Tandem Cyclizations Involving Carbene as an Intermediate: Photochemical Reactions of Substituted 1,2-Diketones Conjugated with Ene-Yne

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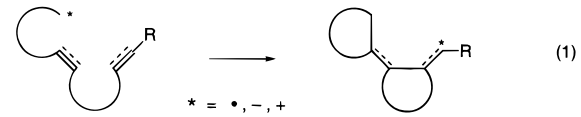
Received March 8, 1999. Revised Manuscript Received June 22, 1999

Abstract: We have investigated photoreactions of a novel system in which a carbene generator and a carbene trap are contained in the same molecule for studying tandem cyclizations involving carbene. The photocyclization of 1,2-diketones conjugated with ene-yne to (2-furyl)carbene was employed as a carbene-generating system. Upon photoirradiation of 1,2-diketones possessing biphenyl and 2-acetyl-1-cyclopentenyl systems as a carbene trapping unit in aprotic solvents, we observed tandem cyclizations via a carbene intermediate to produce fluorenylfuran and bifuran derivative with nearly quantitative yield, respectively. The solvent dependency for the tandem cyclization clearly indicated that 1,2-diketone is equilibrated with (2-furyl)carbene under the steady state photoirradiation conditions. The results reported here indicated that such compounds containing a carbene generator and a trap within a molecule are extremely useful for studying the sequential carbene addition reaction.

Introduction

Tandem or sequential cyclizations involving cations,[1a,2] anions,[1a] radicals,[1,3] and metal carbenoids[4] as well as those catalyzed by transition metals[5] are well-known. Equation 1 represents a general scheme for such reactions, where alkenes or alkynes play a key role as a bridge that mediates a transfer of a reactive intermediate. In contrast, such sequential cyclizations involving a carbene intermediate are not common, although 1,3- and 1,2-carbene migrations are well-known for propargyl[6] and alkenyl[7] carbenes, respectively.



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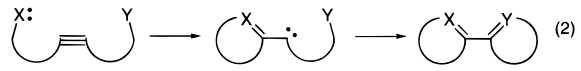
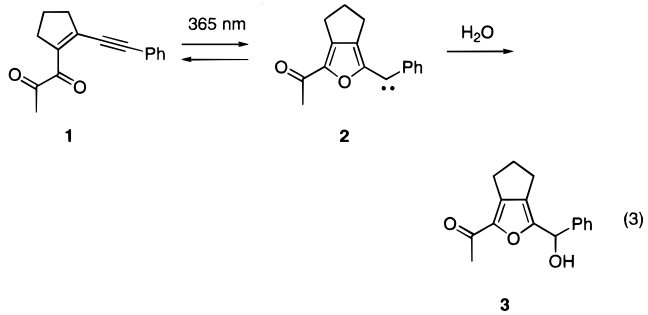


(2)

As a part of our continuing interest for a sequential carbene cyclization, as exemplified in eq 2, we have examined the design and synthesis of such molecular systems which contain two essential molecular units of a carbene generator and a trap. We previously reported a novel photocyclization of 1,2-diketones conjugated with ene-yne **1** to furan derivative **3** via carbene intermediate **2** (eq 3).[8,9] In our preliminary studies on the photocyclization, we proposed an equilibration between **1** and **2** under the steady-state photoillumination conditions.[9] Taking into account the efficiency of the carbene generation from 1,2-diketones in combination with synthetic accessibility, a carbene-generating system such as **4** was connected to the peripheral π systems that can effectively trap the carbene intermediate as exemplified by **5** and **6**. Butadienyl (X = CH_2)[10] and 4-oxa-butadienyl carbenes (X = O)[11] are known to spontaneously undergo 6π electrocyclization to produce cyclopentadiene and furan derivatives, respectively (eq 4).



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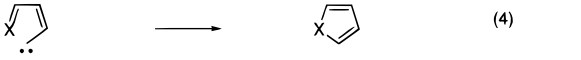

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We herein describe a novel photoinduced tandem cyclization of **5** and **6** involving a carbene as an intermediate. Upon irradiation, both **5** and **6** undergo a tandem cyclization with high efficiency to produce corresponding fluorenylfuran and bifuran

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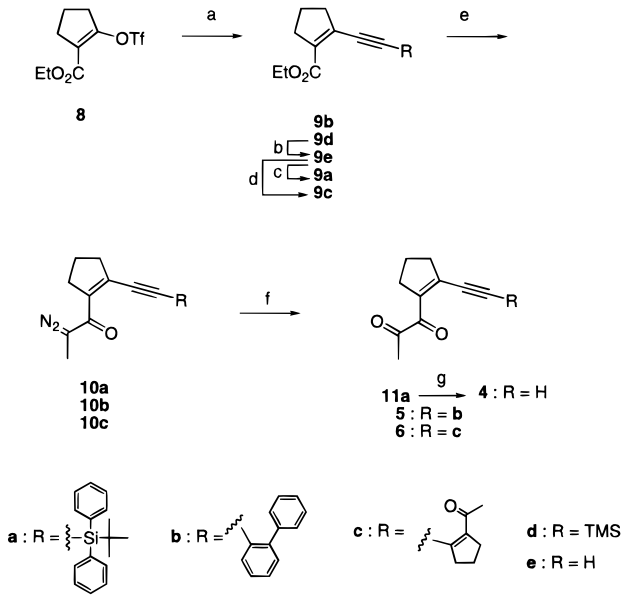
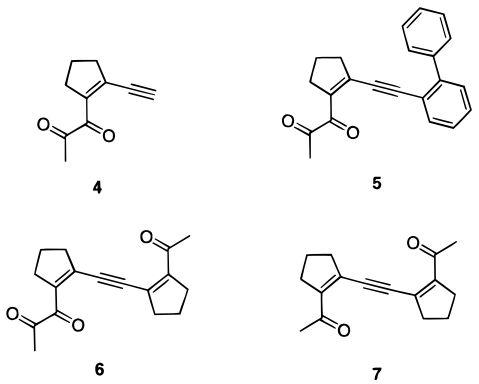
10.1021/ja990763q CCC: $18.00
Published on Web 08/25/1999

Scheme 1[a]



[a] Reagents and conditions: (a) (2-phenylphenyl)acetylene (for **9b**), trimethylsilylacetylene (for **9d**), $PdCl_2(PPh_3)_2$, 2,6-lutidine, CuI, DMF, 56% (for **9b**), 67% (for **9d**); (b) TBAF, AcOH, THF, 82%; (c) lithium hexamethyldisilazide, *t*-$BuPh_2SiCl$, −78 °C, 87%; (d) 2-acetyl-1-cyclopenten-1-yl trifluoromethanesulfonate, $PdCl_2(PPh_3)_2$, 2,6-lutidine, CuI, DMF, 62%; (e) (1) NaOH, H_2O, MeOH, room temperature; (2) $(COCl)_2$, benzene, then CH_3CHN_2, 78% (for **10a**), 37% (for **10b**), 33% (for **10c**); (f) PPh_3, ether, then $NaNO_2$, 2 N HCl, THF, 94% (for **11a**), 52% (for **5**), 46% (for **6**), 49%; (g) TBAF, AcOH, THF, 79%.

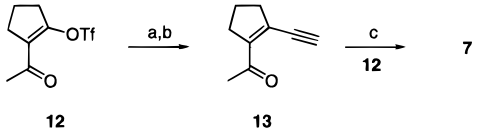
derivatives, respectively. These studies demonstrated that 1,2-diketones conjugated with ene-yne are actually equilibrated with the (2-furyl)carbene under steady state photoillumination conditions, and molecular systems containing carbene generator and a trap within a molecule are widely applicable to sequential carbene addition reactions.



