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Highly Efficient Photochemical Generation of a Triple Bond: Synthesis, Properties, and Photodecarbonylation of Cyclopropenones

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UV irradiation of alkyl-, aryl-, and heteroatom-substituted cyclopropenones results in the loss of carbon monoxide and the formation of quantitative yields of corresponding alkynes. The quantum yield of the photochemical decarbonylation reaction ranges from 20% to 30% for alkyl-substituted cyclopropenones to above 70% for the diphenyl- and dinaphthylcyclorpopenones. Rapid formation (<5 ns) and then a somewhat slower decay (ca. 40 ns) of an intermediate in this reaction was observed by using laser flash photolysis. The DFT calculations allowed us to identify this intermediate as a zwitterionic species formed by a cleavage of one of the carbon–carbon bonds of the cyclopropenone ring. The latter then rapidly loses carbon monoxide to produce the ultimate acetylenic product. Despite their high photoreactivity, cyclopropenones were found to be thermally stable compounds with the exception of hydroxy- and methoxy-substituted cyclopropenones. The latter undergo rapid solvolysis in hydroxylic solvents even at room temperature. The application of this reaction to the in situ generation of the enediyne strucutre was illustrated by the photochemical preparation of benzannulated enediyne **12**.

Introduction

The development of enediyne-based photonucleases, which is underway in our group, requires robust and efficient methods for the photogeneration of a triple bond. We have already utilized photochemical decarbonylation of hydroxycyclopropenones for the generation of short-lived ynol[1] intermediates and decided to explore the suitability of this reaction for the preparation of stable acetylenes. The preparation of the first cyclopropenone, diphenylcyclopropenone, was reported independently in 1959 by Breslow et al.[2] and Vol'pin et al.[3] Cyclopropenones received considerable attention due to their possible description as aromatic compounds.[4] The discovery of cyclopropenone-containing natural antibiotic penitricin,[5] as well as cyclopropenone-based protease inhibitors,[6] renewed interest in this class of cyclic ketones. The chemical reactivity of the cyclopropenone ring is dominated by two processes:[4] (1) nucleophilic attack on the carbonyl carbon with the formation of acrylic acid derivatives[7] and (2) decarbonylation to alkynes under high-temperature pyrolysis or in the presence of various catalysts.[8] Acetylenes were also observed as intermediates[1,9] or were even isolated[7,10] in photolysis of some cyclopropenones. In this work we report synthesis, properties, and photochemistry of the series of cyclopropenones **1a–n** and **12**.

	R	R'		R = R'
a	H	$n\text{-}C_5H_{11}$	**j**	Ph
b	H	$n\text{-}C_4H_9$	**k**	p-MeO-C_6H_4
c	CH_3	$n\text{-}C_4H_9$	**l**	2,4-$(MeO)_2$-C_6H_3
d	Ph	$n\text{-}C_4H_9$	**m**	Mesityl
e	Ph	OH	**n**	1-Naphthyl
f	Ph	NHPh		
g	OH	2-Br-4-MeO-C_6H_3		
h	OCH_3	2-Br-4-MeO-C_6H_3		
i	Ph	2-Br-4-MeO-C_6H_3		
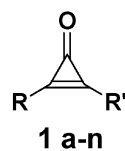
Synthesis. We have explored three different approaches to a cyclopropenone structure: (1) alkylation of aromatic compounds with trichlorocyclopropenium

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SCHEME 1[a]
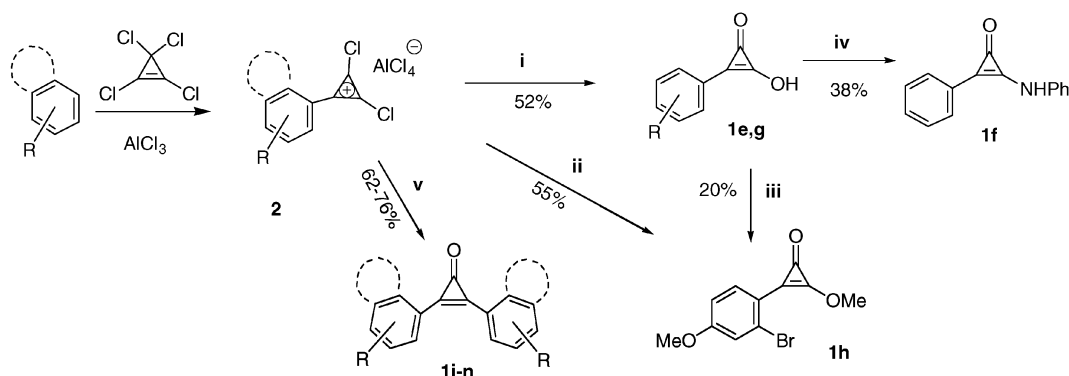
[a] Reagents and conditions: (i) acetone−water mixture, 0 °C; (ii) (1) MeOH, (2) HCl$_{conc}$; (iii) diazomethane; (iv) (1) SOCl$_2$, (2) aniline; (v) (1) ArH, (2) H$_2$O.

