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An Experimental and Computational Investigation of (α-Methylbenzylidene)carbene

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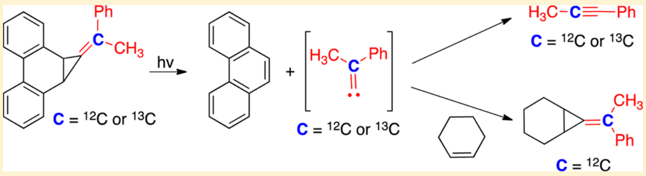
S Supporting Information

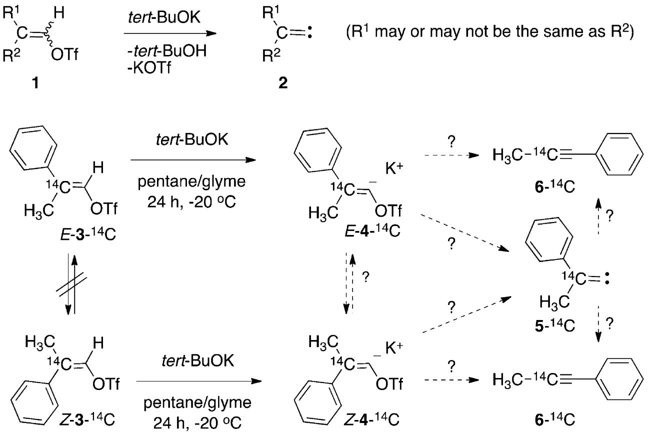
ABSTRACT: Photolysis of 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene, in C_6H_6 (or C_6D_6), at ambient temperature, produces (α-methylbenzylidene)carbene which undergoes a facile Fritsch−Buttenberg−Wiechell (FBW)-type rearrangement to 1-phenylpropyne. The alkyne results exclusively from a 1,2-phenyl shift as evident from the use of a ^{13}C-labeled precursor. This experimental result is consistent with CCSD(T)/cc-pVTZ//B3LYP/6-31+G* calculations which reveal that a 1,2-phenyl shift in the singlet carbene needs to overcome a barrier of only 3.8 kcal/mol whereas the 1,2-methyl shift has to surmount a much larger barrier of 11.9 kcal/mol. The alkyne remains the predominant product when the photolysis is carried out in cyclohexene but the carbene-alkene cycloadduct could be detected, albeit in low yield, in the photolysate.



INTRODUCTION

Stang and co-workers have previously noted that treatment of primary vinyl triflates (**1**) in solution with a strong base such as potassium *tert*-butoxide offered a convenient route to "free" alkylidenecarbenes (**2**).[1] In particular, they reported[2] that labeled (α-methylbenzylidene)carbene (**5**-^{14}C), generated from either the *E* or *Z* triflate (**3**-^{14}C), underwent a Fritsch−Buttenberg−Wiechell (FBW)-type rearrangement[3] to 1-phenylpropyne-^{14}C (**6**-^{14}C) with exclusive migration of the phenyl group (Scheme 1). The lack of stereoselectivity in these rearrangements, and the fact that the two starting triflates did not interconvert during the reaction, was taken to suggest that both precursors produced the free carbene **5**-^{14}C as a common intermediate, which subsequently rearranged to the observed alkyne **6**-^{14}C via a 1,2-phenyl shift.

Scheme 1. Reaction of *E*- and *Z*-3 Triflates with *tert*-BuOK Leads to the Same Alkyne 6[2]



The authors did note, however, that even though the two triflate starting materials did not interconvert during the reaction, the interconversion of the carbenoids derived from these precursors, namely *E*-**4**-^{14}C and *Z*-**4**-^{14}C, could not be ruled out.[4] This possibility has elicited some concern as to whether both precursors do, in fact, afford the same intermediate.[5] It has been pointed out, for example, that one starting triflate could form the "free" carbene whereas the other can only produce a carbenoid, and both of these intermediates prefer to undergo a 1,2-phenyl shift.[5] Another complication stems from the fact that the FBW rearrangement of carbenoids to form alkynes can occur with very little anti/syn stereoselectivity.[5] Thus, in many instances, ascertaining the true nature of the product-forming intermediates involved in the α-elimination of various vinyl substrates can pose vexing mechanistic questions; carbenoids, free carbenes, and other possible species will all need to be carefully considered.[5,6]