Results

Synthesis of Substituted 1,2-Diketones. We have synthesized 1,2-diketones **4**, **5**, and **6** and reference compound **7** according to the method previously reported for the synthesis of **1** (Scheme 1).[8,9] The palladium-catalyzed cross coupling of enol triflate **8** with (2-phenylphenyl)acetylene[12] produced ene-yne esters **9b**. The coupling of **8** with trimethylsilylacetylene produced **9d**, which was desilylated to **9e**. Silylation of **9e** with *tert*-butyldiphenylchlorosilane produced **9a** and the cross coupling with 2-acetyl-2-cyclopenten-1-yl trifluoromethanesulfonate gave **9c**. Three-step sequence for an ester hydrolysis of **9a**−**c**, acid chloride formation, and diazoethane addition afforded α-diazo ketones **10a**−**c**, which were transformed into 1,2-diketones **11a**, **5**, and **6** by treating with triphenylphosphine and sodium nitrite in aqueous acid, respectively.[13] Diketone **4** was obtained by desilylation of **11a**. Similarly, C_2 symmetric diketone **7** was obtained by a sequential coupling of enol triflate **12** with trimethylsilylacetylene (Scheme 2).

Scheme 2[a]



[a] Reagents and conditions: (a) $Me_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, 2,6-lutidine, CuI, DMF, 93%; (b) TBAF, AcOH, THF, 73%; (c) **12**, $PdCl_2(PPh_3)_2$, 2,6-lutidine, CuI, DMF, 36%.

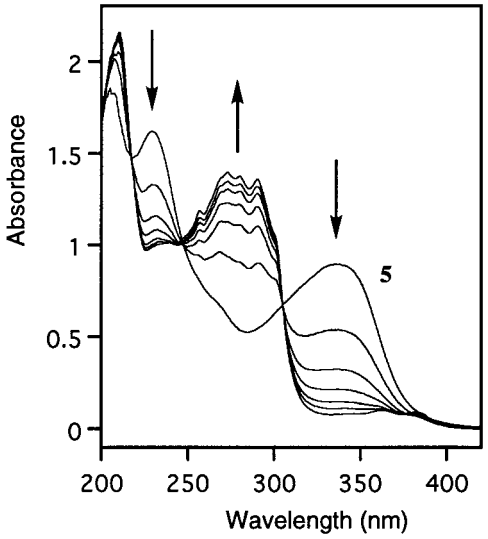
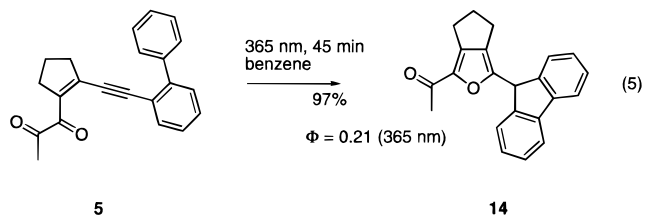


Figure 1. Spectral change during the photoirradiation of **5** (6.25×10^{-5} M) in acetonitrile with 382 nm light obtained from a monochromator (0, 100, 200, 300, 400, 500, and 800 counts of irradiation time). The photocyclization has completed in 800 counts irradiation.

Photoreactions in Aprotic Solvents. We carried out photoreactions of **5** and **6** in benzene at 365 nm with a transilluminator. The photoreaction of **5** produced a single product in an almost quantitative yield (eq 5). We observed clear isosbestic



(5)

points on UV spectral change during the photoirradiation with 382 nm light isolated from a monochromator (Figure 1). The molecular formula of the product determined by HRMS was $C_{22}H_{18}O_2$, which was the same as that of starting **5**. The ^1H NMR spectra of the product showed a characteristic singlet at 5.28 ppm (Figure 2) that was directly attached to the carbon

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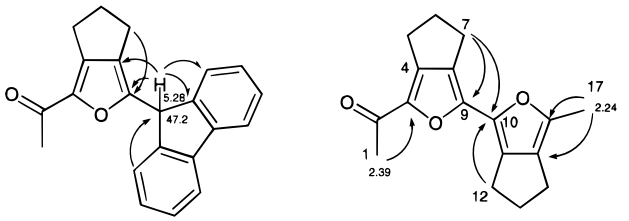


14 **15**

Figure 2. The key C−H correlations observed in the HMBC spectra of **14** and **15**.

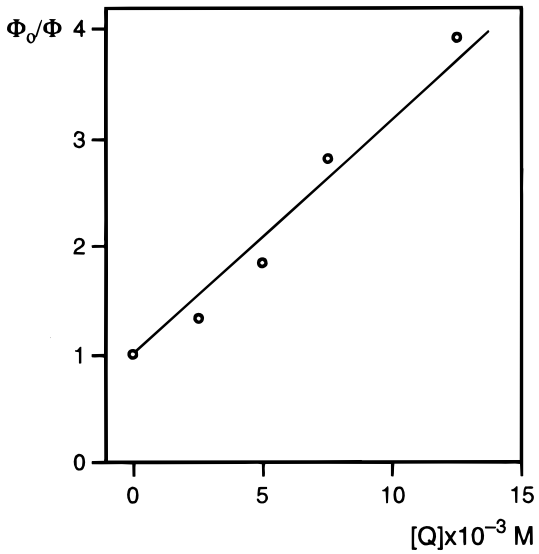
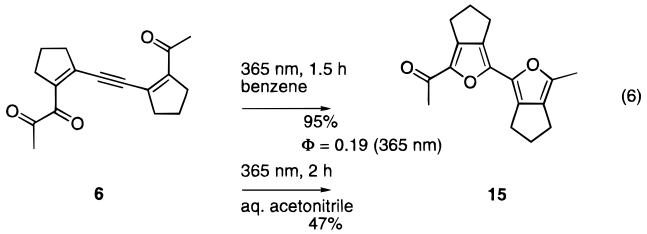


Figure 3. Stern−Volmer plot of relative quantum yields for the photocyclization of **5** in the presence of triplet quencher (*E*,*E*)-1,4-diphenyl-1,3-butadiene. The quantum yield measurements were carried out with **5** (1 mM) in the presence of the quencher (0, 2.5, 5, 7.5, and 12.5 mM) in acetonitrile at 382 nm. The relative quantum yield (Φ_o/Φ) was plotted against quencher concentration [Q].

observed at 47.2 ppm in the ^{13}C NMR spectra. We observed seven aromatic carbons attached to a hydrogen (−CH═) in ^{13}C NMR of **5**, but only four of such carbons were detected in the product, indicating that there is a symmetric structure in the product with regard to the aromatic rings. On the basis of these data and the long-range C−H correlations observed in the HMBC spectra (Figure 2), we identified the product as fluorenylfuran **14**. The quantum yield for the disappearance of **5** in acetonitrile at 365 nm was 0.21, and the photocyclization was quenched by (*E*,*E*)-1,4-diphenyl-1,3-butadiene. Stern−Volmer analysis at 382 nm irradiation showed a linear correlation between relative quantum yields and quencher concentrations with a correlation coefficient (*r*) of 0.985 with a slope ($k_q\tau$) of 227 M^{-1} (Figure 3).