SCHEME 2
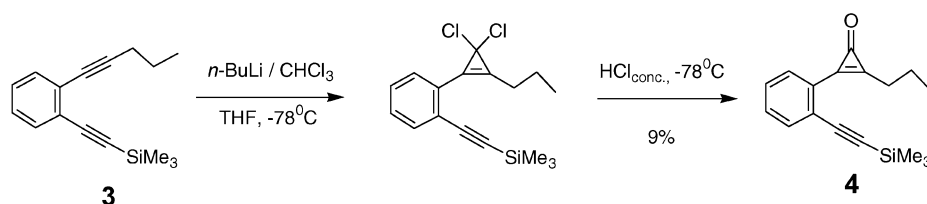
cation followed by hydrolysis (Scheme 1); (2) dihalocy-clopropanation of acetylenes and hydrolysis of intermediate hem-dihalocyclopropenes (Scheme 2); and (3) introduction of substituents into 2- and 3-positions of cyclopropenone acetal followed by deprotection of the carbonyl group (Scheme 3).

The reaction of tetracholorocyclopropene with anhydrous aluminum chloride generates the trichlorocyclopropenium cation, which is then used in Friedel−Crafts alkylation of aromatic compounds to produce an aryldichlorocyclopropenium cation **2** (Scheme 1). Controlled hydrolysis of the latter in an acetone−water mixture at 0 °C produces arylhydroxycyclopropenone **1e**,**g** in moderate yields.[11] Quenching of the salt **2** with methanol followed by hydrolysis with concentrated hydrochloric acid allowed us to prepare arylmethoxycyclopropenone **1h**. The dimethylacetal of **1h** is likely an intermediate in this reaction. Dialkyl acetals of cyclopropenones are known to be extremely susceptible to hydrolysis with a sub-millisecond lifetime in aqueous solution.[12] The ester **1h** was alternatively prepared by esterification of aryl-hydroxycyclopropenone **1g** with diazomethane (Scheme 1).

The treatment of phenylhydroxycyclopropenone **1e** with thionyl chloride converts it into unstable[11b] aryl-chlorocyclopropenone. Quenching of the latter with aniline produces 2-phenyl-3-*N*-phenylaminocyclopropenone **1f** (Scheme 1).[13]

The reaction of the arylcyclopropenium salt **2** with the second equivalent of the aromatic compound results in a subsequent Friedel−Crafts alkylation to produce symmetric[4,8] (**1j**−**n**) or nonsymmetric[10d] (**1i** and **12**) diaryl-cyclopropenones (Schemes 1 and 5).

Cyclopropanation of acetylenic compounds with dichloro-[14] or fluorochlorocarbenes[15] results in the formation of gem-dihalosubstituted cyclopropenes. The latter are then hydrolyzed to corresponding cyclopropenones. Using this method, we were able to conduct a regio-selective cyclopropanation of o-dialkynyl substituted benzene **3** to produce cyclopropenone **4** (Scheme 2). Unfortunately, the conversion in the cyclopropanation step of this reaction was low and o-alkynylphenylcyclopropenone **4** was found to be unstable.

Cyclopropenones are susceptible to a nucleophilic attack, which limits the range of reactions that can be used to achieve the desired structural modification. Use of cyclopropenone acetal allows us to mask the reactivity of the cyclopropenone moiety. Simple dimethyl or diethyl acetals of cyclopropenones are rather unstable and undergo a facile hydrolysis even in neutral solution.[12] The neopentyl glycol acetal possesses much higher kinetic stability and was chosen as the protecting group for the preparation of alkyl-substituted cyclopropenones. The 1,3-dichloroacetone was converted into acetal **6** by treating it with neopentyl glycol in the presence of *p*-toluene-sulfonic acid. The reaction of **6** with sodium amide in liquid ammonia results in a cyclization/dehydrohalogenation reaction and formation of the sodium salt of cyclopropenone acetal **7**. The latter can be quenched by

(10) (a) Breslow, R.; Altman, L. J.; Krebs, A.; Mohacsi, E.; Murata, I.; Peterson, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1326. (b) Agranat, I.; Barak, A.; Pick, M. P. *J. Org. Chem.* **1973**, *38*, 3064. (c) Eicher, T.; Schmieder, V. *Synthesis* **1989**, 372. (d) Weidner, C. H.; Wadsworth, D. H.; Knop, C. S.; Oyefesso, A. I.; Hafer, B. L.; Hartman, R. J.; Mehlenbacher, R. C.; Hogan, S. C. *J. Org. Chem.* **1994**, *59*, 4319.

(11) This procedure has been used for the preparation of a series of arylhydroxycyclopropenones: (a) Chicos, J. C.; Patton, E.; West, R. *J. Org. Chem.* **1974**, *39*, 1647. Also see ref 1. Direct quenching of arylcyclopropenium cation with water, on the other hand, results in ring openinig and formation of 2-aryl-3-chloroacrylic acid: (b) West, R.; Zecher, D. C.; Tobey, S. W. *J. Am. Chem. Soc.* **1970**, *92*, 168.

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(14) Dehmlow, E. V.; Dehmlow, S. S.; Marschner, F. *Chem. Ber.* **1977**, *110*, 154.