Given these circumstances, the generation of **5** by an alternative route that excludes the possibility of carbenoids and other surrogate species might provide a clearer mechanistic insight into the chemistry of this carbene. Perhaps one approach could be a "reagent-free" photolysis of a suitable precursor to generate **5**. Unfortunately, the literature reveals a conspicuous paucity of photochemical methods for generating alkylidenecarbenes, a limitation attributed to the difficulty in preparing appropriate precursors.[7] Some of the earlier accounts include a photofragmentation route that proved to be rather inefficient with a reported yield of <5%,[8] approaches aimed at generating specific alkylidenecarbenes in a matrix,[7,9] and photolysis of an indane-based precursor to prepare polyynes in solution.[10]

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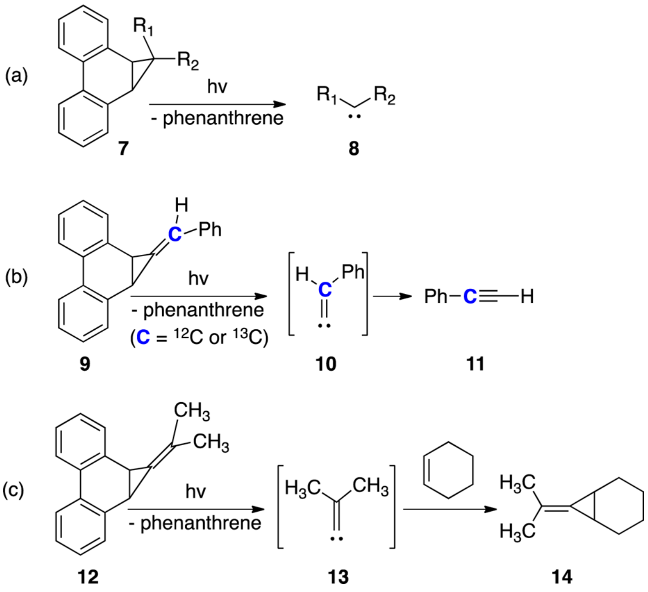
Scheme 2. Photochemical Generation of Carbenes from Cyclopropanated Phenanthrenes



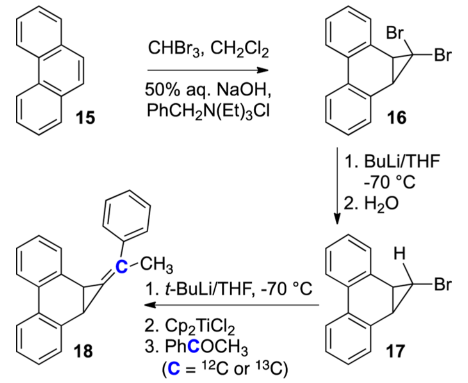
As a number of laboratories, including ours, have demonstrated, cyclopropanated phenanthrene derivatives such as **7** can be photolyzed to produce carbenes **8** (Scheme 2a).[11] It seemed to us, therefore, that by suitably modifying **7** we might be able to address the need for convenient and generally applicable photochemical routes to alkylidenecarbenes. Our approach proved successful, and we recently reported the first use of a phenanathrene-based precursor to produce an alkylidenecarbene as exemplified by the photolysis of **9**, which gave phenylacetylene **11** via benzylidenecarbene **10** (Scheme 2b).[12] Using a ^{13}C labeled precursor, we showed that **11** originated entirely from a 1,2-hydrogen shift, a result that is consistent with DFT and coupled-cluster calculations.[12] Furthermore, the hydrogen migration in **10** was found to be too rapid for the carbene to undergo intermolecular trapping reactions with alkenes. In a subsequent paper, we demonstrated that a similar approach could be used to produce a "trappable" carbene, dimethylvinylidene (**13**), by photolyzing **12**, with the carbene being intercepted by cyclohexene to form adduct **14** (Scheme 2c).[13]

In this work, we report the use of a phenanthrene-based precursor for the photochemical generation of (α-methylbenzylidene)carbene (**5**) and show, using ^{13}C-labeling studies, that the carbene undergoes a facile FBW-type rearrangement by a 1,2-phenyl shift. We also show that despite an overwhelming preference for alkyne formation, the carbene may be trapped by cyclohexene but in low yield. In addition, a computational analysis of the singlet and triplet gap in **5** and the potential energy surface for the rearrangement of singlet **5** are presented. The results of these calculations are fully consistent with the experimental observations.