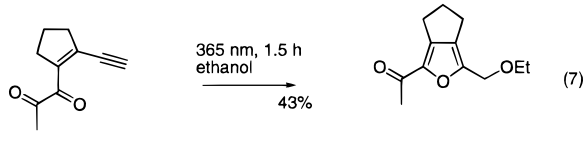
Photoirradiation of **6** for 1.5 h at room temperature also produced a single product (eq 6). The ^{1}H NMR spectra of the



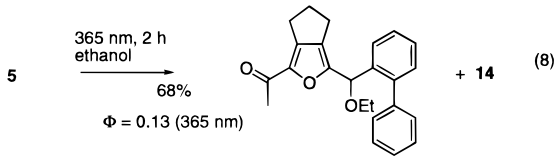
6 **15** (6)

product showed two methyl signals at 2.24 and 2.39 ppm with a small upfield shift from those observed at 2.40 and 2.48 ppm for **6** (Figure 2). It was apparent from the ^{13}C NMR spectra that two acetylenic carbons and two of three carbonyl carbons did not exist in the product, but there are eight sp^2 carbons in addition to one carbonyl carbon instead. HRMS of the product indicated a molecular formula of $C_{17}H_{18}O_3$, which is the same as that of starting **6**. We confirmed the structure of the product as bifuran **15** by observing long-range C−H correlations in the HMBC spectra between C9−H7, C10−H7, and C10−H12 (Figure 2). Other 1,2-diketones **1** and **4** were recovered unchanged under the photoirradiation conditions. Attempts to trap the intermediate carbene by external alkenes also resulted in a recovery of starting material. We examined the direct and triplet-sensitized photoreactions of C_2 symmetric diketone **7**, but no significant product was obtained, indicating that the 1,2-diketone chromophore is indispensable for the carbene generation.

Photoreactions in Protic Solvents. 1,2-Diketone **4** undergoes a smooth photocyclization in ethanol to produce **16** (eq 7).



4 **16** (7)



5 **17** (8)

Protonation of the initially formed (2-furyl)carbene intermediate followed by a solvent addition to the resulting cation would rationalize the formation of **16**.[14,15] With regard to the photoreaction of 1,2-diketones **5** and **6**, a competition between the carbene trapping by electrocyclization and the protonation with solvents may be conceivable. Photoirradiation of **6** in aqueous acetonitrile produced bifuran **15** as a major product in 47% isolated yield (eq 6). We could not isolate the product derived from protonation of the initially formed furylcarbene. In sharp contrast, photoirradiation of **5** in ethanol produced furan derivative **17** possessing an ethoxyl group α to the furan ring in 68% yield together with a trace amount of **14** (eq 8). The quantum yield for the disappearance of **5** in ethanol was 0.13, which is about 60% of that observed for the cyclization to **14** in benzene. Protonation of the intermediate carbene with ethanol is a bimolecular reaction, whereas a carbene trapping by the internal biphenyl subunit was an unimolecular reaction. Therefore, the efficiency for the formation of **17** should be dependent on the ethanol concentration. Actually, photoreactions of **5** in a mixed solvent of ethanol and benzene produced both **14** and **17** with the ratio being dependent on ethanol concentration (Table 1). A normalized ratio of the two products was 13:87 in 50% ethanol in benzene, whereas the ratio became 58:42 when the benzene−ethanol ratio was 32:1.

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Table 1. Product Distribution in the Photoreactions of **5** at a Different Concentration of Ethanol in Benzene[a]

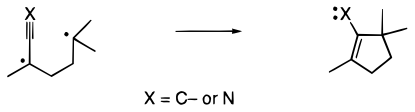
ethanol−benzene	**14**[b]	**17**[b]	ethanol−benzene	**14**[b]	**17**[b]
1:1	13	87	1:32	58	42
1:2	16	84	1: 64	76	24
1:8	26	74	1:128	95	5
1:16	44	56			

[a] Photoreaction of **5** was carried out in the indicated solvent mixture (2 mL). Product ratio was determined by ^{1}H NMR. NMR analysis of the crude products indicated that both **14** and **17** were the predominant products in all runs. [b] The ratio of two products was normalized.

Discussions

Synthetic Accessibility. As illustrated in Scheme 1, 1,2-diketones conjugated with ene-yne were readily synthesized from the corresponding α-diazo ketones. A most significant feature on the synthetic scheme was that various π conjugated subunits were directly connected to the carbene-forming carbon by using palladium-catalyzed cross coupling reactions.

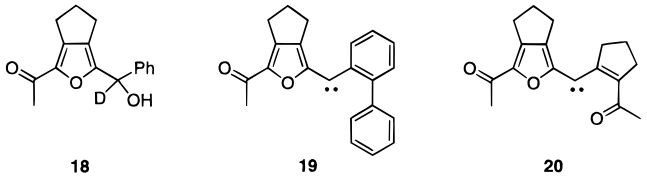
Mechanism for the Carbene-Generating Step. The photocyclizations described here are reminiscent of the cyclization of the propargyl 1,4-diradicals to produce the cycloalkenyl carbenes[11b,16,17] as well as of the related cyclization producing nitrenes as we reported earlier (eq 9).[18] It was well rationalized



(9)

that such cyclizations proceed via triplet diradicals.[16] The photocyclization of **5** in the presence of varying amounts of (*E,E)*-1,4-diphenyl-1,3-butadiene (E_T = 177 kJ/mol)[19] as a triplet quencher showed a linear correlation between the relative quantum efficiency and quencher concentrations with a Stern−Volmer slope of 227 M^{-1}. However, it was not quenched by (*E*)-stilbene with E_T of 227 kJ/mol. If we assume that the quenching by 1,4-diphenyl-1,3-butadiene is diffusion controlled ($\sim 10^{10}$ M^{-1} s^{-1}), the lifetime of excited triplet **5** is 23 ns. The fact that C_2 symmetric diketone **7** did not cyclize under both direct and triplet-sensitized conditions indicated that the 1,2-diketone chromophore is essential for the cyclization. We concluded that the photocyclization of the 1,2-diketones conjugated with ene-yne proceeded from its lowest triplet excited state. The quantum yields for the disappearance of **5** in both benzene and ethanol were 0.21 and 0.13, respectively.

Solvent Dependency for the Carbene Reaction. In aprotic solvents, 1,2-diketones **1** and **4** were photostable, but they efficiently produced corresponding furan derivatives **3** and **16** in protic solvents by solvent incorporation. Such remarkable solvent dependency was due to the irreversible trapping of the intermediate carbene by protic solvents. The direct evidence for the carbene protonation[14,15] followed by trapping of the resulting cation with solvent was obtained in the photoreaction of **1** in deuterium oxide (99.8% D) and acetonitrile. We isolated deuterated furan derivative **18** with D content of more than 95%.



18 **19** **20**

Photoirradiation of 1,2-diketones **5** and **6** in the aprotic solvents produced fluorenylfuran **14** and bifuran **15**, respectively, with high efficiency via 6π electrocyclization of the initially formed (2-furyl)carbenes **19** and **20** (eqs 5 and 6). It is obvious that the formation of **14** involves a 1,5-H shift after electrocyclization. In sharp contrast to the photoreaction in aprotic solvents, (2-furyl)carbene species **19** was trapped by protonation in ethanol to produce **17** (eq 8). The ratio of two products **14** and **17** in the photoirradiation of **5** in a mixed solvent of ethanol and benzene was dependent on ethanol concentration. With decreasing ethanol concentration, the amount of **17** decreased with a concomitant increase of **14**, indicating that both products would be derived from a common carbene intermediate **19**.