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SCHEME 3[a]
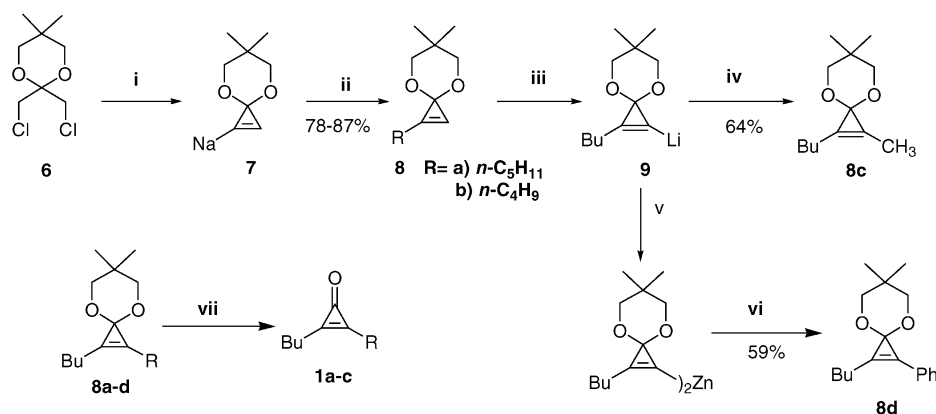
[a] Reagents and conditions: (i) NaNH₂ in NH₃; (ii) *n*-C₅H₁₁Br or *n*-C₄H₉Br, Et₂O, −78 °C; (iii) *n*-BuLi, HMPA, THF, −78 °C; (iv) CH₃I, THF, −78 °C; (v) ZnCl₂, THF, −78 °C; (vi) 5% Pd(PPh₃)₄, PhI; (vii) Amberlist 15, acetone.

TABLE 1. Comparison of Structural Parameters of Phenyl- and Diphenylcyclopropenones Calculated by Using the DFT B3LYP Hybrid Functional with Crystal Structure Data

parameter	phenylcyclopropenone (R = H)		diphenylcyclopropenone (R = Ph)		
	6-31+G(d,p)	6-311+G(3df,2p)	6-31+G(d,p)	6-311+G(3df,2p)	X-ray[20]
C_1−O (Å)	1.216	1.200	1.222	1.211	1.225 (1.226)[a]
C_1−C_2 (Å)	1.430	1.420	1.420	1.420	1.417 (1.409)
C_1−C_3 (Å)	1.420	1.410			
C_2−C_3 (Å)	1.350	1.356	1.370	1.360	1.349 (1.354)
C_2−Ph (Å)	1.440	1.447	1.440	1.440	1.447 (1.452)
∠$C_2C_1C_3$ (deg)	56.8	56.6	57.6	57.3	56.9 (57.4)
∠C_3C_2Ph (deg)	146.6	146.3	149.9	149.9	150.6 (149.3)
∠C_1C_2H (deg)	145.2	145.0			
ϕC_3C_2Ph (deg)	0.0	0.0	0.0	0.0	2.2 (6.3)

[a] Data in parentheses represent the crystal structure of the diphenylcyclopropenone monohydrate.[20b]

ammonium chloride and then water to give the acetal of the parent cyclopropenone.[16]

Reaction of the sodium salt **7** with *n*-butyl or *n*-amyl bromide produces 2-alkylcyclopropenone acetals **8a** and **8b**. Acetal **8b** was deprotonated with *n*-BuLi to give salt **9**, which in turn reacted with methyl iodide to yield the acetal of 2-butyl-3-methylcyclopropenone (**8c**). Lithium salt **9** can also be transmetalated with zinc chloride to produce an organozinc derivative. The latter undergoes palladium-catalyzed coupling with iodobenzene to give 2-butyl-3-phenylcyclopropenone acetal **8d**. Cyclopropenones are acid-sensitive compounds and deprotection of acetals **8** should be conducted under mild conditions. We found that trans-acetalization in acetone catalyzed by the Amberlist 15 ion-exchange resin gives the best results.

Structure. Cyclopropenones are planar compounds with a potentially "aromatic" character.[17] The structural feature that supports the notion of cyclopropenone aromaticity is elongation of the endocyclic double bond in the parent cyclopropenone (1.332 Å)[18] in comparison with

cyclopropene itself (1.296 Å).[19] This double bond is even longer in diphenylcyclopropenone (1.349 Å)[20] according to the X-ray data shown in Table 1. This phenomenon is probably due to the additional conjugation of the double bond with an aromatic system. We have conducted DFT geometry optimization of phenylcyclopropenone and diphenylcyclopropenone (**1j**) using the B3LYP hybrid functional with 6-31+G(d,p) and 6-311+G(3df,2p) basis sets. Both methods produce optimized structural parameters (shown in Table 1), which are in good agreement with the X-ray data. The 6-311+G(3df,2p) basis set, however, gives a better description of the electronic properties, as the length of the C_2−C_3 double bond is closer to the experimental value and the dipole moment calculated by using the 6-311+G(3df,2p) basis set (5.31 D) is in better agreement with the experimental value (5.08 D[21a] and 5.14 D[21b]) than results obtained with a smaller set (5.42 D). In other words, the DFT method used in the present work describes the geometry and electronic structure of

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(21) (a) Takahashi, K.; Nishijima, K.; Takase, K.; Katagiri, S. *Tetrahedron Lett.* **1983**, *24*, 205. (b) Breslow, R.; Eicher, T.; Krebs, A.; Petersom, R. A.; Posner, J. *J. Am. Chem. Soc.* **1965**, *87*, 1320.

phenyl-substituted cyclopropenones reasonably well, especially when using the extended triple-ζ basis set.

