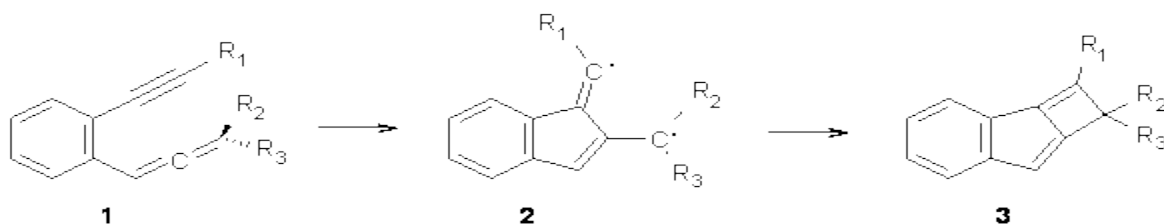


STEPWISE CYCLIZATION OF ALLENE-YNES

Continuing their studies of ene-yne cyclizations, the Schmittel group examined the apparent [2+2] cyclization of the allene-yne **1**.¹ They proposed that it first closed the diradical **2** and then in a second step the four-member ring is formed, giving **3**.



a: R₁=Ph, R₂=R₃=H

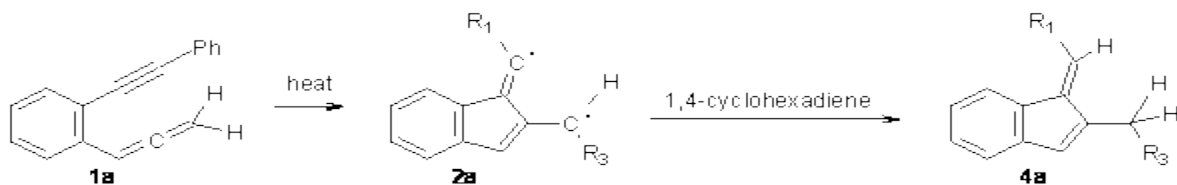
b: R₁=Ph, R₂=H,

R₃=t-Bu

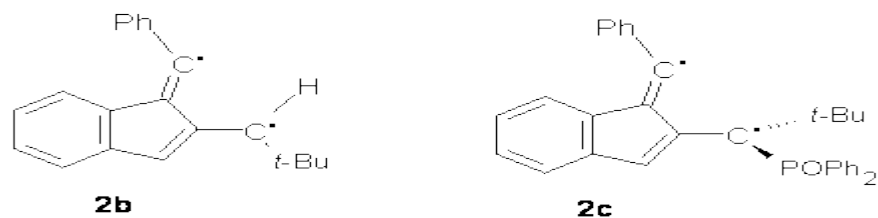
c: R₁=Ph, R₂=POPh₂,

R₃=t-Bu

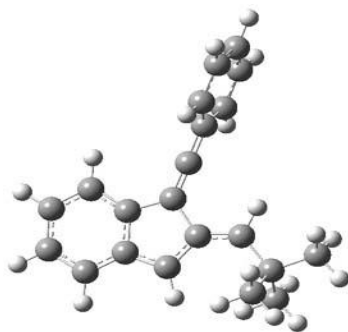
Evidence supporting the intermediate diradical is that heating **1a** in the presence of 1,4-cyclohexadiene gives 11% of the trapped species **4a**. Interestingly, heating **1b** gives 26% of **3b**, while the reaction of **1c** gives 72% of the ring closed product **3c**.



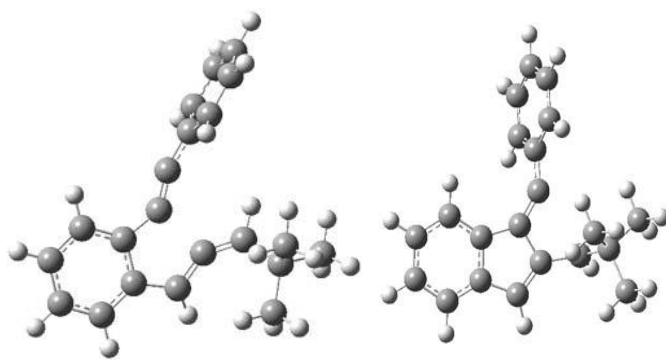
Schmittel suggests the intermediate diradical **2b** is planar, while **2c** is not, and the radical centers are nicely position in the latter compound for quick closure to product.



UBLYP/6-31G(d) computations support the mechanism. The transition state taking **1b** to **2b** (**TS1**, shown in Figure 1) lies $20.2 \text{ kcal mol}^{-1}$ above reactant. The intermediate diradical **2b** is $7.9 \text{ kcal mol}^{-1}$ above reactant **1b**. The second transition state (**TS2**) for closing the four-member ring lies $27.8 \text{ kcal mol}^{-1}$ above reactant, making it the rate determining step. The overall reaction is exothermic by $-12.4 \text{ kcal mol}^{-1}$. The transition state for a single step reaction, taking **1b** directly into **3b** (**TS3**) is very high, $49.0 \text{ kcal mol}^{-1}$ above **1b**, and is therefore non-competitive with the stepwise pathway. These computations suggest a reversible formation of the intermediate, followed by a rate limiting step to making the four-member ring, completely consistent with the experiments.

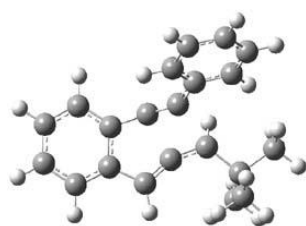


2b



TS1

TS2



TS3

Figure 2. UBLYP/6-31G(d) optimized structures of **2b**, **TS1**, **TS2**, and **TS3**.

Source: <http://comporgchem.com/blog/?p=1645>