It has been known that (2-furyl)carbene undergoes rapid ring-opening rearrangement to *cis*-2-pent-4-ynal (eq 10).[20,21] This

(10)

reaction has shortened the lifetime of (2-furyl)carbene and, consequently, the direct determination by spectroscopic method has not been readily accomplished. The existence of (2-furyl)-carbene as a distinct intermediate was only recently confirmed by IR spectra measurement of the N_2 matrix isolated carbene stabilized by chlorine substitution (R = Cl in eq 10).[22] Theoretical studies on the (2-furyl)carbene revealed that it is a ground-state singlet with the structure being close to the most suitable conformation to undergo the ring-opening rearrangement. The activation energy for the reaction is as low as 9.6 kcal/mol.[23] Taking into account the marked solvent dependency of the cyclization of **1**, **4**, and **5** in addition to the efficient ring-opening rearrangement of (2-furyl)carbenes, it seems very general that the 1,2-diketones conjugated with ene-yne are equilibrated with the (2-furyl)carbenes under the steady-state photoirradiation conditions, i.e., photoproducts are produced when intermediate carbenes are trapped by protic solvents or by intramolecular reactions. The mechanism of photoinduced tandem cyclization of **5** is illustrated in Scheme 3.

Efficiency for the Carbene-Trapping Step. The reaction rates for protonation and electrocyclization are expressed by eq 11, where k_p and k_e are the rate constants for the protonation

$$\frac{d[\mathbf{17}]}{dt} = k_p[\mathbf{19}][\mathrm{EtOH}] \qquad (11)$$

$$\frac{d[\mathbf{14}]}{dt} = k_e[\mathbf{19}]$$

and the electrocyclization steps, respectively. We assume that

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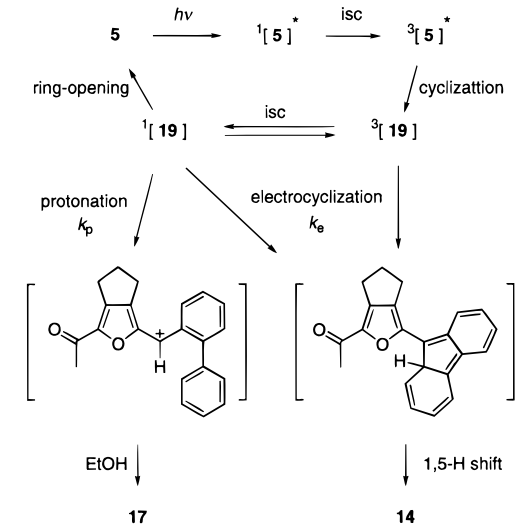
Scheme 3



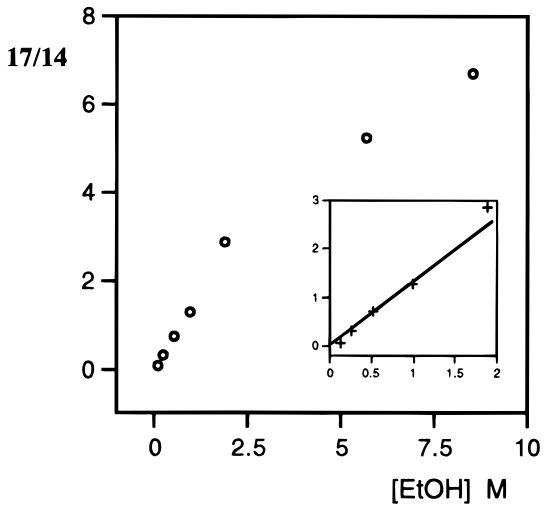


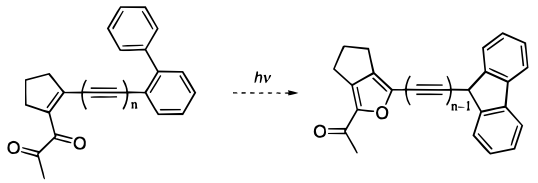
Figure 4. Plots of the ratio of **14** and **17** (**17**/**14**) vs the ethanol concentration [EtOH]. A linear correlation was obtained for the first five plots with a correlation coefficient (*r*) of 0.993 (inset).

the protonation and the electrocyclization of **19** are rate determining for the formation of **14** and **17**, respectively. Accordingly, the relative rate for the two processes would be proportional to the product ratio. This leads to the following equation, showing that the ratio of two products (**17**/**14**) is proportional to the ethanol concentration with a slope of k_p/k_e (eq 12).

$$\frac{[\mathbf{17}]}{[\mathbf{14}]} = \frac{k_p}{k_e}[\mathrm{EtOH}] \qquad (12)$$

A plot of the product ratio against ethanol concentration listed in Table 1 showed a linear correlation at low ethanol concentration (~1.9 M) (Figure 4). The slope (k_p/k_e) is 1.44 with a correlation coefficient (*r*) of 0.993. It has been reported that the singlet arylcarbenes such as xanthlidene[24] and 3,6-dimethoxyfluorenylidene[25] react with alcohols at a diffusion-controlled rate.[14] Therefore, the value of 1.44 for k_p/k_e implies that the 6π electrocyclization of **19** to **14** is also a fast process. In contrast, the photoirradiation of **6** in protic solvents did not produce a detectable amount of solvent-incorporated product. Both compounds **5** and **6** contain carbene-trapping subunits that are different in their electronic character from each other. The enone subunit incorporated into **6** is a strong electron-withdrawing group unlike the biphenyl group in the case of **5**. An efficient formation of **15** from **6** via **20** implies that such an electron-withdrawing substituent does not affect the cyclization rate, but does drastically retard the protonation rate. It has been shown that an electron-withdrawing substituent attached to the carbene center suppressed the carbene protonation due to an increased singlet−triplet energy gap.[14,26] This is likely the reason that we could not isolate the protonated product of carbene **20** in the photoreaction of **6** in aqueous solvents. While it is not certain whether electrocyclization of **19** and **20** proceeds from their singlet and/or triplet states, kinetic studies of 2-biphenylmethlyene in perfluorinated alkane at 77 K indicated that the carbene is ground-state triplet and undergoes cyclization to fluorene under these conditions.[27]

Implication for the Molecular Design of the Sequential Reactions Involving Carbenes. We have designed the molecular systems containing a carbene generator and a trap in the same molecule. The carbene generator **4** can produce furylcarbene on photoirradiation, whereas electrocyclizations of 2-biphenyl and 2-acetylcyclopentenylmethylene are used as a trap. Both carbene generation and trapping steps proceed with high efficiency as demonstrated by the photoreaction of **5** and **6** giving **14** and **15** in almost quantitative yield, respectively. The carbene-generating step is unique because the furyl carbene produced equilibrate with the starting diketone under steady-state photoillumination conditions. Therefore, reactions of **19** and **20** leading to stable products would compete with the ring-opening reaction that requires only 9.6 kcal/mol of the activation energy. Photoreactions of **1** and **4** in benzene resulted in a complete recovery even in the presence of external alkenes as a trap. These results suggest that reactions of furylcarbenes with higher activation energy may be effectively eliminated from a product-forming pathway by the energy threshold. Apparently from the efficient formation of **14** and **15**, intramolecular electrocyclizations can compete with the ring opening of furylcarbenes. These studies clearly demonstrate that a combination of a furylcarbene generator and a trap by electrocyclization is a suitable molecular system for tandem cyclizations involving carbene. Connection of such molecular units with acetylenic bridges may realize a long-range carbene transfer system as illustrated in eq 13.