Both phenylcyclopropenone and **1j** are predicted by DFT calculations to be perfectly planar. X-ray data, on the other hand, show that benzene rings in **1j** are slightly twisted from the plane of the three-membered ring. We believe that this distortion is a result of a packing requirement in the crystal lattice. Planarity of phenyl-cyclopropenone and **1j** means that an efficient conjugation exists between the cyclopropenone ring and the aromatic system. Such conjugation should exert a strong influence on photophysical properties of cyclopropenones with aromatic substituents as discussed below.

Frequency calculations conducted on phenylcyclopropenone and **1j** allowed us to address the long-standing confusion about the nature of the major absorbance band at ca. 1850 cm^{-1} in the infrared spectra of cyclopropenones. On the basis of the solvent dependency, this band has been originally assigned to the ring vibration, while the band at ca. 1630 cm^{-1} has been assigned to the carbonyl stretching vibration.[22] However, the substitution of carbonyl oxygen with the ^{18}O isotope affected the shorter wavelength band more strongly, an observation that suggests reverse assignment.[23] B3LYP/6-311+G (3df,2p) calculations clearly indicate that the absorbance band at 1850 cm^{-1} corresponds to the carbonyl stretching vibration. The band at 1650 cm^{-1} is due to endocyclic double bond stretching vibrations, which in our case is coupled with vibrations of the benzene ring.

Stability. The UV spectra of the aqueous and methanolic solutions of cyclopropenones bearing alkyl (**1a**,**c**) and aryl (**1d**,**k**) substituents show no changes over a period of 12 h at pH 7.0 and 70 °C. This observation indicates that these cyclopropenones are reasonably stable under the given conditions. Cyclopropenone (**1k**) was quantitatively recovered after heating at 130 °C in DMSO solution for 5 h. Samples of cyclopropenones (**1a**–**d**,**i**–**n**) were stored at ca. −10 °C for several months without detectable decomposition. The aminocyclopropenone **1f** is also stable at ambient temperatures in aqueous, methanolic, and THF solutions. In contrast, the oxygen-substituted cyclopropenes **1e** and **1h** are the notable exceptions as they undergo a rapid decomposition in hydroxylic solvents. The lifetime of phenylhydroxycyclopropenone **1e** in methanol at 25 °C is 83 min, while methoxy-substituted cyclopropenone **1h** shows $\tau = 35$ min in methanol at 25 °C and only 17 min at 40 °C (Figure 1).

Photophysical Properties. The UV spectra of alkyl- and dialkyl-substituted cyclopropenones show only tail absorbance above 200 nm, similar to the parent unsubstituted compound.[24] Conjugation of the cyclopropenone system with the benzene ring in **1c** causes the appearance of an intense band at 251 nm (Figure 2, Table 2).

According to the time-dependent DFT B3LYP/6-311+G-(3df,2p)[25] calculation on phenylcyclopropenone, this ab-
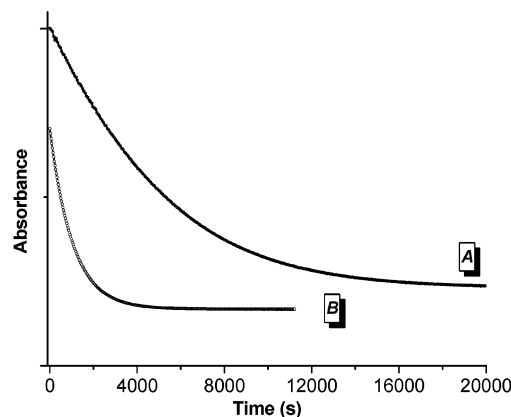

FIGURE 1. Decomposition of cyclopropenones **1e** (A) and **1h** (B) in methanolic solution at 25 °C. The reaction was followed at $\lambda = 250$ nm for **1e** and at $\lambda = 280$ nm for **1h**.
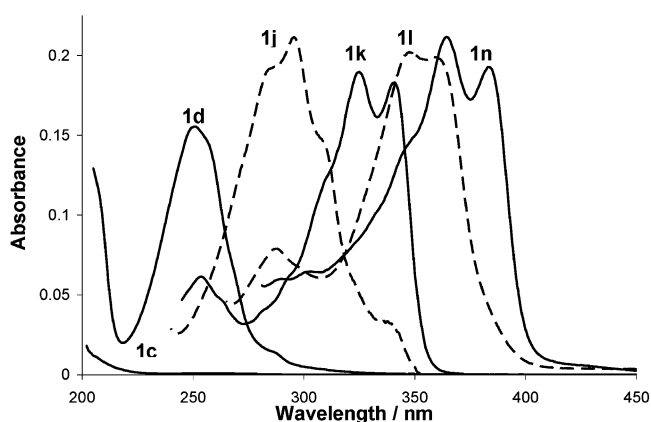

FIGURE 2. UV spectra of ca. 10^{-5} M solutions of cyclopropenones **1c**,**d**,**j**,**k**,**l**,**n** in methanol at 25 °C.

