

The Benzyldenecarbene–Phenylacetylene Rearrangement: An Experimental and Computational Study

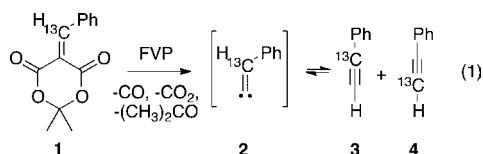
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S Supporting Information

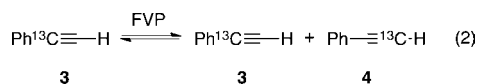
ABSTRACT: Benzyldenecarbene was generated from a new photochemical source, 1-benzylidene-1a,9b-dihydro-1*H*-cyclopropa[*I*]phenanthrene, in deuterated benzene at ambient temperature. The carbene undergoes a facile rearrangement to phenylacetylene and could not be trapped by olefins. Generation of the carbene bearing a ¹³C label at the β-carbon produced phenylacetylene in which the label was found exclusively at the carbon adjacent to the phenyl ring. This overwhelming preference for H shift is consistent with B3LYP and CCSD(T) calculations. The label distribution observed in this work, however, contrasts previously reported high-temperature flash vacuum pyrolysis results where the interconversion of carbene and alkyne leads to the scrambling of labels over both alkynyl (sp) carbons.

Brown et al. have previously noted that flash vacuum pyrolysis (FVP) of ¹³C-labeled benzyldiene malonate **1**, a precursor to labeled benzyldenecarbene (**2**), at 560 °C and 0.1 mm Hg, produced isotopomeric phenylacetylenes **3** and **4** in a 3:1 ratio (eq 1).¹ They were careful to point out, however, that



the observed ratio “cannot be taken as an accurate reflection of the relative migratory aptitudes of hydrogen and phenyl as at this temperature, the migration is reversible”.^{1a}

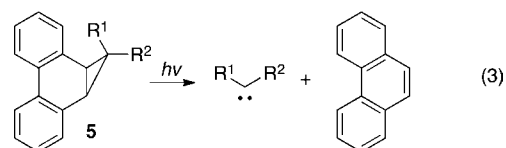
This notion was supported by the fact that when **3** was independently pyrolyzed at 550 °C and 0.05 mm Hg, the pyrolysate contained **3** and **4** in a 9:1 ratio (eq 2).² However,



when the pyrolysis was conducted at 700 °C and 0.02 mm Hg, approximately equal amounts of **9** and **10** were produced.² These experiments led the authors to conclude that under high-temperature FVP conditions, benzyldenecarbene and phenylacetylene were in equilibrium, which led to the observed scrambling of labels. Indeed, this alkylidene–alkyne interconversion, now known as the Brown rearrangement, has evolved into an important process, especially for polycyclic

aromatic compound synthesis.³ Herein we describe the solution chemistry of benzyldenecarbene, generated from a new photochemical precursor, and show that under these conditions, the phenylacetylene results exclusively from a 1,2-hydrogen shift in the carbene. A detailed computational study of the benzyldenecarbene–phenylacetylene system, which agrees with experimental observations, is also presented.

Nearly 50 years ago, it was demonstrated that the cyclopropanated phenanthrene derivative **5** (R¹=R²=H) could be photolyzed to produce methylene with the concomitant loss of phenanthrene (eq 3).⁴ Remarkably, the



potential of this system for generating other carbenes remained untapped for another 25 years before **5** (R¹=R²=Cl) was used in a landmark study to determine the absolute kinetics of dichlorocarbene in solution.⁵ Recently, however, there has been renewed interest in compounds based on **5** as legitimate carbene sources, and several laboratories, including ours, have used such systems to investigate the chemistry of a number of carbenes.⁶