(13)

Experimental Section

General. ^{1}H NMR spectra were measured with Varian Gemini 200 (200 MHz), JEOL JNM α-400 (400 MHz) or JEOL α-500 (500 MHz) spectrometers. The chemical shifts are expressed in ppm downfield from residual chloroform (δ = 7.24) and benzene (δ = 7.15) as an internal standard. ^{13}C NMR spectra were measured with Varian Gemini 200 (50 MHz) and JEOL JNM α-400 (100 MHz) spectrometers. IR spectra were recorded on a Jasco FT-IR-5M spectrophotometer. A Jasco V-550 UV/VIS spectrophotometer was used for the absorption spectra measurements. Mass spectra were recorded on a JEOL JMS SX-102A

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or a JEOL HX-100 spectrometer. A Funakoshi TEL-33 transilluminator was used for irradiation at 365 nm. A Jasco CRM-FD monochromator was used for irradiation at 365 and 382 nm. A Wakogel C-200 was used for silica gel chromatography. Precoated TLC plates Merck silica gel 60 F_{254} was used for monitoring the reactions and also for preparative TLC. Tetrahydrofuran (THF) and ethyl ether (Et_2O) were distilled under N_2 from sodium/benzophenone ketyl prior to use. Dichloromethane (CH_2Cl_2), acetonitrile (CH_3CN), and benzene were distilled from CaH_2 at atmospheric pressure. All other reagents and solvents were used as received.

General Procedures for Palladium-Catalyzed Cross Coupling. Ethyl 2-(2-(2-Phenylphenyl)ethynyl)cyclopent-1-enecarboxylate (9b). To a mixture of enol triflate **8** (862 mg, 3.0 mmol), (2-phenylphenyl)-acetylene[12] (705 mg, 4.0 mmol), bis(triphenylphosphine)palladium(II) chloride (69.4 mg, 0.10 mmol), and 2,6-lutidine (530 mg, 5.0 mmol, 0.58 mL) in deaerated, anhydrous DMF (5 mL) was added cuprous iodide (37.7 mg, 0.2 mmol). The mixture was stirred at ambient temperature for 3 h under nitrogen. The resulting mixture was diluted with saturated NH_4Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (5% ethyl acetate/hexane) to give **9b** (526 mg, 56%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, 3 H, J = 7.1 Hz), 1.83 (quint, 2 H, J = 7.6 Hz), 2.48 (m, 2 H), 2.65 (m, 2 H), 4.14 (q, 2 H, J = 7.1 Hz), 7.24−7.37 (6 H), 7.56−7.59 (3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 22.2, 33.4, 38.9, 60.2, 88.4, 99.5, 121.2, 126.8, 127.3, 127.7, 128.9, 129.1, 129.3, 133.2, 134.2, 137.3, 140.0, 143.7, 164.3; IR (neat) 3266, 2923, 1699, 1211 cm^{-1}; MS *m*/*e* (%) 316 (M^+) (27), 287 (88), 243 (100); HRMS calcd for $C_{22}H_{20}O_2$ (M^+) 316.1462, found 316.1477.

Ethyl 2-(trimethylsilylethynyl)cyclopentenecarboxylate (9d). 9d was obtained as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 9 H), 1.30 (t, 3 H, J = 7.2 Hz), 1.88 (m, 2 H), 2.60−2.71 (4 H), 4.22 (q, 2 H, J = 7.2 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 0.00, 14.4, 22.3, 33.48, 39.6, 60.5, 100.5, 105.6, 133.5, 139.1, 164.3; IR (neat) 2960, 2141, 1720, 1260, 860 cm^{-1}; MS *m*/*e* (%) 236 (M^+) (15), 221 [(M − Me)$^+$] (20), 207 (25); HRMS calcd for $C_{13}H_{20}O_2Si$ (M^+) 236.1232, found 236.1224.

Ethyl 2-(2-(2-Acetylcyclopent-1-enyl)ethynyl)cyclopent-1-enecarboxylate (9c). 9c was obtained as yellow solids: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, 3 H, J = 7.1 Hz), 1.88 (quint, 2 H, J = 7.6 Hz), 1.96 (quint, 2 H, J = 7.7 Hz), 2.56 (s, 3 H), 2.67−2.80 (8 H), 4.21 (q, 2 H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 21.7, 22.2, 29.5, 33.0, 33.5, 38.8, 40.2, 60.4, 95.4, 97.4, 133.2, 133.4, 139.7, 148.1, 164.2, 196.6; IR ($CHCl_3$) 3011, 2361, 1697, 1651, 1376, 1247, 762 cm^{-1}; MS *m*/*e* (%) 272 (M^+) (10), 243 (100), 227 (10); HRMS calcd for $C_{17}H_{20}O_3$ (M^+) 272.1411, found 272.1391.

Ethyl 2-Ethynylcyclopent-1-enecarboxylate (9e). To a solution of **9d** (653 mg, 2.8 mmol) and acetic acid (829 mg, 13.8 mmol) in THF (6 mL) was added TBAF (4.1 mL, 1.0 M in THF, 4.1 mmol) at 0 °C, and the mixture was stirred at ambient temperature for 2 h. The resulting mixture was diluted with saturated $NaHCO_3$ and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (3% ethyl acetate/hexane) to give **9e** (370 mg, 82%) as a brown oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (t, 3 H, J = 7.1 Hz), 1.91 (m, 2 H), 2.61−2.72 (4 H), 3.51 (s, 1 H), 4.21 (q, 2 H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.2, 33.3, 39.1, 60.4, 79.4, 87.3, 133.1, 140.0, 164.0; IR (neat) 3270, 2970, 2100, 1710, 1610 cm^{-1}; MS *m*/*e* (%) 164 (M^+) (64), 136 (65), 119 (100); HRMS calcd for $C_{10}H_{12}O_2$ (M^+) 164.0837, found 164.0840.

Ethyl 2-(4,4-Dimethyl-3,3-diphenyl-3-silapent-1-ynyl)cyclopent-1-enecarboxylate (9a). To a solution of **9e** (2.45 g, 14.9 mmol) in THF (30 mL) was added LHMDS (17.9 mL, 1.0 M in THF, 17.9 mmol) at −78 °C, and the mixture was stirred at 0 °C for 15 min. To this mixture was added *tert*-butylchlorodiphenylsilane (4.92 g, 17.9 mmol) at −78 °C, and the mixture was stirred at −78 °C for 3 h and at 0 °C for another 1 h. The resulting mixture was diluted with saturated NH_4-Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (2% ethyl acetate/hexane) to give **9a** (5.25 g, 87%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (s, 9 H), 1.20 (t, 3 H, J = 7.0 Hz), 1.95 (quint, 2 H, J = 7.6 Hz), 2.74−2.78 (4 H), 4.23 (q, 2 H, J = 7.0), 7.34−7.39 (6 H), 7.81−7.83 (4 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 18.6, 22.1, 27.0, 33.6, 39.7, 60.4, 100.8, 104.4, 127.7, 129.5, 133.1, 134.8, 135.6, 139.9, 164.5; IR ($CHCl_3$) 3011, 2984, 2143, 1696, 1429, 1112, 752, 702 cm^{-1}; MS *m*/*e* (%) 402 (M^+) (2), 345 [(M − *t*-Bu)$^+$] (100), 301 (80); HRMS calcd for $C_{22}H_{21}O_2Si$ [(M − *t*-Bu)$^+$] 345.1310, found 345.1303.

