solution (10 cm^3) of **1–7**, **9**, **13**, and **15** (0.01 mol dm^{-3}) in a pyrex tube. The solution was irradiated at room temperature. The light intensity was determined by stilbene actinometry.[11] These quantum yields are described in Tables 2 and 3.

5.5. MO Calculation

MO calculation was performed using the PM3 method of Hyper Chem from Auto Disk, Inc., or Mac Spartan Plus of Wavefunction, Inc.

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