As there are currently no convenient, readily prepared photochemical sources of alkylidenecarbenes with potential for general applicability, we wondered if it might be feasible to generate such unsaturated carbenes by modifying **5**.⁷ To test this idea, we carried out the synthesis of 1-benzylidene-1a,9b-dihydro-1*H*-cyclopropa[*I*]phenanthrene **8**, a potential precursor to benzyldenecarbene, following a simple three-step procedure described in Scheme 1. First, phenanthrene was treated with bromoform and aqueous sodium hydroxide under phase transfer catalysis conditions, following our improved procedure,⁸ to produce the dibromocarbene adduct **6**. Reaction of **6** with butyllithium at low temperature, followed by quenching of the resulting lithio anion with benzyl bromide, gave the benzylated derivative **7**, likely via an S_N2 process. The relative stereochemical disposition of benzyl and bromo groups in **7** was determined by X-ray crystallography (see Supporting Information, SI) and is consistent with our previous observations of analogous reactions.^{6a} Finally, dehydrobromination of **7** to give the desired precursor **8** was successfully

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Scheme 1. Synthesis of 8

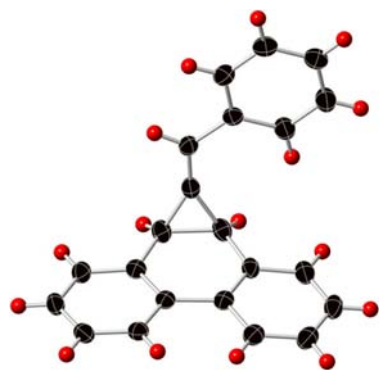
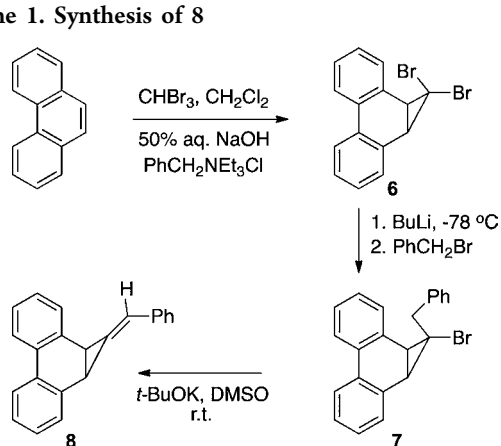
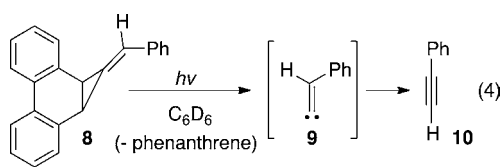


Figure 1. X-ray structure of 8.

accomplished at rt by treatment with potassium *tert*-butoxide in DMSO. The single crystal X-ray structure of 8 is shown in Figure 1.

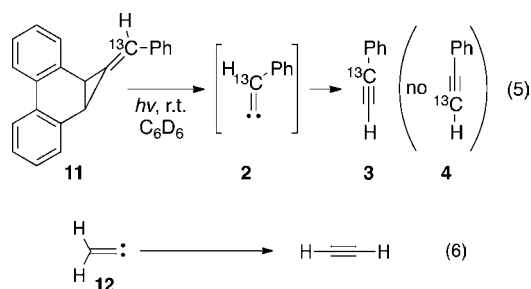
Precursor 8 undergoes photolysis cleanly (~ 315 – 400 nm) in benzene- d_6 at ambient temperature to afford the putative benzylicidene carbene 9, as evident from the quantitative formation of phenylacetylene 10 within 5 h (eq 4).



Furthermore, no trapping products were obtained when the photolysis of 8 was carried out in cyclohexene, *cis*-3-hexene, or 2-methyl-2-butene, presumably because rearrangement of 9 to 10 occurs much more rapidly than intermolecular processes.

We believed that our precursor 8 could be useful in accurately determining the H vs Ph migratory aptitudes in benzylicidene carbene, given that the phenylacetylene derived from 9 is formed under conditions where it cannot revert to the carbene. Accordingly, we prepared 11, the labeled version of 8, by using $\text{Ph}^{13}\text{CH}_2\text{Br}$ in step 2 of Scheme 1. Photolysis of 11 in benzene- d_6 at rt afforded 3 but no 4, demonstrating the exclusive preference for the migration of hydrogen to phenyl in carbene 2 (eq 5).⁹

