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Photochemistry of 1-(propan-2-ylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene

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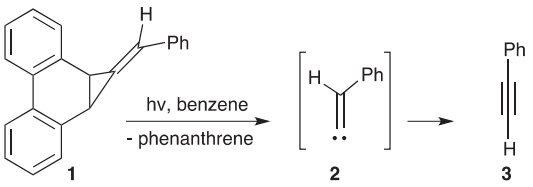
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ABSTRACT

The hydrocarbon, 1-(propan-2-ylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene, affords dimethylvinylidene upon photolysis (~315–400 nm) at ambient temperature, and the carbene may be trapped by cyclohexene. Some of the precursor also rearranged to a non-photolabile isomer via a putative 1,5-sigmatropic shift followed by an electrocyclic ring opening.

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We recently reported that the solution photolysis of methylenecyclopropane (**1**) produces benzylidenecarbene (**2**) with the concomitant loss of phenanthrene (Eq. 1), and the carbene subsequently rearranges into phenylacetylene (**3**).[1] Using a ^{13}C-labeled version of **1**, we also demonstrated that **3** results from migration of the hydrogen rather than the phenyl group. Attempts to intercept the carbene with alkenes proved futile, however, presumably because the 1,2-hydrogen shift is too facile in **2** to allow intermolecular trapping.



(1)

Herein we report that a similar approach may be used to generate a "trappable" vinylidene, using dimethylvinylidene (**4**) as an illustrative example. Previous calculations have shown that **4** is a ground state singlet with a singlet–triplet gap ranging from 44 to 50 kcal/mol depending on the method and basis set employed.[2] Although earlier computational studies indicated that the 1,2-methyl shift in singlet **4** to form 2-butyne has to surmount barriers of about 20 kcal/mol,[3] subsequent calculations have suggested much smaller barriers in the range of 11–13 kcal/mol.[2b,4] Our calculations at the CCSD(T)/cc-pVTZ//B3LYP/6-311++G** level place singlet **4** at 50.4 kcal/mol below the triplet with a barrier to rearrangement of 11.7 kcal/mol (Fig. 1).[5]

Given that the 1,2-methyl migration in singlet **4** has a significant barrier, one might expect the carbene to live long enough to be trapped by alkenes in solution. Indeed, this expectation has been borne out by experiment.[6]

Our synthesis of a phenanthrene-based photochemical precursor to **4**, was accomplished in three quite straightforward steps as shown in Scheme 1. Thus, addition of dibromocarbene to phenanthrene (**5**) under phase transfer catalysis conditions, according to our improved procedure,[7] gave the adduct **6**. This adduct was selectively converted into the monobromo derivative 7 by treatment with *t*-butyllithium at low temperature followed by quenching with water.[8] In the third and final step, we adapted the Petasis procedure[9] by reacting the cyclopropyllithium derived from **7** with titanocene dichloride. Subsequent addition of acetone and work-up led to the desired precursor **8**. The X-ray crystal structure of **8** is shown in Figure 2.[10]

As shown in Scheme 2, photolysis of a solution of **8** (~315–400 nm) in cyclohexene gave the expected adduct **9** (23% yield), along with phenanthrene. A 21% yield of the hydrocarbon **10**, an isomer of the precursor that did not undergo further photolysis, was also observed.According to an earlier report, the photolysis of precursor **11** in cyclohexene also forms **9** albeit in a yield of 3% (by GC).[6j] Interestingly, in a subsequent paper, a larger yield of **9** (35–40% by GC) was reported in the photolysis of a

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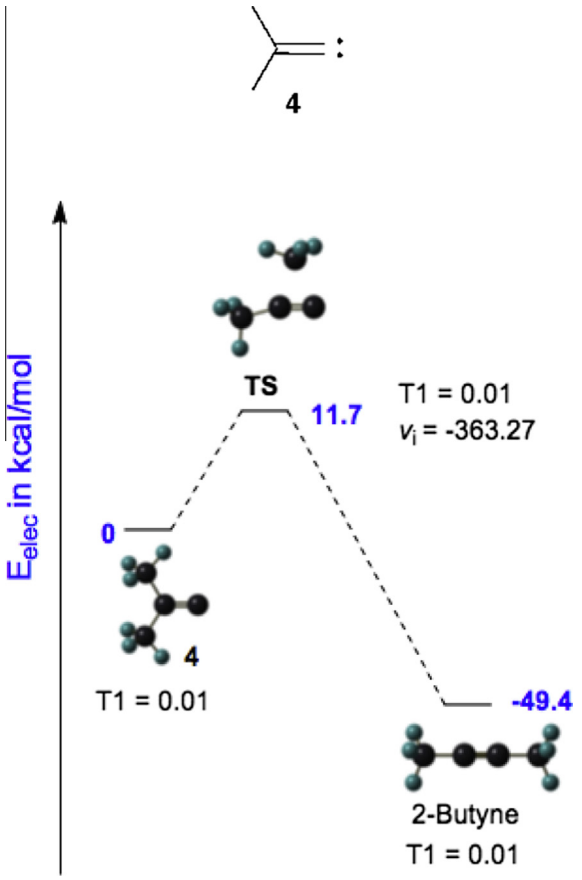
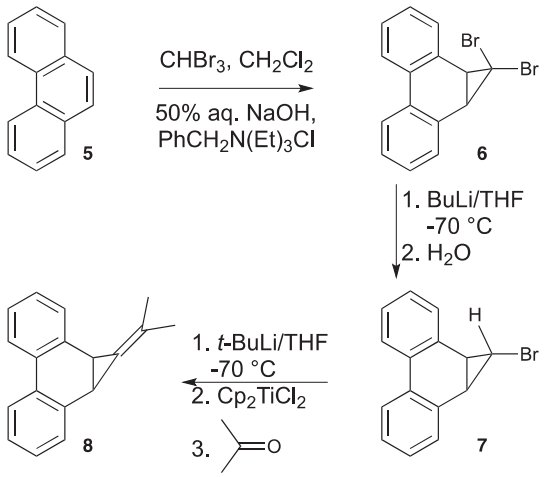
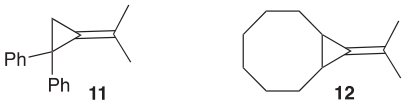


