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Photochemical generation and trapping of 3-oxacyclohexyne†

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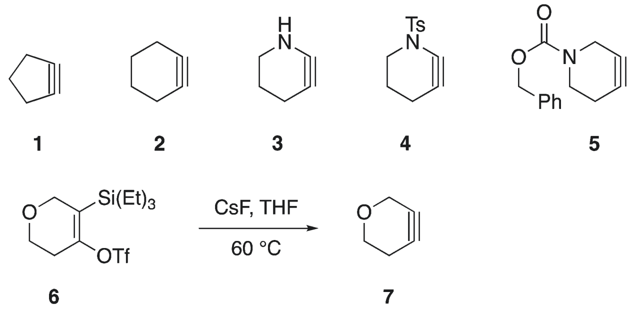
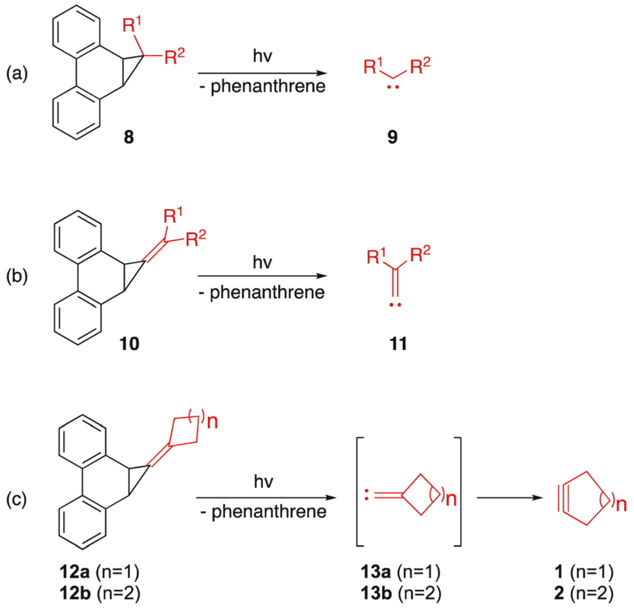
The strained heterocyclic alkyne, 3-oxacyclohexyne, was generated photochemically for the first time using a cyclopropanated phenanthrene precursor, and trapped by cyclopentadienones as Diels–Alder adducts. The precursor initially produced the putative 3-oxacyclopentylidenecarbene that subsequently rearranged to the cycloalkyne. Computational studies indicate that the carbene favors a singlet state, and the barrier for its ring expansion by a 1,2-shift of the carbon proximal to oxygen is lower in energy than the corresponding shift of the distal carbon.

Small-ring strained cycloalkynes have been a source of much fascination to theoreticians and experimentalists alike.[1] The utility of cyclopentyne (**1**)[2] and cyclohexyne (**2**)[2,3] in organic synthesis, including the construction of natural products,[4] is also well documented. By contrast, considerably less is known about strained alicyclic alkynes bearing a heteroatom in the ring. For many years, the matrix-isolated 3-azacyclohexyne **3**[5] remained as the sole exemplar of such a system before the tosyl substituted derivative **4**[6] and the *N*-substituted 4-piperidyne **5**[7] were reported in synthetic contexts to prepare functionalized heterocycles. To the best of our knowledge, the only experimental approach to an oxygen-containing cyclohexyne reported to date is the method devised by Garg and coworkers, who converted the silyl triflate precursor **6** into 3-oxacyclohexyne **7** by a fluoride-induced 1,2-elimination (eqn (1)).[8] This recent work also demonstrated the utility of **7** as a powerful synthetic intermediate for preparing a wide variety of complex oxygen-containing heterocyclic compounds.[8]



(1)

It has long been known that cyclopropanated phenanthrenes such as **8** release carbenes **9** upon photolysis with the concomitant loss of phenanthrene (Scheme 1a).[9] The release of ring strain and aromatization of the central ring of the phe-



Scheme 1 Cyclopropanated phenanthrenes as carbene sources.

