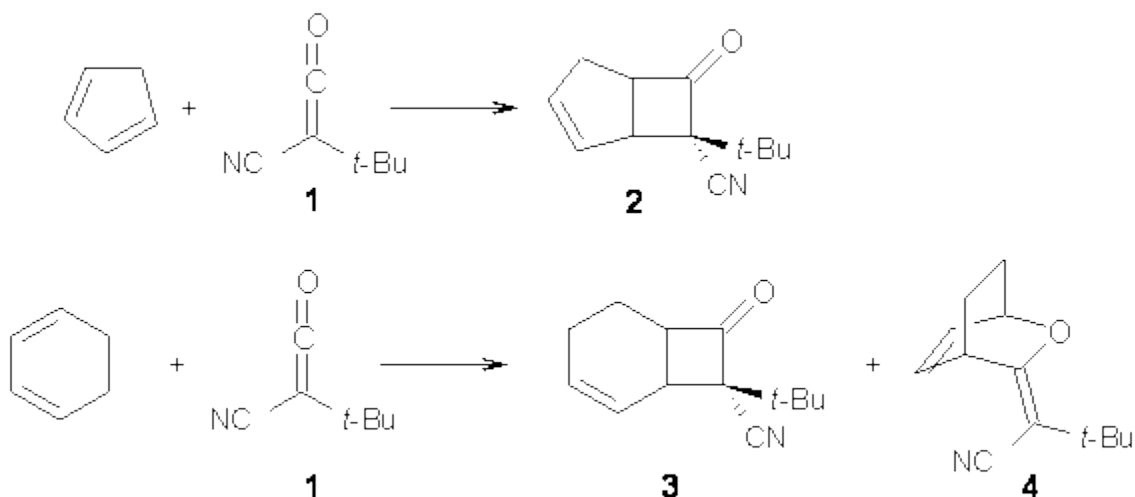


CYCLOADDITIONS OF CYCLODIENES WITH KETENES

One more study of cycloaddition reactions with ketenes that suggest the occurrence of dynamic effects.¹ The reaction of cyclopentadiene with *t*-butylcyanoketene **1** gives cyclobutanone **2** solely. In contrast, the reaction of 1,3-cyclohexadiene with **1** gives the cyclobutanone **3** and a small amount (less than 25%) of the ether **4**. Warming the reaction from -20 °C to 20 °C leads to loss of **3** and an increase in **4**. This is in distinct contrast with the reaction of cyclopentadiene with diphenylketene,² where the ether product is the major product and the cyclobutanone is the minor product (see Chapter 7.3.5.2 in my book).



To help understand this situation, the authors optimized the structures of the critical points on the surface of the cyclohexadiene reaction at MPWB1K/6-31+G(d,p) – though once again, there are no supporting materials so I cannot supply the 3-D structures in the blog! **4** is predicted to be 3.4 kcal mol⁻¹ more stable than **3**, which accounts for it being the thermodynamic product, consistent with experiment. Only two transition states are found. The first TS, with a barrier of 23.2 kcal mol⁻¹, connects reactants with **3**. The second transition state corresponds to the oxy-Cope rearrangement that takes **3** into **4**. This surface is reminiscent of many others that display dynamic effects (again see my book and also these posts). Unfortunately, the authors have not performed any trajectory calculation. But one might expect that most trajectories cross the first transition state and fall into the well associated with **3**. Some of these molecules then go on to cross the second barrier to form **4**. But some trajectories cross the first TS and then veer off into the slightly lower well associated with **4**, being directly formed from reactant. This would be a manifestation of dynamic effects, and is worth further study.

Source: <http://comporgchem.com/blog/?p=707>