TABLE 2.   Extinction Coefficients and Quantum Yields of Photolysis of Cyclopropenones

	λ_{max}/nm (log ϵ)[a]	Φ^a (λ/nm)
1a	259 (1.57)	0.228 ± 0.006 (254)
1c	254 (1.92)	0.26 ± 0.01 (254)
1d	251 (4.18)	0.40 ± 0.01 (350)
1e	260 (4.30), 252 (4.30)	0.26 ± 0.02 (300)
1f	314 (4.43)	0.48 ± 0.02 (350)
1i	340 (4.20)	0.37 ± 0.02 (350)
1j	∼284 (4.28),[b] 295 (4.33), ∼307 (4.16)[b]	0.78 ± 0.07 (350)
1k	∼309 (4.08),[b] 325 (4.28), 340 (4.28)	0.24 ± 0.01 (350)
		0.23 ± 0.01[c] (350)
1l	347 (4.51), 360 (4.49)	0.45 ± 0.02 (350)
1m	273 (4.25), 322 (4.05)	0.36 ± 0.01 (350)
1n	∼347 (4.16),[b] 364 (4.33), 383 (4.29)	0.70 ± 0.02 (350)

[a] Measured in methanol. [b] Shoulder. [c] Measured in hexane

sorbance band corresponds to the HOMO-1 → LUMO transition. The HOMO-1 of phenylcyclopropenone is similar to the HOMO of the styrene[26] with additional involvement of the n-orbital of a carbonyl oxygen. The LUMO of phenylcyclopropenone, on the other hand, looks almost identical to the LUMO of styrene (Figure 3). In fact, the HOMO → LUMO transition of styrene corresponds to the absorbance band at 247 nm (log ϵ =

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(23) Schubert, R.; Ansmann, A.; Bleckmann, P.; Schrader, B. *J. Mol. Struct.* **1975**, *26*, 429.

(24) Breslow, R.; Oda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4787.

(25) The geometry of phenyl- and diphenylcyclopropenones was optimized at the DFT B3LYP/6-311+G(3df, 2p) level by using the Gaussian 98W program as discussed in the Experimental Section.

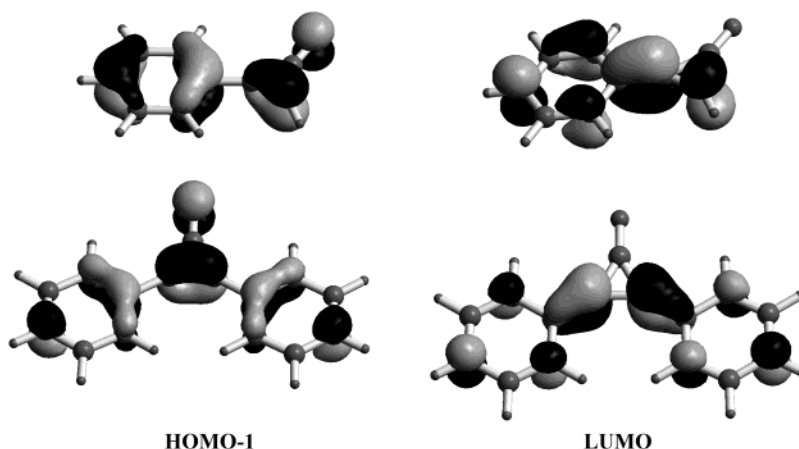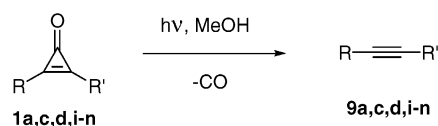(26) Amatatsu, Y. *J. Comput. Chem.* **2001**, *23*, 950.

FIGURE 3. HOMO-1 and LUMO of S_0 of phenylcyclopropenone and diphenylcyclopropenone (**1j**) by B3LYP/6-311+G (3df,2p).

4.17),[27] which is similar to the band observed in the UV spectrum of **1d** (Table 2). Substitution of the alkyl group in **1d** with the second phenyl ring in **1j** results in a 44-nm bathochromic shift of the major band in the UV spectrum (Figure 2, Table 2). TD-DFT calculations predict that this band in the spectrum of **1j** also corresponds to the HOMO-1 → LUMO transition (Figure 3), which closely resembles the HOMO → LUMO transition of stilbene.[28] The red shift of this absorbance band is, however, more pronounced between **1d** and **1j** than between styrene (247 nm in ethanol)[27] and stilbene (278 nm in ethanol).[29] This difference is apparently due to different geometry: phenyl- and diphenylcyclopropenones are planar, as discussed above, while stilbene is twisted with the ca. 43° dihedral angles between both benzene rings and the plane of the double bond.[30] This distortion substantially reduces conjugation in stilbene.

