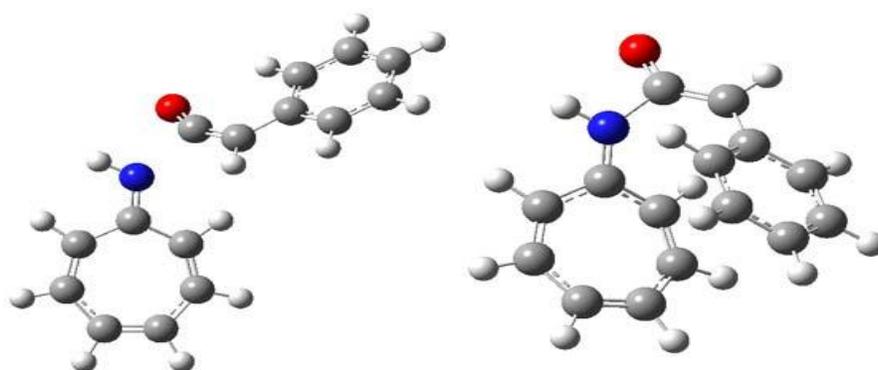
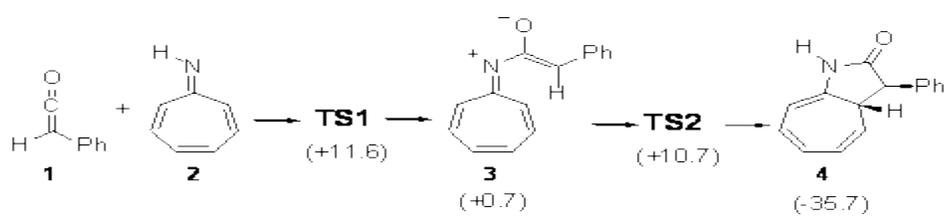


# [8+2] CYCLOADDITION IS STEPWISE

While many pericyclic reactions proceed in a concerted fashion, the stepwise pathway is a distinct possibility. Fernandez, Sierra and Torres report on an interesting [8+2] cycloaddition that is decidedly stepwise, confirmed through trapping of the intermediate zwitterion.<sup>1</sup>

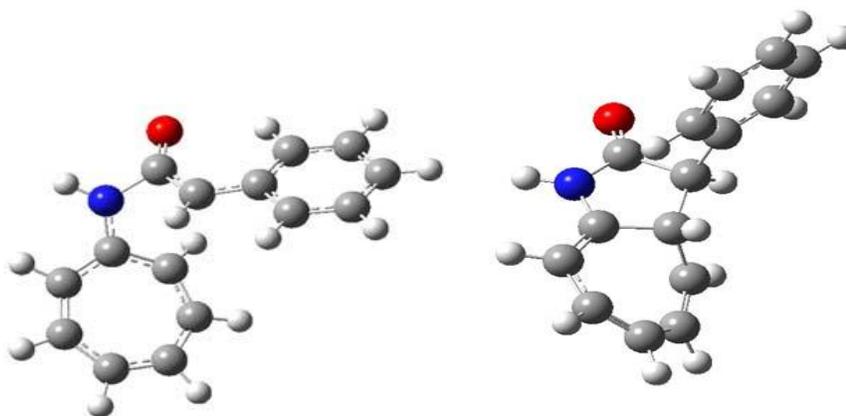
The reaction of **1** with **2** was examined at M06-2x/6-311+G(d) (optimized geometries of the critical points are shown in Figure 1). The first transition state (**TS1**) has nitrogen acting as a nucleophile, attacking the carbonyl carbon of ketene to give **3**. The barrier is 11.6 kcal mol<sup>-1</sup>, and **3** lies 0.7 kcal mol<sup>-1</sup> above reactants. While **3** might be described with a tropyllium cation resonance structure, the ring is in fact non-planar and both the NICS(0) and NICS(1)<sub>zz</sub> values are positive. The ring is therefore antiaromatic, consistent with the endoergonicity of this step. Closure of the zwitterion through **TS2** leads to the formal [8+2] product, with the barrier for this second step slightly lower than the barrier for the first step. Overall, the reaction is quite exothermic.

**Scheme 1** (relative energies in kcal mol<sup>-1</sup>)



**TS1**

**3**



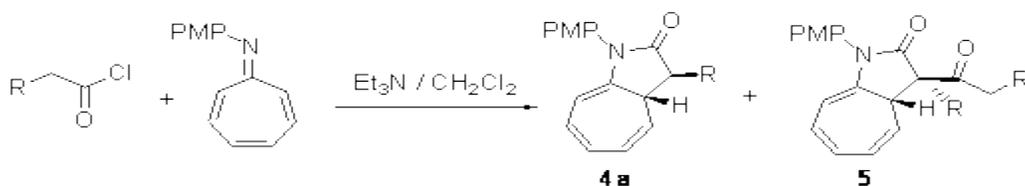
**TS2**

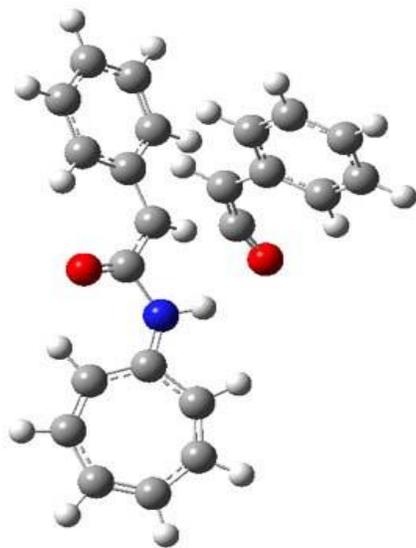
**4**

**Figure 1.** MO6-2x/6-311+G(d) optimized Structures of **3**, **4**, and the transition states leading to them (**TS1** and **TS2**).

Experiments were performed with a variety of acyl chloride precursors to ketenes (Scheme 2), and along with the [8+2] product, a second product (**5**) incorporating 2 equivalents of ketene is found; in fact, if the R group is benzyloxy or t-butyl, **5** is the only observed product. This second product comes about via trapping of the intermediate **3**. Mixing phenylketene with **4a** (where the R group is phenyl) gives no reaction, thus precluding the intermediacy of **4** on the path to **5**. MO6-2x computations of the trapping of **3** with phenylketenes indicates a barrier (**TS3**, see Figure 2) of 9.6 kcal mol<sup>-1</sup>, very close to the barrier height of the second TS for ring closure of the [8+2] pathway, supporting the competition between trapping of the intermediate and progress on to the [8+2] product.

**Scheme 2.**





**TS3**

**Figure 2.** MO6-2x/6-311+G(d) optimized Structures of **TS3**.

Source: <http://comporgchem.com/blog/?p=1591>