RESULTS AND DISCUSSION

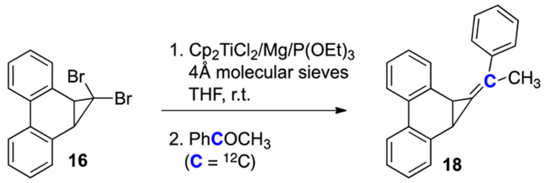
Syntheses of 18 (and 18-^{13}C). Our synthesis of 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**18**), a photochemical precursor to **5**, was initially carried out in three steps as shown in Scheme 3. In the first step, phenanthrene (**15**) was treated with bromoform, base, and a phase transfer catalyst, according to our previously reported procedure,[14] to obtain the dibromocyclopropyl adduct **16**. Subsequent treatment of this adduct with butyllithium at low temperature followed by quenching with water provided the *exo* monobromo derivative **17**.[11b] Finally, the cyclopropyllithium derived from **17** was reacted with titanocene dichloride, following a procedure developed Petasis and Bzowej[15] and then treated with acetophenone to prepare the desired precursor **18**. Using acetophenone labeled with ^{13}C (~100%) at the carbonyl position, in the last step, gave **18**-^{13}C, the precursor to **5**-^{13}C bearing the label (~100%) on the benzylic carbon.

Scheme 3. Synthesis of 18 (and 18-^{13}C), a Phenanthrene-Based Photochemical Precursor to 5 (and 5-^{13}C)



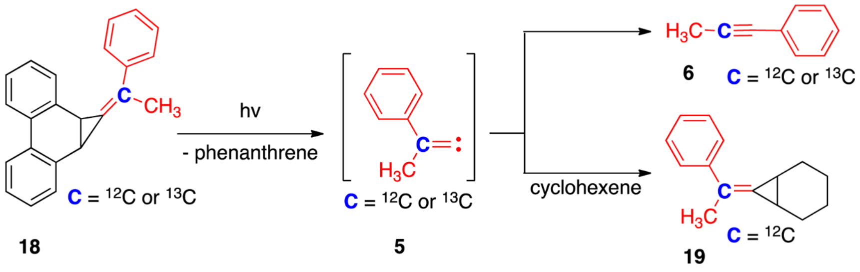
An alternative procedure was subsequently developed to directly obtain **18** from **16** by a modification of the Takeda method.[16] In this room temperature process (Scheme 4), the reagent $Cp_2Ti[P(OEt)_3]_2$, derived from the *in situ* reaction of Cp_2TiCl_2, magnesium, and $P(OEt)_3$, is treated with **16** and subsequently acetophenone to yield the desired precursor **18**.

Scheme 4. An Alternative Synthesis of 18 Directly from 16



Photochemical Experiments. Results of the photolysis of **18** and **18**-^{13}C are summarized in Scheme 5. Thus, a solution of **18** in benzene-d6 was photolyzed (~315 to 400 nm) at ambient temperature, and the reaction was monitored by ^{1}H NMR spectroscopy and GC/MS. The only product isomeric with carbene **5** was 1-phenylpropyne whose identity was confirmed by comparison to an authentic commercial sample. Approximately 13% of **18** was unreacted, and 11% had rearranged to unidentified nonphotolabile isomers[17] of the precursor. Using an internal standard, the yield of the alkyne **5** was determined by integration of ^{1}H NMR signals to be 73%. To determine the relative migratory aptitudes of the phenyl and methyl groups, **18**-^{13}C was photolyzed in benzene-d6. Analysis of the photolysate by ^{13}C NMR confirmed the presence of 1-phenylpropyne-^{13}C bearing the ^{13}C label only on the carbon adjacent to the methyl group. Clearly, the 1,2-phenyl shift in carbene **5**-^{13}C occurs to the complete exclusion of the methyl shift.