Ethyl 2-(2-(2-Acetylcyclopent-1-enyl)ethynyl)cyclopent-1-enecarboxylate (9c). To a mixture of 2-acetylcyclopent-1-enyl trifluoromethansulfonate (1.22 g, 4.2 mmol), **9e** (764 mg, 4.7 mmol), bis(triphenylphosphine)palladium(II) chloride (148 mg, 0.2 mmol), and 2,6-lutidine (680 mg, 6.4 mmol) in deaerated, anhydrous DMF (6 mL) was added cuprous iodide (80.6 mg, 0.4 mmol), and the mixture was stirred at ambient temperature for 6 h under nitrogen. The resulting mixture was diluted with saturated NH_4Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (67% toluene/hexane) to give **9c** (711 mg, 62%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, 3 H, J = 7.1 Hz), 1.88 (quint, 2 H, J = 7.6 Hz), 1.96 (quint, 2 H, J = 7.7 Hz), 2.56 (s, 3 H), 2.67−2.80 (8 H), 4.21 (q, 2 H, J = 7.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 21.7, 22.2, 29.5, 33.0, 33.5, 38.8, 40.2, 60.4, 95.4, 97.4, 133.2, 133.4, 139.7, 148.1, 164.2, 196.6; IR ($CHCl_3$) 3011, 2361, 1697, 1651, 1376, 1247, 762 cm^{-1}; MS *m*/*e* (%) 272 (M^+) (10), 243 (100), 227 (10); HRMS calcd for $C_{17}H_{20}O_3$ (M^+) 272.1411, found 272.1391.

General Procedures for the Preparation of α-Diazo Ketones. 1-(2-(4,4-Dimethyl-3,3-diphenyl-3-silapent-1-ynyl)cyclopent-1-enyl)-2-diazopropane-1-one (10a). To a solution of **9a** (5.12 g, 12.7 mmol) in EtOH (120 mL) and H_2O (60 mL) was added NaOH (2.29 g, 57.2 mmol), and the mixture was stirred at 45 °C for 15 h. After concentration in vacuo, the resulting mixture was diluted with H_2O, washed with ethyl acetate, and acidified with 10% HCl. The mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give crude carboxylic acid (4.40 g, 92%), which was immediately used in the next step. Oxalyl chloride (2.19 g, 17.3 mmol) was added to a solution of the crude carboxylic acid in anhydrous benzene (10 mL), and the mixture was stirred for 4 h at room temperature. Benzene was removed under reduced pressure, and the crude acid chloride (995 mg, 2.7 mmol) was dissolved in 20 mL of anhydrous ether. To a solution of diazoethane prepared from 3.74 g of nitrosourea was added a solution of acid chloride at 0 °C, and the mixture was stirred for 2 h. Concentration of the resulting mixture under reduced pressure gave the crude diazo ketone, which was purified by silica gel chromatography (5% ethyl acetate/hexane) (930 mg, 85%) to give pure **10a** as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (s, 9 H), 1.39 (quint, 2 H, J = 7.6 Hz), 1.67 (s, 3 H), 2.28 (tt, 2 H, J = 7.6, 2.5 Hz), 2.62 (tt, 2 H, J = 7.6, 2.5 Hz), 7.17−7.22 (6 H), 7.90−7.92 (4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.6, 18.8, 22.4, 27.3, 35.1, 38.3, 99.0, 104.4, 128.2, 128.5, 123.0, 133.4, 135.9, 136.0, 148.8, 186.2; IR ($CHCl_3$) 2959, 2931, 2080, 1605, 1570, 1429, 1375, 702 cm^{-1}; MS *m*/*e* (%) 384 [(M − N_2)$^+$] (50), 327 (100); HRMS calcd for $C_{26}H_{28}OSi$ [(M − N_2)$^+$] 384.1908, found 384.1896.

2-Diazo-1-(2-(2-(2-phenylphenyl)ethynyl)cyclopent-1-enyl)propan-1-one (10b). 10b was obtained as a yellow oil: ^{1}H NMR (400 MHz, C_6D_6) δ 1.38 (quint, 2 H, J = 7.7 Hz), 1.61 (s, 3 H), 2.25 (m, 2 H), 2.65 (m, 2 H), 6.96−7.04 (2 H), 7.12−7.23 (4 H), 7.53−7.60 (3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 8.8, 22.3, 35.2, 38.4, 88.3, 98.4, 121.7, 126.5, 127.3, 127.8, 128.3, 129.2, 129.5, 130.0, 133.6, 140.7, 144.4, 146.3, 186.1 (one carbon was not observed by peak overlap); IR (neat) 2928, 2848, 2072, 1583, 1373 cm^{-1}; MS *m*/*e* (%) 327 [(M + H)$^+$] (45), 154 (100); HRMS calcd for $C_{22}H_{19}ON_2$ [(M + H)$^+$] 327.1496, found 327.1482.

2-Diazo-1-(2-(2-(2-acetylcyclopent-1-enyl)ethynyl)cyclopent-1-enyl)propan-1-one (10c). 10c was obtained as yellow solids: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (quint, 2 H, J = 7.6 Hz), 1.95 (quint, 2 H, J = 7.6 Hz), 2.02 (s, 3 H), 2.47 (s, 3 H), 2.63−2.81 (8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.0, 21.7, 22.4, 29.3, 33.2, 35.1, 38.1, 40.3, 94.1,

96.2, 126.1, 132.8, 147.6, 148.0, 196.2 (we could not observe two carbons.); IR ($CHCl_3$) 3699, 3022, 3011, 2077, 1653, 1610, 1590, 1571, 1211, 761, 747 cm^{-1}; MS *m/e* (%) 254 [$(M - N_2)^+$] (100), 226 (20), 211 (35); HRMS calcd for $C_{17}H_{18}O_2$ [$(M - N_2)^+$] 254.1306, found 254.1310.

General Procedures for the Preparation of 1,2-Diketones. 1-(2-(4,4-Dimethyl-3,3-diphenyl-3-silapent-1-ynyl)cyclopent-1-enyl)propane-1,2-dione (11a). To a solution of **10a** (801 mg, 1.9 mmol) in anhydrous ether (30 mL) was added triphenylphosphine (1.02 g, 3.9 mmol), and the mixture was stirred at ambient temperature for 3 h. After concentration in vacuo, the resulting mixture was diluted with THF (30 mL). The THF solution was added to sodium nitrite (402 mg, 5.8 mmol) and cooled to 0 °C. To the mixture was added 2 N HCl (4.6 mL, 9.1 mmol), and the reaction mixture was stirred at 0 °C for 1 h. The resulting mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (3% ethyl acetate/hexane) to give **11a** (727 mg, 94%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9 H), 1.99 (quint, 2 H, $J = 7.7$ Hz), 2.20 (s, 3 H), 2.77 (tt, 2 H, $J = 7.7$, 2.4 Hz), 2.85 (tt, 2 H, $J = 7.7$, 2.4 Hz), 7.35−7.42 (6 H), 7.72−7.74 (4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 22.0, 25.8, 27.1, 32.5, 40.7, 102.8, 105.3, 127.9, 129.8, 132.4, 135.6, 138.8, 143.4, 191.5, 200.8; IR ($CHCl_3$) 1712, 1649, 1110, 820, 777, 741 cm^{-1}; MS *m/e* (%) 400 (M^+) (3), 357 [$(M - COCH_3)^+$] (40), 343 (25); HRMS calcd for $C_{24}H_{25}OSi$ [$(M - COCH_3)^+$] 357.1673, found 357.1665.

1-(2-(2-(2-Phenylphenyl)ethynyl)cyclopent-1-enyl)propane-1,2-dione (5). 5 was obtained as yellow solids: ^1H NMR (400 MHz, $CDCl_3$) δ 1.93 (quint, 2 H, $J = 7.5$ Hz), 2.31 (s, 3 H), 2.63 (tt, 2 H, $J = 7.7$, 2.2 Hz), 2.72 (tt, 2 H, $J = 7.7$, 2.4 Hz), 7.30−7.65 (9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 26.1, 31.9, 39.8, 87.3, 103.2, 120.3, 127.3, 127.7, 128.0, 129.2, 129.6, 129.9, 133.1, 140.0, 140.6, 141.5, 144.3, 192.0, 202.0; IR ($CHCl_3$) 2924, 2360, 2342, 2331, 1714, 1639 cm^{-1}; MS *m/e* (%) 314 (M^+) (32), 271 [$(M - COCH_3)^+$] (100); HRMS calcd for $C_{22}H_{18}O_2$ (M^+) 314.1306, found 314.1293.