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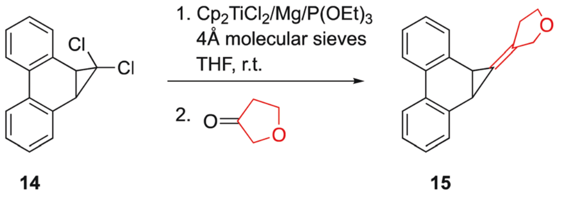
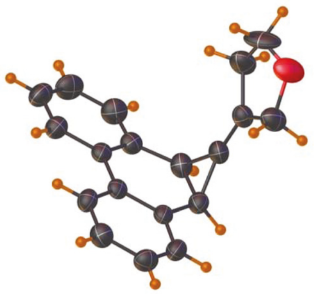
nanthrene byproduct contribute to the driving force for carbene extrusion in this process. In recent years, we have extended the utility of this system to related precursors **10** to produce alkylidenecarbenes **11** (Scheme 1b).[10] Subsequently, we employed precursors **12a** and **12b** to produce **1** and **2** respectively,[11] presumably by the Fritsch–Buttenberg–Wiechell (FBW)-type rearrangement[12] of the intermediate carbenes **13a** and **13b** (Scheme 1c). In this work, we demonstrate the utility of an analogous approach to successfully generate **7**, for the first time by a photochemical route.

To prepare **15**, the desired photochemical precursor to **7**, the known dichloro derivative **14** was first synthesized from phenanthrene following a literature procedure.[13] Subsequently **14** was converted into **15** by adapting a convenient one-pot method developed by Takeda *et al.* (eqn (2))[14] albeit in a modest yield of 36%. The structure of **15** was determined by X-ray crystallography and is shown in Fig. 1 along with salient crystallographic data.[15]



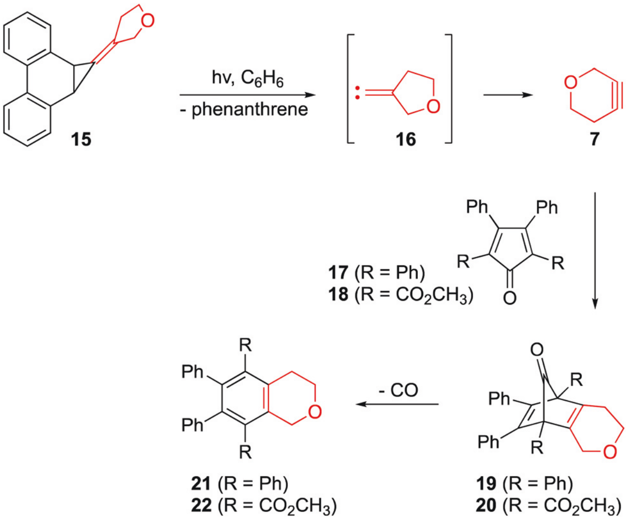
(2)

The photolysis of a solution of **15** in benzene (Rayonet reactor; ~315 to 400 nm; ambient temperature; 31 hours) in the presence of tetraphenylcyclopentadienone (**17**) led to the known adduct **21**[8] in a yield of 20%.[16] This result, summarized in Scheme 2, is rationalized by **15** releasing the putative carbene **16** which then undergoes a FBW rearrangement to produce **7**. The Diels–Alder reaction of **7** with **17** initially gives **19** which subsequently loses CO to form **21**. A similar trapping study using the cyclopentadienone **18** also gave the adduct **22** in an yield of 16%,[16] presumably through the intermediacy of the initially formed **20**. The X-ray structure of **21** and **22** and their key crystallographic data are shown in Fig. 2.[17]



Crystal system	Monoclinic
Space group	$P2_1$
a/b/c/ Å	10.482/5.173/12.755
α/β/γ/ °	90/98.5/90
Volume/ Å^3	684.1
Z	2
Final R indexes [I>=2σ (I)]	R_1 = 0.0452, wR_2 = 0.0946
Final R indexes [all data]	R_1 = 0.0748, wR_2 = 0.1066

Fig. 1 X-ray structure of **15** and key crystallographic data.



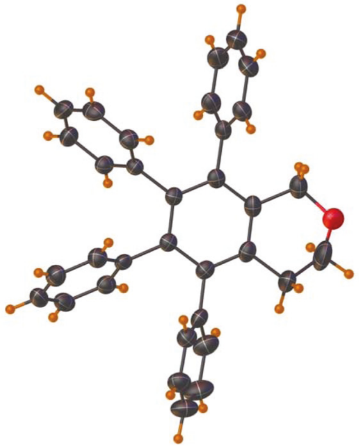
Scheme 2 Photolysis of **15** in the presence of trapping agents **17** and **18**.