Scheme 5. Photolysis of 18 and 18-^{13}C in Benzene-d6 Lead to 6 and 6-^{13}C Respectively[a]



[a]The position of the label in **6**-^{13}C points to an exclusive 1,2-phenyl shift in carbene **5**-^{13}C. The intermediacy of **5** is implicated by the formation of adduct **19** when the precursor is photolyzed in cyclohexene.

It has been previously observed that alkylidenecarbenes bearing an alkyl and aryl substituent are difficult to trap in an intermolecular fashion due to a facile aryl shift, unless the aryl moiety contains a strong electron-withdrawing substituent such as the nitro group.[5,18] Nonetheless, we attempted to intercept carbene **5** by photolyzing **18** in cyclohexene. Although the alkyne **6** remained the overwhelmingly major product, we observed that **19**, the adduct of **5** and cyclohexene, was also formed albeit in a low yield of 1.5% (by NMR). The identity of **19** was established by comparison to an authentic sample that was independently synthesized following the route shown in Scheme 3, but beginning with cyclohexene instead of phenanthrene.

Computational Studies. In tandem with the experimental work described above, we carried out a computational investigation into the structure of **5** and its rearrangement pathways. Alkylidenecarbenes are known to possess singlet ground states,[19] and calculations using hybrid density functional methods such as B3LYP[20] and M062X,[21] with the 6-311+G** basis set, indicate that carbene **5** conforms to that paradigm. Interestingly, two minima were located for singlet **5** with B3LYP/6-311+G** and were nearly isoenergetic. One form, designated as **5s-pl** in Figure 1, has all the carbons essentially in one plane whereas the nonplanar form, **5s-npl**, has the phenyl plane twisted away from the plane of the remaining three carbons by 72.6°. The **5s-pl** form was only 0.13 kcal/mol lower in energy than **5s-npl**, after applying zero-point vibrational energy (ZPVE) corrections. On the other hand, only one minimum was located for the triplet, **5t**, which was found to be planar and 37 kcal/mol above **5s-pl**. The reaction energy, after applying ZPVE corrections, for the conversion of **5s-pl** into the alkyne **6** was computed to be −52.7 kcal/mol, and the barriers for the methyl and phenyl shifts were 10.3 and 2.6 kcal/mol, respectively. The structures of the two transition states are also shown in Figure 1. These barriers reflect the greater ease with which phenyl migrates relative to the methyl group. Calculations at the M062X/6-311+G** level of theory gave similar results with one notable exception in that the transition state energy for the phenyl shift was slightly lower than that of the carbene itself. The results of calculations at these two theoretical levels are summarized in Table 1.

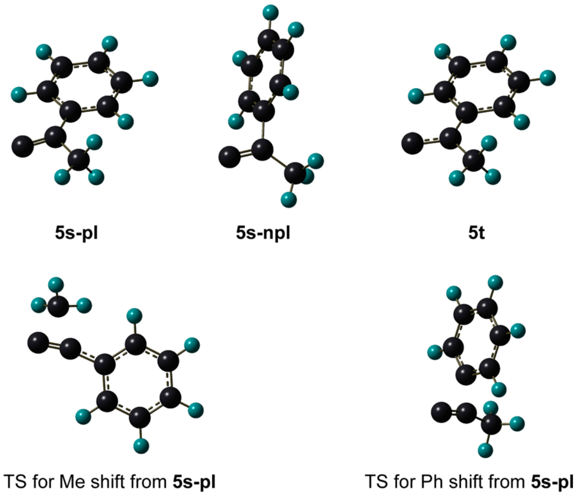


Figure 1. B3LYP/6-311+G** structures of singlet (planar and nonplanar) and triplet **5** are shown in the top row. The bottom row shows the transition states for the methyl and phenyl shifts respectively starting from the lower energy singlet **5s-pl**.

