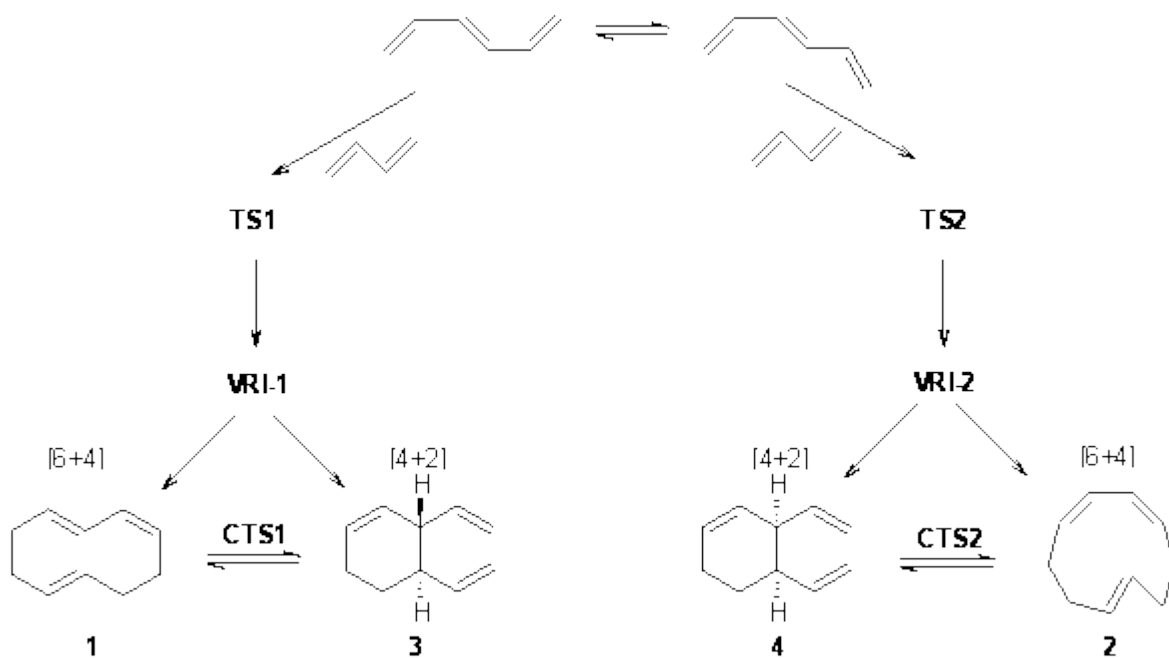


[6+4] AND [4+2] CYCLOADDITIONS: UNUSUAL POTENTIAL ENERGY SURFACES

Alder and co-workers have published a substantial theoretical study of potential [6+4]-cycloaddition reactions.¹ There is much too much to summarize from this study, but I highlight here an interesting result that is consistent with one of the themes of the book and blog: unusual potential energy surfaces.

They examined two [6+4]-cycloaddition routes involving 1,3,5-hexatriene with 1,3-butadiene to give **1** and **2**. These products are shown in Figure 1. A competing [4+2]-cycloaddition is also possible, giving rise to **3** and **4**.

Interestingly, only one TS is found leading to **1/3** and one TS leading to **2/4**. (These TSs are also shown in Figure 1.) This is reminiscent of many examples from the book and blog where a single TS seems to lead to 2 different products. A valley-ridge inflection point divides the surface between **1** and **3** (**VRI-1**), and a second valley-ridge inflection point separates **2** from **4** (**VRI-2**). In addition a Cope transition state (**CTS1**) takes **1** into **3**, and a second TS (**CTS2**) takes **2** into **4**.