In addition to the experimental work described above, we carried out computational studies on **16** and its conversion into **7**.[18] Initially we performed hybrid density functional theory calculations (B3LYP/6-31+G*),[19] which revealed that singlet carbene **16** is more stable than the triplet, by about 41 kcal mol^{-1} (after applying zero-point vibrational energy correction), observation that is consistent with the known tendency of alkylidenecarbenes to show an overwhelming preference for the singlet ground state.[20]

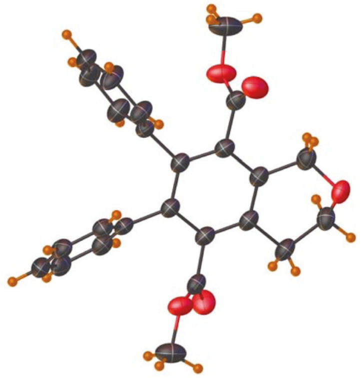
We then turned our attention to the mechanism by which singlet **16** undergoes ring-expansion to produce **7**. Although this is a formal 1,2 shift of one of the two C–C bonds connected to the endocyclic sp^2 carbon, those two bonds are non-equivalent. Thus, it was of interest to determine whether there might be a preference to move bond ***a*** or ***b*** in **16** (Scheme 3) to form the strained alkyne **7**.

As summarized in Fig. 3, coupled-cluster calculations[21] at the CCSD(T)/cc-pVTZ//B3LYP/6-31+G* level of theory suggest that there is, indeed, a preference to shift bond ***a***, which is closer to the oxygen, rather than bond ***b*** (farther away from the oxygen) when singlet **16** rearranges into **7**. These calculations indicate that the transition state for the rearrangement of **16** into **7** by a 1,2-shift of bond ***a*** is about 3.9 kcal mol^{-1} lower than that for moving bond ***b***. Further efforts to experimentally verify the computational results by using appropriately labelled precursors are planned as future work in our laboratory.

In conclusion, we have reported a convenient and readily prepared phenanthrene-based precursor **15** to serve as a photochemical source of 3-oxacyclohexyne **7**. Photolysis of benzene solutions of **15** in the presence of cyclopentadienones **17** and **18** led to the corresponding adducts **21**[8] and **22** respectively. The strained alkyne is likely formed from the ring expansion

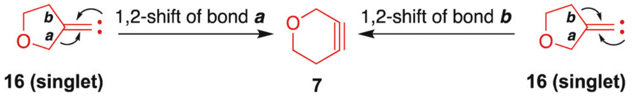


Crystal system	Monoclinic
Space group	$P2_1/c$
a/b/c/ Å	13.469/12.454/14.312
α/β/γ/ °	90/91.7/90
Volume/ $Å^3$	2399.7
Z	4
Final R indexes [I>=2σ (I)]	R1 = 0.0509, wR2 = 0.0945
Final R indexes [all data]	R1 = 0.1172, wR2 = 0.1158



Crystal system	Monoclinic
Space group	$P2_1/n$
a/b/c/ Å	10.528/14,232/14.053
α/β/γ/ °	90/105.3/90
Volume/ $Å^3$	2031.1
Z	4
Final R indexes [I>=2σ (I)]	R1 = 0.0462, wR2 = 0.1024
Final R indexes [all data]	R1 = 0.0737, wR2 = 0.1157

Fig. 2 X-ray structures of **21** (left) and **22** (right) with their key crystallographic data.



Scheme 3 Two different pathways for the rearrangement of singlet carbene **16** into **7**.

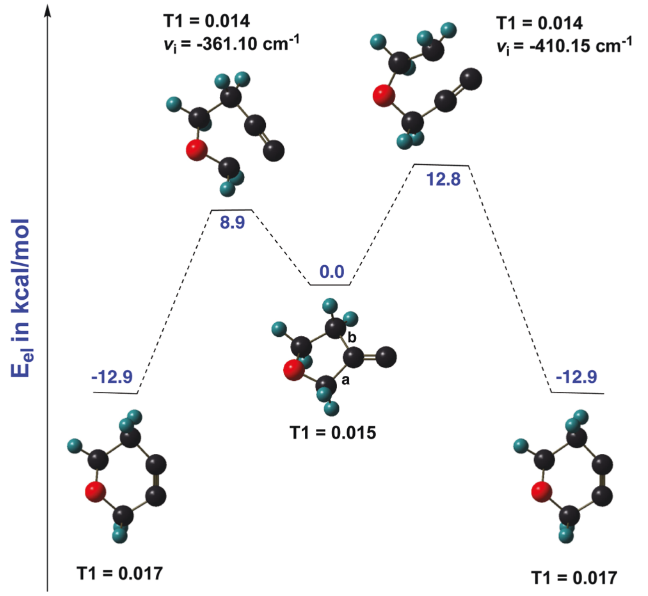


Fig. 3 The potential energy surface for the rearrangement of **16** into **7** computed at CCSD(T)/cc-pVTZ//B3LYP/6-31+G*. The *T1* diagnostic values (CCSD) for all structures and the imaginary frequencies for the transition states are also noted.