Table 1. Computed Relative Energies in kcal/mol, after Zero-Point Vibrational Energy Corrections, for the Potential Energy Surface of Carbene 5 and Alkyne 6

entity	(R/U)B3LYP/6-311+G**	(R/U)M062X/6-311+G**
5s-pl[a,b]	0	0
5s-npl[a,b]	0.13	0.26
5t[b,c,d]	37.04	38.87
6[a,b]	−52.73	−51.34
TS$_{\text{Me shift}}$[a,e,f]	10.31	8.27
TS$_{\text{Ph shift}}$[a,e,f]	2.56	−0.18

[a]Restricted method. [b]No imaginary frequency. [c]Unrestricted method. [d]Spin expectation values $\langle S^2 \rangle$ = 2.000. [e]One imaginary frequency. [f]Transition states for the conversion of **5s-pl** into **6**.

Figure 2 depicts the potential energy surface connecting **5s-pl** with alkyne **6** at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level of theory. T1 diagnostic values[22] of the stationary points are all <0.02 indicating well-behaved species with no significant multireference character. In this case, too, the barrier for phenyl shift (3.78 kcal/mol) is substantially smaller than that for the methyl shift (11.9 kcal/mol) and the reaction energy is −50.8 kcal/mol.

CONCLUSIONS

This work reports the chemistry of (*α*-methylbenzylidene)-carbene which was photochemically generated in solution from 1-(1-phenylethylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene. The carbene undergoes a facile rearrangement to 1-phenylpropyne, and a ^{13}C labeling experiment reveals that the alkyne is formed exclusively from a phenyl shift. The carbene may be also intercepted by cyclohexene to produce a cycloadduct, albeit in low yield. Computational investigations

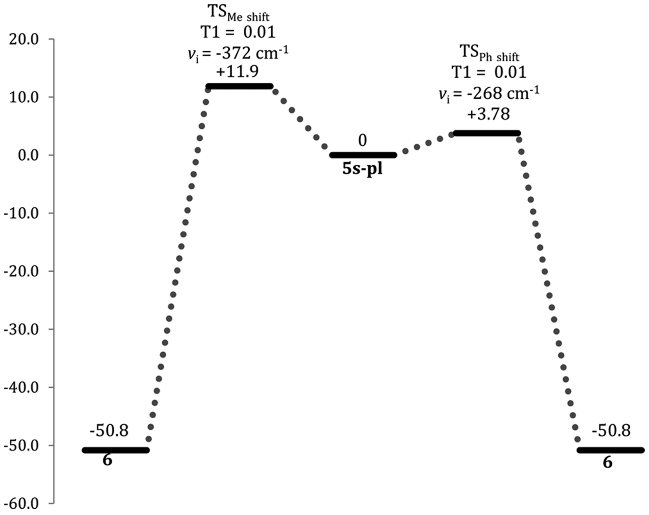


Figure 2. Two pathways for the rearrangement of **5s-pl** into alkyne **6**, computed at CCSD(T)/cc-pVTZ//B3LYP/6-311+G**, showing relative energies (in kcal/mol), T1 diagnostic values (CCSD),[22] and imaginary frequencies for the transition states.

at various levels of theory reveal that the singlet carbene has two, nearly isoergetic conformers, both of which are substantially lower in energy than the triplet. In accord with observed experimental results, calculations also show that the lower energy singlet carbene has a significantly smaller barrier for a phenyl shift compared to that necessary for a methyl shift. It is conceivable that phenanthrene-based methylenecyclopropane precursors, such as those described in this work, could provide attractive photochemical routes to other unsaturated carbenes. Research along these lines is currently underway in our laboratory.