Figure 1. Energetics of the rearrangement of singlet **4** (C_{2v}) to 2-butyne (D_{3h}) at CCSD(T)/cc-pVTZ//B3LYP/6-311++G**. T1 diagnostic values for each structure and the lone imaginary frequency for the transition state are also noted. Further, the vibrational mode of the imaginary frequency is consistent with the 1,2-migration of the methyl group.



Scheme 1. Synthesis of 1-(propan-2-ylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*] phenanthrene (**8**), a photochemical precursor to dimethylvinylidene **4**.

cyclohexene solution of **12** with a 450 W Hanovia lamp despite the precursor not having any absorption maxima above 200 nm.[6d]



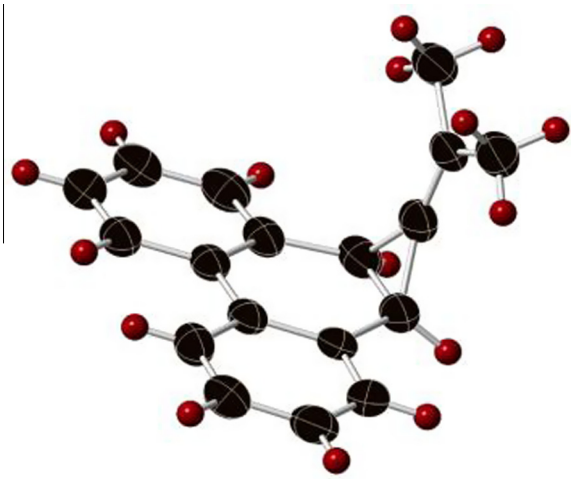
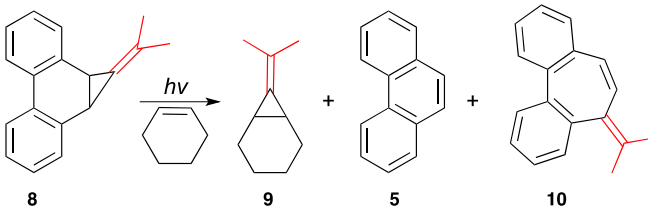
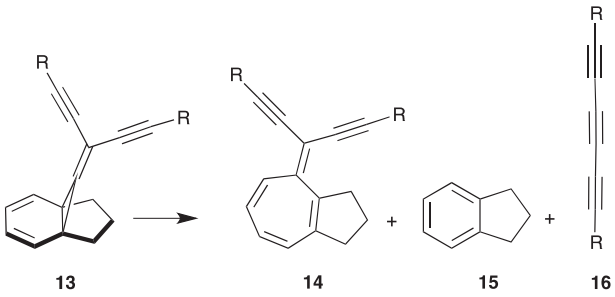


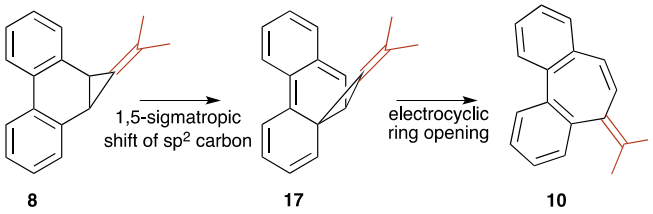
Figure 2. Single-crystal X-ray structure of precursor **8**.[10]



Scheme 2. Results from the photolysis of **8** in the presence of cyclohexene.



Scheme 3. Rearrangement and fragmentation of **13**.



Scheme 4. Proposed mechanism for the rearrangement of **8** into **10**.

The formation of **10** is reminiscent of the process by which precursor **13** has been suggested to yield compound **14** (Scheme 3), in addition to indan **15** and the triyne **16**.[11] Thus, an analogous rearrangement mechanism would involve a 1,5-sigmatropic shift in **8** to form **17** followed by an electrocyclic ring opening to afford **10** (Scheme 4).

In conclusion, we have shown that 1-(propan-2-ylidene)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**8**) may be photolyzed in solution to afford dimethylvinylidene (**4**), and the carbene can be trapped by cyclohexene. In a broader sense, although considerable research effort has been expended on carbene chemistry over the past several decades, it is important to note that convenient, reliable, and generally applicable photochemical methods to produce vinylidenes in solution still remain elusive. Perhaps this conspicuous void in the literature might explain why important techniques such as time resolved laser flash photolysis, to our knowledge, have not been applied to the investigation of these unsaturated carbenes. In this context, cyclopropanated phenanthrene systems such as **8** have the potential to serve as versatile precursors to vinylidenes. We anticipate that the relatively straightforward preparation of such precursors, their stability, and ease of handling will stimulate further research into the chemistry of these remarkable reactive intermediates.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.10.064.

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