Experiment and theory both indicate that the simplest alkylidene, vinylidene (12), is a ground-state singlet with a ΔE_{ST} of ~ 48 kcal/mol.¹⁰ Indeed, the potential energy surface for the singlet vinylidene–acetylene rearrangement (eq 6) has



been a subject of intense computational scrutiny over the years.¹¹ Recent calculations, at the CBS/CCSD(T) level with core correlation effects included, suggest a barrier of 2.08 kcal/mol for conversion of vinylidene into acetylene and a ΔE_{rxn} of -46.54 kcal/mol.^{11a}

While the barrier for 1,2-hydrogen shift in 12 is small, it has been suggested that it could be even smaller in 9, perhaps due to the assistance provided by the phenyl ring.^{7a} Our computational investigation into the structure of 9 and its rearrangement to 10 appears to support such a notion.¹² B3LYP¹³ calculations (Table 1), including zero-point energy

Table 1. Computed Relative Energies in kcal/mol, with Zero-Point Energy Corrections, of 9s and 9t Benzylicidene carbene, Phenylacetylene 10, and Transition States for the Conversion of 9s to 10 via H and Ph Shifts^a

entity	B3LYP/6-31G*	B3LYP/6-31+G*	B3LYP/6-31+G**	B3LYP/aug-cc-pVDZ
9s ^{b,c}	0	0	0	0
9t ^{c,d,e}	+38.43	+37.70	+38.37	+38.90
10 ^{b,c}	-46.15	-45.01	-44.64	-43.71
TS _{1,2-H} ^{b,f}	-0.82	-0.45	-1.35	-1.78
TS _{1,2-Ph} ^{b,f}	+8.79	+8.92	+9.30	+10.24

^aComputational details are provided in the SI. ^bRB3LYP. ^cNo imaginary frequencies. ^dUB3LYP. ^eSpin expectation values $\langle S^2 \rangle = 2.000$. ^fOne imaginary frequency.

corrections, indicate that the singlet carbene, 9s, is much more stable than its triplet counterpart (9t), with ΔE_{ST} values ranging from 37.70 [(U)B3LYP/6-31+G*] to 38.90 kcal/mol [(U)B3LYP/aug-cc-pVDZ]. The ΔE_{rxn} for conversion of 9s to 10 varied from -43.71 (B3LYP/aug-cc-pVDZ) to -46.15 kcal/mol (B3LYP/6-31G*). Furthermore, while the 1,2-phenyl shift has to overcome a modest barrier, ranging from 8.79 (B3LYP/6-31G*) to 10.24 kcal/mol (B3LYP/aug-cc-pVDZ), transition state energies for the 1,2-hydrogen shift pathway are all just below 9s, varying from -0.45 (B3LYP/6-31G*) to -1.78 kcal/mol (B3LYP/aug-cc-pVDZ). The preference for 1,2-hydrogen shift in 9s to give 10 is overwhelming, and other processes, such as 1,2-phenyl shift, much less intermolecular reactions, are not competitive under these conditions.

A similar situation is also encountered when energies are computed at the CCSD(T)/cc-pVTZ//B3LYP/6-31+G** level of theory (Figure 2). Stationary points on the potential energy surface are all well behaved with little, if any, multireference character (all T1 diagnostic values < 0.02). The transition state for the 1,2-hydrogen shift remains slightly below that of the starting material by -1.43 kcal/mol, whereas the 1,2-phenyl shift needs to overcome a barrier of 8.45 kcal/mol. The ΔE_{rxn} of -48.24 is comparable to the DFT calculations.

The observed trend may be rationalized by examining the structure of 9s which already appears “predisposed” for the 1,2-

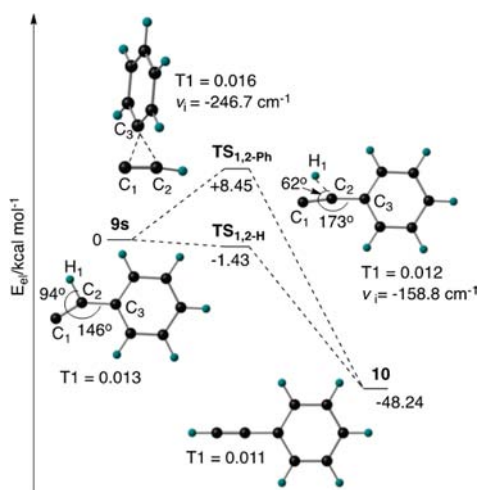
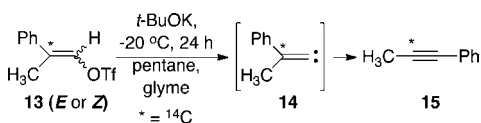