■ EXPERIMENTAL METHODS

General Experimental Procedures. Solvents and all other reagents used were obtained from commercial sources. Tetrahydrofuran (THF) was dried by passage through two columns (2 ft ×4 in) of activated alumina. Unless otherwise noted, all reactions were carried out under an argon atmosphere in oven-dried glassware. The synthesis of *exo*-1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**17**)[11b] and 7-bromobicyclo[4.1.0]heptane[23] was carried out following literature procedures. Flash chromatography was performed on an automated system with prepacked silica gel columns (70–230 mesh). NMR spectra were recorded at 500 MHz for ^{1}H and 125 MHz for ^{13}C in the indicated solvent. The shifts are reported in δ ppm and referenced to either tetramethylsilane (TMS) (for ^{1}H NMR spectra) or the signal from the solvent. FTIR spectra were acquired with an attenuated total reflectance (ATR) accessory. 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 were obtained on a direct analysis in-real-time–time-of-flight (DART-TOF) mass spectrometer. Melting points were recorded on a digital hot plate and are uncorrected.

*1-(1-Phenylethylidene)-1a,9b-dihydro-1H-cyclopropa[l]-phenanthrene (**18**).* A solution of *exo*-1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene[11b] (2.70 g, 10 mmol) in anhydrous THF (80 mL) was cooled to −70 °C with stirring. Then, *tert*-butyllithium (13 mL, 1.7 M in pentanes, 22 mmol) was added dropwise, while keeping the temperature below −60 °C. After stirring at −70 °C for 30 min, bis(cyclopentadienyl)titanium(IV) dichloride (1.1 g, 4.4 mmol) was added to the reaction mixture. Stirring was continued at −70 °C for another 15 min after which the reaction mixture was slowly allowed to warm up to 0 °C. After 90 min of stirring between 0 and 5 °C in an ice–water bath, acetophenone (2.5 mL, 20 mmol) was added. The cooling bath was removed, and reaction mixture was refluxed for 12 h. After cooling, the contents of the flask were adsorbed onto silica gel and directly purified by column chromatography using hexanes as eluent. Colorless solid (436 mg, 15% yield); mp: 135–136 °C; ^{1}H NMR (500 MHz, benzene-d6) δ 7.71 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.41–7.36 (m, 2H), 7.30 (dd, J = 7.5, 1.5 Hz, 1H), 7.23 (dd, J = 7.4, 1.6 Hz, 1H), 7.15–7.07 (m, 4H), 7.07–7.01 (m, 1H), 7.01–6.94 (m, 2H), 3.07 (br d, J = 7.8 Hz, 1H), 2.79 (br d, J = 7.9 Hz, 1H), 1.90 (br t, J = 2.0 Hz, 3H); ^{13}C NMR (125 MHz, benzene-d6) δ 139.3, 133.1, 132.6, 129.7, 129.5, 129.1, 128.8, 128.0, 127.9, 127.8, 127.7, 127.5, 126.8, 126.3, 126.0, 124.2, 124.0, 123.5, 25.0, 20.6, 18.2; FTIR: ν 3063, 2977, 1598, 1484, 1439 cm^{-1}; LRMS (EI): m/z 294 (M$^+$), 279, 178. HRMS: m/z (M+1)$^+$ calcd for $C_{23}H_{19}$: 295.1487; found: 295.1483

*1-(1-Phenylethylidene)-1a,9b-dihydro-1H-cyclopropa[l]-phenanthrene-^{13}C (**18**-^{13}C).* The ^{13}C-labeled precursor was prepared using Ph^{13}COCH$_3$, instead of PhCOCH$_3$, in the procedure described above and using the same purification method. Colorless solid (131 mg, 13% yield); mp: 127–129 °C; ^{1}H NMR (500 MHz, benzene-d6) δ 7.73 (dd, J = 8.1, 1.2 Hz, 1H), 7.71–7.67 (m, 1H), 7.39 (m, 2H), 7.31 (dd, J = 7.5, 1.5 Hz, 1H), 7.24 (dd, J = 7.4, 1.5 Hz, 1H), 7.14–7.08 (m, 4H), 7.08–7.02 (m, 1H), 6.98 (qd, J = 7.6, 1.5 Hz, 2H), 3.09 (br d, J = 8.2 Hz, 1H), 2.81 (br d, J = 7.8 Hz, 1H), 1.90 (dt, J = 6.4, 1.5 Hz, 3H); ^{13}C NMR (125 MHz, benzene-d6) δ 123.98; FTIR: ν 3063, 2977, 1598, 1484, 1439 cm^{-1}; LRMS (EI): m/z 295 (M$^+$), 280, 178. HRMS: m/z (M + 1)$^+$ calcd for $C_{22}{}^{13}CH_{19}$: 296.1520; found: 296.1519.