1-(2-(2-(2-Acetylcyclopent-1-enyl)ethynyl)cyclopent-1-enyl)propane-1,2-dione (6). 6 was obtained as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.90 (quint, 2 H, $J = 7.7$ Hz), 2.00 (quint, 2 H, $J = 7.7$ Hz), 2.40 (s, 3 H), 2.48 (s, 3 H), 2.68−2.81 (8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.1, 26.0, 29.4, 32.5, 33.3, 39.6, 39.7, 95.5, 98.3, 131.8, 138.6, 143.2, 149.4, 190.9, 197.0, 200.9; IR ($CHCl_3$) 3896, 2358, 1713, 1648, 1603, 746 cm^{-1}; MS *m/e* (%) 270 (M^+) (95), 227 (100), 199 (35); HRMS calcd for $C_{17}H_{18}O_3$ (M^+) 270.1255, found 270.1243.

1-(2-Ethynylcyclopent-1-enyl)propane-1,2-dione (4). To a solution of **11a** (96.1 mg, 0.2 mmol) and acetic acid (72.0 mg, 1.2 mmol) in THF (5 mL) was added TBAF (0.5 mL, 1.0 M in THF, 0.5 mmol) at 0 °C, and the mixture was stirred at ambient temperature for 16 h. The resulting mixture was diluted with saturated $NaHCO_3$ and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (3% ethyl acetate/hexane) to give **4** (30.7 mg, 79%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (quint, 2 H, $J = 7.7$ Hz), 2.40 (s, 3 H), 2.74 (t, 4 H, $J = 7.7$ Hz), 3.59 (s, 1 H); ^{13}C NMR (100 MHz, C_6D_6) δ 22.0, 25.8, 32.6, 40.0, 78.9, 90.5, 135.2, 144.5, 191.5, 200.2; IR ($CHCl_3$) 3302, 1715, 1650, 1588, 1349, 1215, 779, 732 cm^{-1}; MS *m/e* (%) 162 (M^+) (12), 119 (100), 91 (25); HRMS calcd for $C_{10}H_{10}O_2$ (M^+) 162.0680, found 162.0684.

1-(2-Ethynylcyclopentenyl)ethan-1-one (13). To a mixture of 2-acetyl-1-cyclopent-1-enyl trifluoromethanesulfonate (**12**) (2.77 g, 9.63 mmol), bis(triphenylphosphine)palladium(II) chloride (203 mg, 0.3 mmol), and 2,6-lutidine (1.54 g, 14.5 mmol) in deaerated, anhydrous DMF (6 mL) were added ethynyltrimethylsilane (1.04 g, 10.6 mmol) and cuprous iodide (110 mg, 0.6 mmol). The mixture was stirred at ambient temperature for 15 h under nitrogen. The resulting mixture was diluted with saturated NH_4Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (3% ethyl acetate/hexane) to give 1-(2-(trimethylsilylethynyl)cyclopentenyl)ethan-1-one (1.85 g, 93%) as a red oil: ^1H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 9 H), 1.83 (quint, 2 H, $J = 7.7$ Hz), 2.53 (s, 3 H), 2.63−2.72 (4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.4, 21.7, 29.5, 32.9, 40.3, 101.6, 108.5, 133.6, 148.6, 196.7; IR ($CHCl_3$) 2905, 1651, 1585, 1374, 1252, 742 cm^{-1}; MS *m/e* (%) 206 (M^+) (80), 191 (100), 163 (20); HRMS calcd for $C_{12}H_{18}OSi$ (M^+) 206.1126, found 206.1133.

To a solution of the above ketone (907 mg, 4.4 mmol) and acetic acid (1.32 g, 22.0 mmol) in THF (7 mL) was added TBAF (6.6 mL, 1.0 M in THF, 6.6 mmol) at 0 °C, and the mixture was stirred at ambient temperature for 12 h. The resulting mixture was diluted with saturated $NaHCO_3$ and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (2% ethyl acetate/hexane) to give **13** (432 mg, 73%) as a brown solid: ^1H NMR (400 MHz, $CDCl_3$) δ 1.86 (quint, 2 H, $J = 7.7$ Hz), 2.53 (s, 3 H), 2.65−2.75 (4 H), 3.64 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 29.4, 32.9, 40.2, 80.2, 89.6, 132.4, 149.0, 196.5; IR ($CHCl_3$) 3302, 3017, 1657, 1589, 1265, 1215, 762, 743 cm^{-1}; MS *m/e* (%) 134 (M^+) (65), 119 (100), 91 (40); HRMS calcd for $C_9H_{10}O$ (M^+) 134.0731, found 134.0723.

1-(2-(2-(2-Acetylcyclopent-1-enyl)ethynyl)cyclopent-1-enyl)ethan-1-one (7). To a mixture of enol triflate **12** (199 mg, 0.7 mmol), bis(triphenylphosphine)palladium(II) chloride (24.2 mg, 0.03 mmol), and 2,6-lutidine (111 mg, 1.0 mmol) in deaerated, anhydrous DMF (4 mL) were added **13** (102 mg, 0.8 mmol) and cuprous iodide (13.1 mg, 0.07 mmol). The mixture was stirred at ambient temperature overnight under nitrogen. The resulting mixture was diluted with saturated NH_4Cl and extracted with ethyl acetate. The extract was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (2% ethyl acetate/toluene) to give **7** (66.2 mg, 36%) as a yellow oil: ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (quint, 4 H, $J = 7.5$ Hz), 2.51 (s, 6 H), 2.70−2.79 (8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 29.4, 33.3, 39.9, 97.4, 132.5, 148.5, 196.0; IR (neat) 2921, 2842, 1651, 1605, 1418, 1251 cm^{-1}; MS *m/e* (%) 242 (M^+) (100), 227 (13), 199 (24); HRMS calcd for $C_{16}H_{18}O_2$ (M^+) 242.1307, found 242.1306.

Photoreaction of 5 in Benzene. 1-(3-Fluoren-9-yl-2,4,5,6-tetrahydro-2-oxapentalenyl)ethan-1-one (14). A solution of **5** (31.4 mg, 0.10 mmol) in anhydrous benzene (10 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 1.1 h. The solvent was removed under reduced pressure, and the resulting mixture was purified by silica gel chromatography (10% ethyl acetate/hexane) to give **14** (30.5 mg, 97%) as yellow solids:^1H NMR (400 MHz, $CDCl_3$) δ 1.83 (t, 2H, $J = 7.1$ Hz), 2.15 (quint, 2 H, $J = 7.5$ Hz), 2.41 (s, 3 H), 2.75 (t, 2 H, $J = 7.0$ Hz), 5.28 (s, 1 H), 7.29 (dt, 2 H, $J = 7.5$, 1.2 Hz), 7.39 (t, 2 H, $J = 7.5$ Hz), 7.56 (dd, 2 H, $J = 7.5$, 0.7 Hz), 7.75 (d, 2 H, $J = 7.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 26.0, 26.5, 31.2, 47.2, 120.0, 125.5, 127.3, 127.9, 130.7, 140.9, 143.0, 143.2, 144.8, 148.4, 185.6; IR ($CHCl_3$) 2925, 2854, 1742, 1666, 1561, 1449, 1396, 738 cm^{-1}; MS *m/e* (%) 314 (M^+) (90), 271 [$(M - COCH_3)^+$] (100); HRMS calcd for $C_{22}H_{18}O_2$ (M^+) 314.1306, found 314.1319.