Figure 2. PES for the rearrangement of singlet benzylidene carbene (**9s**) to phenylacetylene (**10**) at CCSD(T)/cc-pVTZ//B3LYP/6-31+G** including energies, T1 diagnostic values (CCSD), and imaginary frequencies (for transition states).

hydrogen shift (Figure 2). The angles around C2 are substantially distorted from what might be expected for a formally sp^2 carbon. In particular, the H1–C2–C1 angle is severely compressed to 94° , whereas the C1–C2–C3 angle is quite large at 146° . In $TS_{1,2-H}$, the C1–C2–C3 has essentially become linear at 173° , and the H1–C2–C1 angle has decreased further to 62° as the migrating hydrogen leaves C2 and approaches the C1 terminus. Thus, very little motion seems required to tip the hydrogen over from C2 to C1 as **9s** proceeds toward **10**. On the other hand, shifting the phenyl is considerably more difficult. In **9s**, the phenyl ring is coplanar with the C1–C2 internuclear axis. In $TS_{1,2-Ph}$, however, the plane of the phenyl ring is essentially orthogonal to the C1–C2 bond (Figure 2). To achieve such a geometry, the phenyl ring will need to twist out of plane in **9s**, presumably disrupting stabilizing conjugation with the C1–C2 π system.

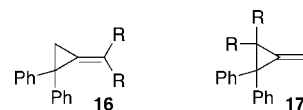
These observations provide an interesting contrast to an earlier report by Stang et al. who showed that ^{14}C -labeled (*E*)- and (*Z*)-2-phenylpropenyltriflates (**13**), when individually treated with potassium *tert*-butoxide in pentane/glyme for 24 h at $-20^\circ C$, produced a common carbene intermediate **14** and resulted in exclusive phenyl migration to afford [$2-^{14}C$]-1-phenylpropyne (**15**) (Scheme 2).¹⁴ Thus, our present work, together with Stang's observations, provides confirmatory evidence for the $H \gg Ph \gg CH_3$ trend in migratory aptitudes in the rearrangement of vinylidenes.

Scheme 2. Stang's Demonstration of the Exclusive Migration of Phenyl, Relative to Methyl, in Carbene 14



It has been reported before that photofragmentation of methylenecyclopropanes (**16**, $R = H, D, CH_3$) affords the corresponding vinylidenes but in yields $<5\%$.¹⁵ Furthermore, photolysis of **16** is complicated by the methylenecyclopropane rearrangement that converts it into **17**, a source of acetylene via vinylidene (**12**). In this context, the ease with which precursor

8 releases carbene **9**, and the complete absence of precursor rearrangements, is particularly noteworthy. This may be attributed to the fact that extrusion of the carbene from **8** is accompanied by aromatization of the central ring in phenanthrene, which provides an important driving force for the reaction. Such a driving force is unavailable to **16** and **17**. We are currently investigating the scope and limitations of analogs of **8** to determine whether such precursors could serve as a general source of alkylidene carbenes.



In conclusion, benzylidene carbene, generated from a new photochemical precursor, undergoes a facile rearrangement to phenylacetylene. The carbene could not be trapped by cyclohexene, *cis*-3-hexene, or 2-methyl-2-butene. Using a ^{13}C -labeled precursor, it was demonstrated that phenylacetylene results exclusively from a 1,2-hydrogen shift in the carbene, and the 1,2-phenyl shift is not competitive. Calculations show that the carbene is a ground-state singlet that is more stable than the triplet by ~ 38 kcal/mol. Furthermore, the barrier for hydrogen migration in the singlet carbene to form the alkyne is essentially nonexistent. The activation energy for phenyl shift, however, is much larger by comparison (~ 8 – 10 kcal/mol).

■ ASSOCIATED CONTENT

Supporting Information

Procedures, characterization data, computational details, and full ref 12. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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