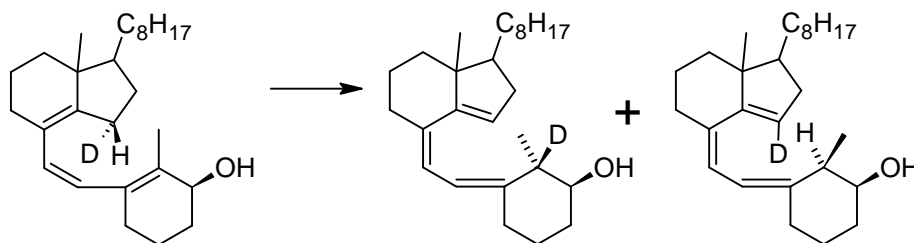
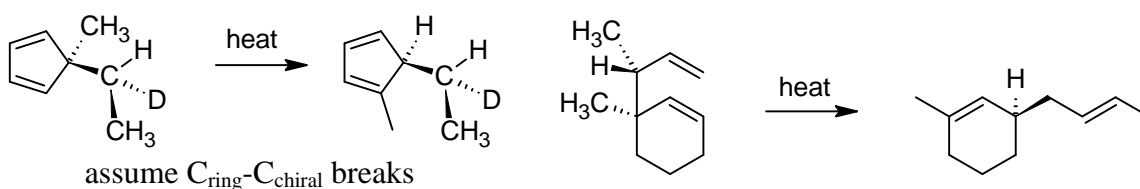


1.

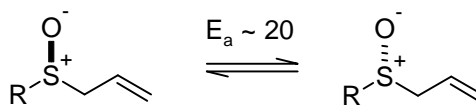
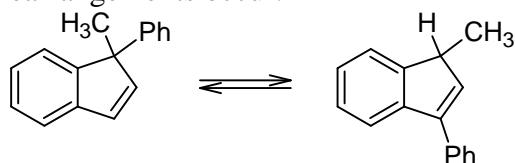
Can the following reactions occur as one-step sigmatropic rearrangements? Perform a complete analysis for each before answering “yes” or “no”. In other words, provide:

- the $[m, n]$ label
- a drawing of the reaction mechanism using curved arrows and the number of electrons participating in the reaction
- whether the rearrangement is *suprafacial* or *antarafacial* with respect to participating pi system(s)
- whether the rearrangement can be viewed as a *migration* reaction, and if it can, whether the migration occurs with *retention* or *inversion* at the migrating group
- whether the transition state is Hückel or Möbius
- whether the rearrangement is allowed or forbidden



2.

Draw plausible mechanisms for the reactions shown below. Both mechanisms include at least one thermally allowed sigmatropic rearrangement; include an $[m, n]$ label wherever these rearrangements occur.



This is a two-step mechanism. It may help to know that sulfoxides that *lack* an allylic group do not easily racemize ($E_a \sim 40$ kcal/mol).

3.

Calculate the HF/3-21G reaction energy and barrier for the [1,5]-H migration shown below. Include ZPE corrections (use FREQSCALE=0.9 in the **Options** box). Is the transition state geometry consistent with the Hammond postulate? Does H migrate as a proton, atom, or hydride?