Conjugation of cyclopropenone with extended aromatic systems, such as in bis-α-naphthylcyclopropenone (**1n**), produces an even stronger effect, shifting λ_{max} another 70 nm versus diphenylcyclopropenone (**1j**). The absorption envelope for diaryl-substituted cyclopropenones usually contains two peaks and a shoulder (Figure 2, Table 2), which can be attributed to a coupling of the aromatic ring vibrations to the electronic transition. Introduction of donor p-methoxy substituents into benzene rings (**1k**) of diphenylcyclopropenone results in the red shift of ca. 30 nm (Table 1). This effect is similar to the one observed in the stilbene family (e.g., 4,4′-dimethoxystilbene, 296 nm in ethanol)[31] but is much stronger. Additional electron-donating substituents in bis-(2,4-dimethoxyphenyl)-cyclopropenone (**1l**) increase the red shift by another 20 nm.

While the position and the structure of the major UV band strongly depends on the nature of the aromatic substituent, cyclopropenones **1d**, **1j**, **1k**, **1l**, **1m**, and **1n** show similar extinction coefficients (Table 2).

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SCHEME 4

No phosphorescence could be detected but a weak fluorescence can be observed at room temperature in methanolic solutions of cyclopropenones **1j**,**k**,**n** with use of 300 and 350 nm excitation light. The fluorescence spectrum is identical in shape to the spectrum of corresponding photoproducts, i.e., diarylacetylenes **9j**,**k**,**n**, which are intensely fluorescent. We believe that the weak fluorescence of these cyclopropenones is due to their photodecomposition by the excitation source. The absence of phosphorescence and fluorescence of diarylcyclopropenones indicates a fast nonradiative depopulation of excited states and is in agreement with the high quantum yield of photodecarbonylation (Table 2). This observation is in sharp contrast with styrene[32] and stilbene,[33] which are strongly luminescent.

Photochemistry. Photolysis of cyclopropenones studied in this work resulted in a remarkably clean decarbonylation reaction. The irradiation of cyclopropenones **1a**,**c**,**d**,**i**−**n** with UV light produced a quantitative yield of corresponding alkynes (Scheme 4).

It should be noted that diaryl-substituted acetylenes produced in the photolysis of cyclopropenones **1i**−**n** are also photoreactive and can undergo secondary photoreactions. However, the high quantum yield of cyclopropenone photolysis allowed us to terminate the irradiation before significant contamination of the reaction mixtures occurs.

The quantum efficiency of photochemical decarbonylation of cyclopropenones **1a**,**c**−**f**,**i**−**n** was determined by using ferrioxalate chemical actinometry. This reaction was found to be very efficient with quantum yields in the range from 23% to almost 80%. Alkyl-substituted cyclopropenones have the lowest quantum efficiency, while conjugation of the cyclopropenone system with unsubstituted aromatic systems results in the highest

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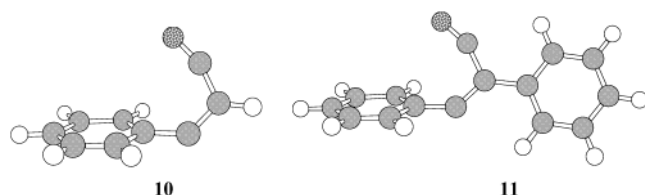
FIGURE 4. B3LYP/6-31+G(d,p) geometries corresponding to the local minima on the potential energy surface of decarbonylation of phenyl- and diphenylcyclopropenones.

quantum yield. Interestingly, substituents at the benzene rings reduce the quantum yield, e.g., **1j** versus **1i**, **1k**, or **1l**. This effect is apparently due to increased efficiency of the vibronic deactivation of the excited state.

Theoretical analysis of the reactivity of the parent cyclopropenone with density functional,[17,34] as well as the reactivity of several alkyl or heteroatom-substituted
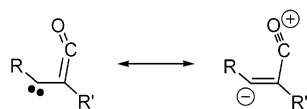
cyclopropenones using Hartree−Fock calculations with or without Møller−Plesset correlation energy correction (MP2),[35] predict an intermediate in the decarbonylation reaction. The structure of this intermediate is described as having both ketenylcarbene and zwitterion features.[17,35]

We have conducted a relaxed scan of the potential energy surface (PES) relevant to decarbonylation of phenylcyclopropenone in terms of C^2-C^1 and C^3-C^1 bond length at the B3LYP/6-31+G(d,p) level. In agreement with previous results, we found that the simultaneous elongation of both bonds results in a rapid rise in potential energy and corresponds to a maximum on PES. Two saddle points found on the PES correspond to the geometry where one bond is elongated to ca. 2.1 Å, while the other remains virtually unchanged. Cleavage of the C^2-C^1 cyclopropenone bond, i.e., next to phenyl, requires somewhat less energy and leads to the local minimum. The B3LYP/6-31+G(d,p) optimized geometry corresponding to this minimum on the reaction pathway of phenyl- and diphenylcyclopropenones is shown in Figure 4.

It is interesting to note that cleavage of the C_1-C_2 bond resulting in the formation of intermediates **10** and **11** is also accompanied by a change in the relative position of phenyl and R (Ph or H) substituents at the double bond. In the starting cyclopropenone these groups are locked in the cis position by a cyclic structure, while in the intermediate, the C_2-C_3 double bond has trans geometry.