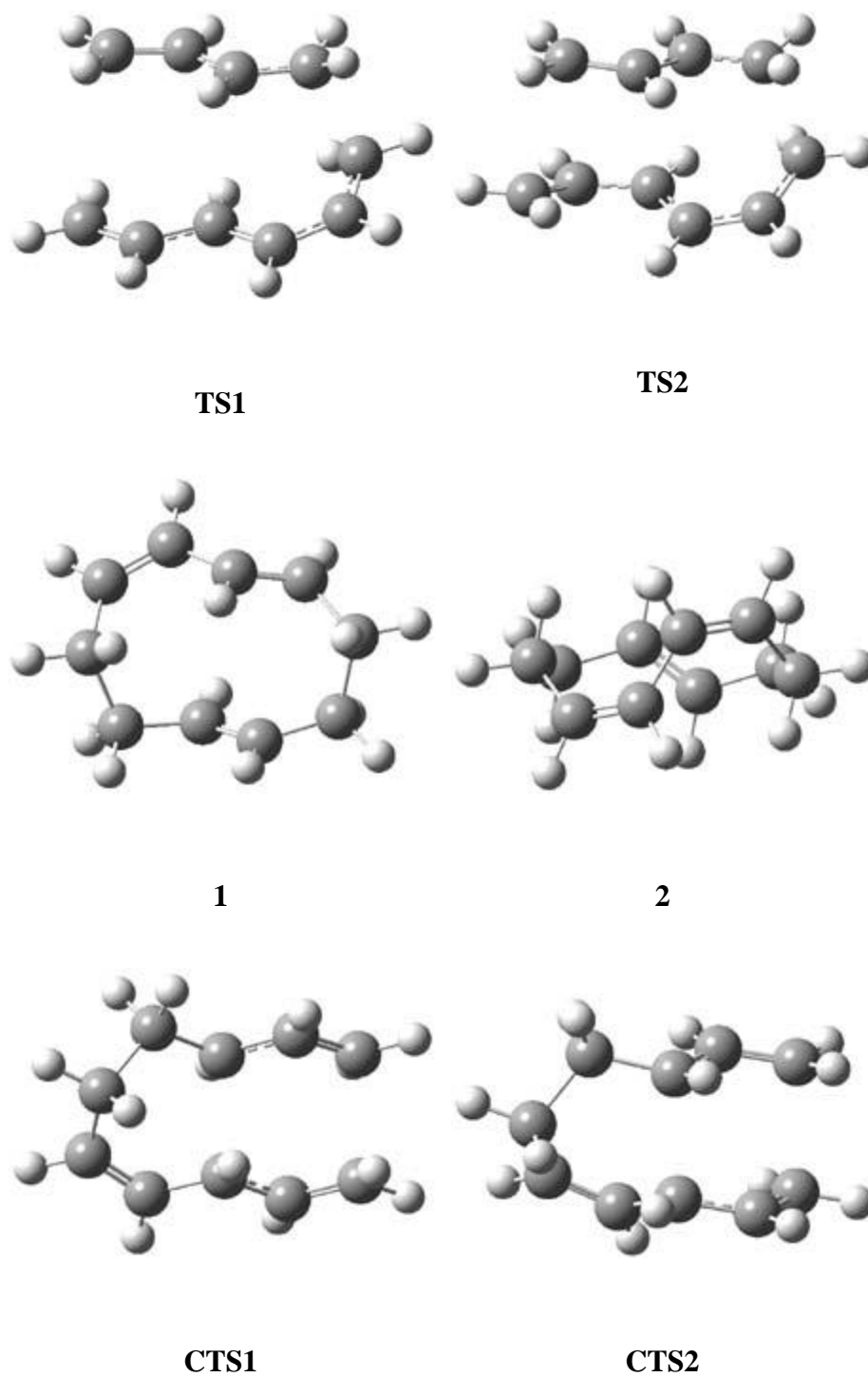


Figure 1. B3LYP/6-31G* optimized structures of the TSs and products of the reaction of 1,3,5-hexadiene with 1,3-butadiene.¹

This type of surface requires study of the dynamics to truly predict what the outcome will be of the reaction. Unfortunately, the low barriers for the Cope rearrangements along with **3** and **4** being much more stable than **1** and **2** indicates that the [6+4] product is unlikely to be observed. Nonetheless, this is yet another example of an unexpected PES.

Source: <http://comporgchem.com/blog/?p=1020>