of the putative carbene **16**, which is initially extruded from the **15**. We are currently investigating the possibility of intercepting the carbene directly with alcohols and/or alkenes. Unlike conventional nitrogenous precursors such as diazo compounds and diazirines, **15** is safer, shelf-stable, and easier to handle. Furthermore, we are planning on synthesizing alternative precursors based on indan, rather than phenanthrene, as analogous indan-compounds are also known to extrude carbenes upon decomposition.[22] We anticipate that the availability of these cyclopropane precursors based on aromatic systems should provide a much-needed impetus to the investigation of other strained carbocyclic and heterocyclic alkynes by techniques such as matrix isolation spectroscopy and time-resolved laser flash photolysis. Such studies are also being pursued in our laboratory.

Experimental section

General procedures

Tetrahydrofuran was dried by passage through two columns (2 ft × 4 in) of activated alumina. All other solvents and reagents were used as obtained from commercial sources. The synthesis of precursor **15** was carried out under an argon in oven-dried glassware. Flash chromatography was performed on an automated system with pre-packed silica gel columns (70–230 mesh). NMR spectra were recorded in $CDCl_3$ at

500 MHz for proton and 125 MHz for carbon. The shifts are reported in δ ppm and referenced to either tetramethylsilane (TMS) or the proton signal from residual $CHCl_3$. GC/MS data were obtained with a capillary gas chromatograph interfaced with a quadrupole, triple-axis mass selective detector operating in the electron impact (EI) mode. High resolution mass spectra (HRMS) were obtained in a positive ion mode with a time-of-flight mass spectrometer interfaced with an electrospray ionization (ESI) source. FTIR spectra were acquired with an attenuated total reflectance (ATR) accessory. The photolysis reactions were carried out in a sealed glass vial using a Rayonet photochemical reactor equipped with 16 12-inch 8 W lamps with output centered at ~350 nm (range ~315 to 400 nm).

Synthesis of precursor 15

Bis(cyclopentadienyl)titanium(IV) dichloride (4.5 g, 18.1 mmol) was added to magnesium turnings (450 mg, 18.5 mmol) and 4 Å molecular sieves (1.05 g) in anhydrous THF (30 mL). Triethyl phosphite (6.2 mL, 3.6 mmol) was added to the dark brown reaction mixture. The color of the reaction mixture turned dark green within 15 minutes. Stirring was continued for 3 hours at room temperature. A solution of **14**[13] (1.57 g, 6.0 mmol), dissolved in THF (15 mL), was then added to the dark green reaction mixture. After stirring for an additional 20 minutes, dihydro-3(2*H*)-furanone (0.232 mL, 3.0 mmol) was added to the mixture and stirring continued for 1 hour. The dark orange mixture was purified by flash chromatography on silica gel (hexanes) to obtain 93.6 mg of **15**. Yield: 36%. ^1H NMR (500 MHz, chloroform-*d*) δ 8.02–7.94 (m, 2H), 7.44–7.40 (m, 1H), 7.39–7.35 (m, 1H), 7.32–7.24 (m, 4H), 4.35 (dt, J = 12.9, 1.5 Hz, 1H), 4.11–4.03 (m, 1H), 3.91 (dt, J = 8.0, 6.0 Hz, 1H), 3.73 (dt, J = 8.3, 7.1 Hz, 1H), 3.17 (m, 2H), 2.70–2.53 (m, 1H), 2.38 (m, 1H); ^{13}C NMR (125 MHz, chloroform-*d*) δ 132.7, 132.7, 129.3, 129.2, 128.9, 128.8, 128.2, 127.9, 127.8, 126.2, 126.2, 123.4, 123.4, 115.5, 69.3, 68.6, 30.8, 22.3, 21.8; FTIR (ATR, neat): ν 3065, 2839, 1486, 1444, 1041, 911, 770, 729 cm^{-1}; LRMS (EI): *m/z* 260 (M^+), 231, 215, 178. HRMS (ESI) calculated for $C_{19}H_{17}O$ $[M + H]^+$: 261.1274, found 261.1271.