*7-(1-Phenylethylidene)bicyclo[4.1.0]heptane (**19**).* 7-Bromobicyclo[4.1.0]heptane[23] (1.07 g, 6.1 mmol) was dissolved in anhydrous THF (80 mL) in an oven-dried round-bottom flask at −70 °C. A solution of *tert*-butyllithium (8 mL, 1.7 M in pentanes, 14 mmol) was added into the flask dropwise, while keeping the temperature below −60 °C. The reaction was stirred at −70 °C for 30 min, and bis(cyclopentadienyl)titanium(IV) dichloride (0.72 g, 2.8 mmol) was added to the reaction mixture. After continued stirring for 5 min at this temperature, the temperature was raised to 0 °C. Acetophenone (1.5 mL, 12 mmol) was added after 90 min of stirring at between 0 to 5 °C. Reaction was refluxed at 70 °C for 22 h. The resulted mixture was purified by silica gel column chromatography using hexanes as the eluent. Pale yellow liquid (99 mg, 8.2% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, J = 8.3, 1.5 Hz, 2H), 7.52–7.36 (m, 2H), 7.27 (d, J = 7.3 Hz, 1H), 2.29 (s, 3H), 2.01 (ddt, J = 8.8, 6.8, 2.0 Hz, 1H), 1.96–1.81 (m, 4H), 1.70 (ddt, J = 8.9, 7.1, 1.6 Hz, 1H), 1.39–1.26 (m, 3H), 1.26–1.16 (m, 1H); ^{13}C NMR (125 MHz, Chloroform-*d*) δ 140.4, 131.5, 128.2, 126.2, 125.4, 122.5, 22.4, 21.9, 21.5, 21.4, 18.8, 15.6, 11.0.; LRMS (EI): m/z 198 (M$^+$), 183. HRMS: m/z (M +1)$^+$ calcd for $C_{15}H_{19}$: 199.1487; found: 199.1474.

Procedures for Photolysis. The precursor **18** (100 mg) was dissolved in benzene-d6 (2 mL) in a glass vial. Photolysis was carried out for 12 h in a Rayonet photochemical reactor equipped with 16 12-in. 8 W lamps with output centered at ~350 nm (range ~315 to 400 nm). The progress of the photolysis was monitored periodically by GC/MS. Following photolysis, an internal standard (4-bromoanisole) was added and the yield of 1-phenylpropyne (**6**) was determined to be 73%. About 13% of **18** remained unreacted, and 11% had been converted into nonphotolabile isomers of the precursor. The ^{13}C-labeled precursor (25 mg) was also photolyzed in benzene-d6 in an analogous manner but in an NMR tube, and monitored periodically by NMR spectroscopy. The identity of the alkyne in the photolysate was confirmed as [2-^{13}C]-1-phenylpropyne by comparison to the previously reported spectra of this compound.[24] For the trapping experiment, **18** (76 mg) was dissolved in cyclohexene (5 mL) in a glass vial and photolysis was carried out for 6 h. The identity of the trapped product, **19**, was established by comparing the GC/MS of the photolysate with that of an independently synthesized authentic sample. The yield of the adduct was determined to be ~1.5% using an internal standard. In all photolysis experiments, phenanthrene was identified as a byproduct by GC/MS and/or NMR.

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Computational Methods. All calculations were carried out with Gaussian 09[25] 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. An intrinsic reaction coordinate calculation was also carried out at the B3LYP/6-311+G(d,p) level of theory to verify that the transition states connected the correct minima.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01143.

> Copies of spectroscopic and GC/MS data for new compounds **18**, **18**-^{13}C, and **19**; Cartesian coordinates and energies for **5**, **9**; the transition states for phenyl and methyl shift in **5**; and results of IRC calculations (PDF)

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Notes

The authors declare no competing financial interest.

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