

SELECTED ANSWERS

1. Notice that the first two rearrangements are almost certainly energetically favorable because the alkene products are more highly substituted than the reactants.

The labeling of [1,m] and [3,3] transition states deserves a little comment:

- [1,m] reactions are migrations. The migrating group can migrate with retention or inversion. These labels do not apply, however, if the migrating group is an atom, e.g., H, because configuration is not defined at an isolated atom.
- [3,3] reactions are rearrangements formally involving two pi systems in the transition state. You must identify whether the transition state is suprafacial or antarafacial with respect to each pi system (two labels required).
- Any reasonable geometry for a [3,3] and [2,3] rearrangement requires a transition state that is suprafacial with respect to both pi systems (see [posted transition state models for Claisen \[3,3\]](#)). This leads automatically to a Huckel array of orbitals. These rearrangements will be allowed if they involve 6 electrons.

2. A pericyclic rearrangement can be included in a reaction mechanism if it will occur at an appreciable rate under the experimental conditions. This usually means that the rearrangement should be:

1. orbital-symmetry allowed
2. the first half ($\text{rct} \rightarrow \ddagger$) should not suffer from any diabolical characteristics (increased hindrance, strain, etc.)
3. and the rearrangement should not be too unfavorable, e.g., a 3° carbocation should not produce a 1° carbocation.

It is very tempting to draw a [1,3] migration for the first mechanism, but this migration is orbital-symmetry forbidden. You must draw two [1,5] migrations instead (notice that the first one will probably be slower since it is unfavorable):