In fact, according to DFT calculations, there are no energy minima corresponding to cis isomers of **10** and **11**. The structure of intermediates **10** and **11**, in our opinion, is better described by the zwitterionic rather than the ketenylcarbene form. The ESP calculations predict that C_2 atoms in both molecules carry a substantial negative charge (ca. −0.7), while C_1 is positively charged (ca. +0.4). The phenyl ring at C_2 in optimized
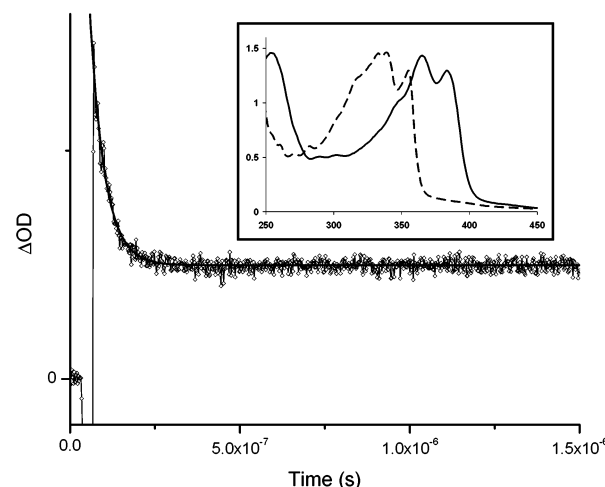

FIGURE 5. Absorbance change at 320 nm produced by laser flash photolysis of an ca. 10^{-4} M solution of **1n** in methanol. $\lambda_{\text{excit}} = 355$ nm. The solid line represents the least-squares fitting to a single-exponential expression. The insert shows spectra of the starting material (**1n**, solid line) and the product (bis-α-naphthylacetylene, dashed line) in methanol.

structures lies in the orthogonal plane to the vinyl anion/ carbene system. This observation is in sharp contrast with structures of other singlet carbenes where the phenyl group always lies in the plane of the carbene stabilizing the vacant p-orbital.[36] In addition, it is known that singlet carbenes react with methanol at a rate close to the diffusion control limit. We have conducted photochemical decarbonylation of cyclopropenones in neat methanol but were unable to detect any O−H insertion products or other products that could be derived from carbene or ketene functionality.

Results of nanosecond laser flash photolysis ($\lambda_{\text{excit}} = 355$ nm) of bis-α-naphthyl-cyclopropenone **1n** in methanol support the formation of the intermediate in the decarbonylation reaction. We observed an instant (on the time scale of the instrument) rise in absorbance following the laser pulse and then somewhat slower decay, which fits first-order rate law well. Changes of absorbance at 320 nm after the laser pulse are shown in the Figure 5.

The intermediate has a lifetime of ca. 40 ns and a broad absorbance spectrum. The latter observation is also more in agreement with the zwitterionic structure of the intermediate rather than ketenylcarbene. Saturation of the methanolic solution of cyclopropenone **1n** with oxygen prior to photolysis did not quench the formation of the transient or acetylenic product and did not affect the lifetime of the former. This observation allows us to conclude that photodecarbonylation of cyclopropenone **1n** proceeds via the singlet exited state and that the intermediate also has a singlet multiplicity. Decay of this intermediate results in the formation of a residual absorbance, which does not change in time (Figure 5). At this wavelength (320 nm) the acetylenic product **9n** absorbs stronger than the starting cyclopropenone **1n** (see insert in Figure 5) and the residual absorbance apparently corresponds to the acetylene **9n** formed in the reaction.

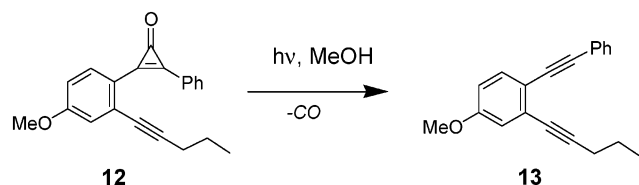(34) Nguyen, L. T.; De Proft, F.; Nguyen, M. T.; Geerlings, P. *J. Org. Chem.* **2001**, *66*, 4316.

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SCHEME 5

32%
12

~ 20%

SCHEME 6

12   **13**
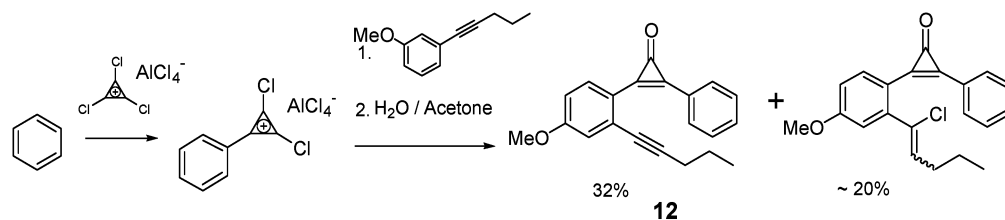
Photochemical Generation of the Enediyne System. To test the applicability of the photochemical decarbonylation of cyclopropenones to the in situ generation of the enediyne structure, we explored the photochemistry of 2-(4′-methoxy-2′-(1-pentynyl)phenyl)-3-phenylcyclopropenone **12**. This photoactivatable precursor of benzannulated enediyne **13** was prepared by using the tetrachlorocyclopropene route. One equivalent of benzene was alkylated with trichlorocyclopropenium cation to give phenyldicholorocyclopropenium cation. The latter was used to alkylate 1-(3-methoxyphenyl)-pentyne-1. After hydrolysis of the reaction mixture in aqueous acetone, we have isolated cyclopropenone **12** and the product of addition of hydrogen chloride across the triple bond of the former (Scheme 5).