Photolysis of 15

Precursor **15** (100 mg, 0.385 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (**17**, 148 mg, 0.385 mmol) were dissolved in 5 mL benzene, placed in the Rayonet photochemical reactor (~315 to 400 nm) and irradiated for 31 hours. The dark purple reaction mixture was purified by flash chromatography on silica gel (hexanes) to obtain 33 mg of **21**.[8] Yield: 20%. ^1H NMR (500 MHz, chloroform-*d*) ^1H NMR (500 MHz, chloroform-*d*) δ 7.23–7.17 (m, 4H), 7.16–7.05 (m, 6H), 6.96–6.67 (m, 10H), 4.55 (s, 1H), 3.91 (t, J = 6 Hz, 2H), 2.64 (t, J = 6 Hz, 2H). ^{13}C NMR (125 MHz, chloroform-*d*) δ 140.8, 140.3, 140.0 (2 carbons), 139.5, 139.1, 138.9, 137.9, 132.4, 131.4 (2 carbons), 131.1, 130.4, 130.1, 127.9, 127.8, 126.7 (2 carbons), 126.4, 125.5, 125.4, 68.3, 65.5, 28.7 (24 of 25 carbon signals found with likely overlap of one signal); FTIR (ATR, neat): ν 2923, 2850, 1441, 1109, 1072, 794, 736 cm^{-1}; LRMS (EI): *m/z* 438 (M^+), 361, 315, 252. HRMS (ESI) calculated for $C_{33}H_{27}O_5$ $[M + H]^+$: 439.2056, found 439.2068.

An analogous photolysis with 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**18**), for about 49 hours, produced the adduct **22** in an yield of 16%. ^1H NMR (500 MHz, chloroform-*d*) δ 7.14–7.11 (m, 6H), 7.03–6.92 (m, 4H), 4.84 (s, 2H), 4.02 (t, J = 5.8 Hz, 2H), 3.48 (s, 1H), 3.44 (s, 1H), 2.91 (t, J = 5.8 Hz, 2H).^{13}C NMR (125 MHz, chloroform-*d*) δ 169.1, 168.6, 138.2, 138.1, 137.7, 137.6, 136.1, 132.2, 132.1, 130.3, 130.1, 130.0, 127.7, 127.2 (two signals), 66.6, 64.8, 52.2, 52.1, 26.4 (20 of 21 carbon signals found with likely overlap of one signal); FTIR (ATR, neat): ν 2944, 1724, 1200, 1152, 1116, 765, 754 cm^{-1}; LRMS (EI): *m/z* 402 (M^+), 370, 282, 252. HRMS (ESI) calculated for $C_{25}H_{23}O_5$ $[M + H]^+$: 403.1540, found 403.1538.

Computational studies

All calculations were carried out with Gaussian 09[18] using the methods and basis sets described in the text. The stationary points obtained from geometry optimizations were verified as minima (zero imaginary frequency) or transition states (one imaginary frequency) by subsequent frequency calculations.

X-ray diffraction experiments

X-ray data were acquired at 173 K on a Bruker D8 Quest Eco diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and PHOTON 50™ CMOS (complementary metal–oxide semiconductor) detector. The Bruker Apex 3 suite of programs was used to collect diffraction data.[23] The data reduction software package Bruker SAINT+[24] was used to integrate the frames with a narrow-frame algorithm and the multi-scan method (SADABS)[25] was used to correct the data for absorption effects. Processing of data was carried out with the Olex2 suite of programs.[26] The Bruker SHELXTL software package[27] was used to perform structure solution by direct methods, and refinement by full-matrix least-squares on F^2. All nonhydrogen atoms were refined anisotropically with suggested weighting factors and the hydrogens were calculated on a riding model. All cif files were validated with the checkCIF/Platon facility of IUCr that was accessed with Olex2.[26] X-ray graphics were also produced with Olex2.[26]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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15 CCDC number for compound **15**: 1560816.†

16 This represents the final yield of isolated product following work up and purification. Substantial photodegradation of the precursor to unidentified, non-photolabile isomers was also observed in the photolysate mixture.

17 CCDC number for compound **21**: 1561188; for compound **22**: 1573403.†

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