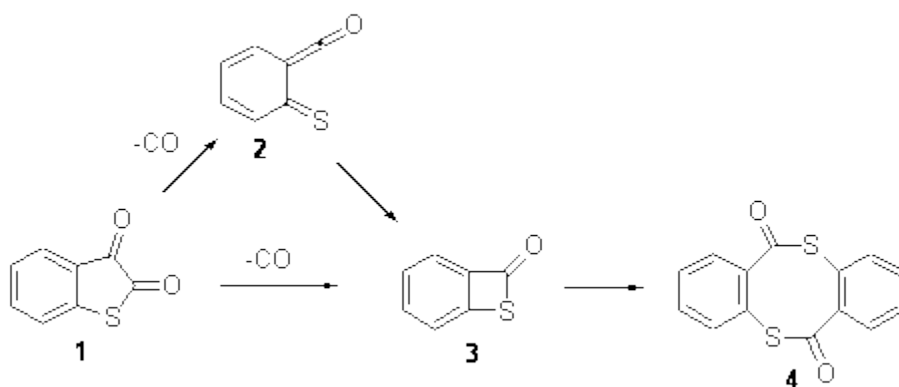


NEW PSEUDOPERICYCLIC REACTION

Birney has published another study of a pseudopericyclic reaction to complement the many I discuss in Chapter 3.4. Here he looks at that decarbonylation of benzothiophenedione **1**, which if analogous to the furandione will first give the ketene **2** before forming **3**.¹ Upon gentle heating, **3** dimerizes to **4**. Interestingly, **2** has not been detected.²



2 does not exist as a local minimum on the B3LYP/6-31G(d,p) or G3MP2B3 surfaces; rather all optimizations collapse to **3**. However, when optimized with PCM with the dielectric of DMSO, **2** is a local minimum.

The transition state for loss of CO from **1** leads directly to **3**. This TS (**TS1-3**, see Figure 1) is non-planar, unlike for the analogous reaction of the furandione. **TS1-3** does not correspond with a pseudopericyclic reaction.

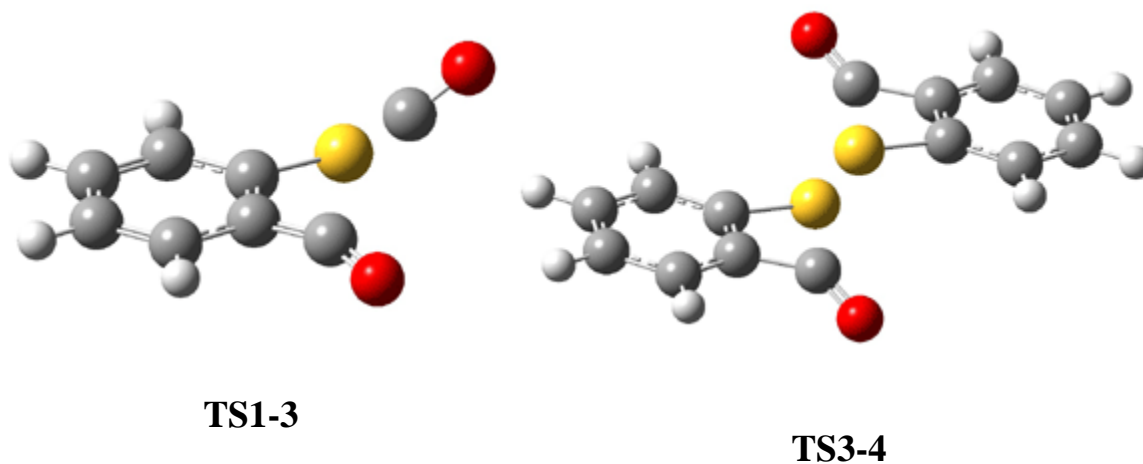


Figure 1. B3LYP/6-31G(d,p) optimized geometries of **TS1-3** and **TS3-4**.¹

The transition state for the dimerization of **3** (**TS3-4**), also shown in Figure 1, appears to be a $[2\sigma + \sigma]$ cyclization, which is thermally forbidden. However, analysis of the molecular orbitals indicates the interaction of sets of orthogonal orbitals, exemplary of a pseudopericyclic reaction. The barrier for this reaction, $17.9 \text{ kcal mol}^{-1}$, is consistent with an allowed pseudopericyclic process.

Source: <http://comporgchem.com/blog/?p=61>