Photoreaction of 6 in Benzene. 1-(3-(2,4,5,6-Tetrahydro-2-oxapentalenyl)-2,4,5,6-tetrahydro-2-oxapentalenyl)ethan-1-one (15). A solution of **6** (5.6 mg, 0.02 mmol) in anhydrous benzene (2.1 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 1.5 h. The solvent was removed under reduced pressure, and the resulting mixture was purified by silica gel chromatography (10% ethyl acetate/hexane) to give **15** (5.3 mg, 95%) as yellow solids: ^1H NMR (400 MHz, $CDCl_3$) δ 2.24 (bs, 3 H), 2.39 (s, 3 H), 2.33−2.40 (2 H), 2.42−2.47 (2 H), 2.48−2.53 (2 H), 2.77−2.82 (4 H), 2.87 (t, 2 H, $J = 7.4$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.9, 23.0, 24.3, 24.9, 26.2, 26.2, 31.5, 32.0, 129.4, 130.3, 133.8, 134.5, 141.2, 142.2, 143.2, 145.1, 197.7; IR ($CHCl_3$) 1640, 1627, 1209 cm^{-1}; MS *m/e* (%) 270 (M^+) (100), 227 [$(M - COCH_3)^+$] (65); HRMS calcd for $C_{17}H_{18}O_3$ (M^+) 270.1255, found 270.1220.

Photoreaction of 4 in Ethanol. 1-(3-(Ethoxymethyl)-2,4,5,6-tetrahydro-2-oxapentalenyl)ethan-1-one (16). A solution of **4** (18.1 mg, 0.11 mmol) in ethanol (6 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 1.5 h. The solvent was removed under reduced pressure, and the resulting mixture

was purified by silica gel chromatography (13% ethyl acetate/hexane) to give **16** (10.0 mg, 43%) as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, 3 H, J = 7.0 Hz), 2.37 (s, 3 H), 2.41 (quint, 2 H, J = 7.1 Hz), 2.64 (t, 2 H, J = 7.5 Hz), 2.84 (t, 2 H, J = 7.3 Hz), 3.53 (q, 2 H, J = 7.0 Hz), 4.42 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.1, 23.4, 26.2, 26.5, 31.7, 66.3, 67.3, 133.9, 143.3, 143.7, 146.5, 186.5; IR ($CHCl_3$) 2971, 1669, 1569, 1360, 1093 cm^{-1}; MS *m*/*e* (%) 208 (M^+) (90), 193 (14), 179 (15), 163 (100), 137 (98); HRMS calcd for $C_{12}H_{16}O_3$ (M^+) 208.1099, found 208.1100.

Photoreaction of 5 in Ethanol. 1-(3-(Ethoxy(2-phenylphenyl)-methyl)-2,4,5,6-tetrahydro-2-oxapentalenyl)ethan-1-one (17). A solution of **5** (31.4 mg, 0.10 mmol) in ethanol (10 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 2 h. The solvent was removed under reduced pressure, and the resulting mixture was purified by silica gel chromatography (13% ethyl acetate/hexane) to give **17** (24.4 mg, 68%) as a colorless oil and a trace amount of **14**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, 3 H, J = 7.0 Hz), 2.13 (m, 1 H), 2.20−2.31 (5 H), 2.32 (s, 3 H), 2.75−2.81 (2 H), 3.33−3.41 (2 H), 5.37 (s, 1 H), 7.14−7.42 (8 H), 7.66 (dd, 1 H, J = 7.7, 1.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 23.8, 25.9, 26.4, 31.4, 64.6, 73.7, 127.2, 127.4, 127.7, 127.8, 128.1, 129.1, 129.9, 133.7, 136.2, 140.4, 141.7, 143.2, 143.4, 148.3, 186.7; IR ($CHCl_3$) 2924, 2359, 1669, 1071 cm^{-1}; MS *m*/*e* (%) 360 (M^+) (52), 331 (58), 317 (62), 271 (100); HRMS calcd for $C_{24}H_{24}O_3$ (M^+) 360.1724, found 360.1736.

Photoreaction of 6 in Aqueous Acetonitrile. A solution of **6** (8.1 mg, 0.03 mmol) in acetonitrile (1.5 mL) and H_2O (1.5 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 2 h. The solvent was removed under reduced pressure, and the resulting mixture was purified by silica gel chromatography (10% ethyl acetate/hexane) to give **15** (3.8 mg, 47%).

Photoreaction of 1 in Deuterium Oxide To Give 18. A solution of **1** (9.8 mg, 0.04 mmol) in CH_3CN (2.1 mL) and deuterium oxide (2.1 mL) was irradiated with a transilluminator (365 nm) through a Pyrex filter at room temperature for 40 min. After concentration in vacuo, the resulting mixture was extracted with ethyl acetate, washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was purified by silica gel chromatography (20% ethyl acetate/hexane) to give **18** (6.4 mg, 61%) as a colorless oil: ^{1}H NMR (200 MHz, C_6D_6) δ 2.01−2.33 (4 H), 2.35 (s, 3 H), 2.78 (t, 2 H, J = 7.5 Hz), 7.27−7.45 (5H); IR ($CHCl_3$) 3738−3334, 1663, 1656, 1221, 763, 736 cm^{-1}; MS *m*/*e* (%) 257 (M^+) (100), 240 [(M − OH)$^+$] (45), 214 [(M − $COCH_3$)$^+$] (80); HRMS calcd for $C_{16}H_{15}O_3D$ (M^+) 257.1160, found 257.1161.

Photoreaction of 7. A solution of **4** (10.0 mg, 0.04 mmol) in benzene (4.1 mL) was irradiated with a transilluminator (365 nm) for 3 h. In another experiment, the same solution of **7** containing Michler's ketone (11.4 mg, 0.04 mmol) was photoirradiated for 1 h. A ^{1}H NMR spectrum of the crude photolysate obtained from both experiments showed complete recovery of **7**.

Quantum Yield Measurements. An acetonitrile solution (2 mL) of **5** (1 mM) in a Pyrex flask containing benzene as an internal standard was illuminated at 365 nm obtained from the monochromator for 25 counts by an integrator equipped with the monochromator. The monochromator was calibrated by the chemical actinometer of phenylglyoxylic acid (Φ = 0.72 at 365 nm)[19] under identical conditions. The amount of produced **14** was measured by HPLC analysis. Under these conditons, diketone **5** was converted to **14** in 7.7%, whereas phenylglyoxylic acid was transformed to benzaldehyde in 26.1%. The quantum yield for the photocyclization of **5** to **14** was calculated as 0.21. Similary, the quantum yields for the disappearance of **5** in ethanol and **6** in benzene at 365 nm irradiation were measured as 0.13 and 0.19, respectively.

Triplet Quenching. Triplet quenching for the photocyclization of **5** (1 mM) was carried out in the presence of (*E*,*E*)-1,4-diphenyl-1,3-butadiene (0, 2.5, 5.0, 7.5, and 12.5 mM) in acetonitrile at 382 nm obtained from the monochromator. Photoirradiation was carried out for 50 counts by an integrator equipped with the monochromator. Relative quantum yields (Φ_0/Φ) for the cyclization in the presence of the quencher were 1.33 (2.5 mM), 1.84 (5.0 mM), 2.83 (7.5 mM), and 3.92 (12.5 mM). The Stern−Volmer slope was 227 M^{-1}.

JA990763Q