The 350-nm irradiation of **12** results in the quantitative formation of enediyne **13** (Scheme 6). The photodecarbonylation of **12** is an efficient reaction with a quantum yield of 0.56.

Conclusions. We have shown that alkyl- or aryl-substituted cyclopropenones are thermally stable compounds but undergo photochemical decarbonylation to acetylenes with high quantum and chemical yield. The decarbonylation reaction is a stepwise process where cleavage of one bond in the cyclopropenone structure results in the formation of a short-lived zwitterionic intermediate, which then loses carbon monoxide to produce the ultimate acetylenic product. Aryl-substituted and especially diaryl-substituted cyclopropenones can be activated with a 350 nm or longer wavelength light and can be used for the development of photonucleases. The applicability of cyclopropenone photochemistry to the generation of the enediyne system has been illustrated with the example of photochemical preparation of benzannulated enediyne **13**.

Experimental Section

Photolytic Experiments. Analytical photolyses were performed by irradiation of ca. 10^{-4} M solutions of cyclopropenones in a 1 cm quartz cell, using a RMR-600 Rayonet photochemical reactor equipped with a carousel and three sets of eight lamps with λ_{max} of emission at 254, 300, and 350 nm. Reaction mixtures were then analyzed by HPLC. Preparative photolyses were conducted by the irradiation of methanolic solutions of ca. 100 mg of cyclopropenones, using a 16 lamp (with $\lambda_{emission}$ = 254 or 350 nm) Rayonet photochemical reactor

in a quartz vessel equipped with an immersible cooling finger. The consumption of starting material was followed by TLC. After the irradiation solvent was removed in a vacuum, products were analyzed by NMR spectroscopy. Determination of a quantum yield was performed with a ferrioxalate chemical actiniometer.[37] The laser flash photolysis experiments were carried out with use of a frequency tripled (355 nm) output of a Q-switched Nd:YAG laser as the excitation source. The setup of the laser system and time-resolved UV spectrometer was described previously.[38]

Thermal reactions of cyclopropenones were monitored with a UV−vis spectrometer equipped with a thermostatable cell holder. Substrate concentrations in the reacting solutions were ca. 10^{-4} M, and the temperature of these solutions was controlled with 0.05 °C accuracy. Observed first-order rate constants were calculated by least-squares fitting of a single-exponential function.

Materials. Moisture- and oxygen-sensitive reactions were carried out in flame-dried glassware under an argon atmosphere. Tetrahydrofuran and diethyl ether were distilled from sodium, and dichloromethane was distilled from phosphorus pentoxide under argon immediately before use. Hexanes used in column chromatography was distilled from sodium, and ethyl acetate and acetone were distilled from anhydrous calcium chloride. HMPA was distilled from calcium hydride and stored under argon. Diphenylcyclopropenone (**1j**) was obtained from Aldrich and recrystalized from ethanol. All other reagents were used as purchased. Purification of products by column chromatography was performed with use of 40−63 μm silica gel. 2-Butylcyclopropenone (**1b**),[16] phenylhydroxycyclopropenone (**1e**),[9a] and 1,3-dichloroacetone acetal (**6**)[16] were prepared according to previously reported procedures. Preparation of compounds **1a−n**, **8a**, **12**, and **13** is described in the Supporting Information.

Theoretical Procedures. Density functional theory calculations were carried out with the Gaussian 98 program.[39] Geometries were pre-optimized, using the B3LYP hybrid functional and 6-31+G(d,p) basis set, and then reoptimized (in the case of phenyl- and diphenylcyclopropenones) with the extended triple-ζ basis at the B3LYP/6-311+G(3df,2p) level. Zero-point vibrational energy (ZPVE) corrections, required to correct the raw relative energies to 0 K, were obtained from B3LYP/6-311+G(3df,2p) frequency calculations. Analytical second derivatives were computed to confirm each stationary point to be a minimum by yielding zero imaginary vibrational frequencies. These frequency analyses are known to overes-

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timate the magnitude of the vibrational frequencies. Therefore, we scaled the frequencies by 0.9772.[40] The vertical excitation energies were evaluated by using the Random Phase Approximation for a time-dependent DFT calculation method,[41] at the TD-B3PW91/6-311++G(3df,2p) level.

Supporting Information Available: Preparation of cyclopropenones **1a**–**n** and, **12**; spectroscopic data for compounds **1a**–**n**, **9d**–**n**, **12**, and **13**; ^{1}H, ^{13}C NMR, and IR spectra of unknown compounds (**1a,c,d,g,h,i,n**); Gaussian 98 output files for DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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