

PSEUDOPERICYCLIC [3,3]- SIGMATROPIC REARRANGEMENT

Duncan has discovered a pseudopericyclic [3,3]-sigmatropic rearrangement,¹ and what is particularly interesting is how rare this seems to be! Using CASSCF/6-31G* computations of Reactions 1-9, only Reaction 1 is found to be pseudopericyclic. (The transition state for this reaction is shown in Figure 1). This characterization is based largely on the shapes of the active MOs, one of which displays two orbital disconnections. In addition, this transition state is much more planar than is typical for a [3,3]-rearrangement. Dihedral angles are about 20 ° in the TS for reaction 1, while in the other reaction TSs, their dihedral angles are about 50 ° or even larger. This is consistent with Birney's contention that pseudopericyclic reactions have nearly planar TSs. The activation barrier for Reaction 1 is also quite small, 19.4 kcal mol⁻¹, much lower than for Reactions 2 (26.2 kcal mol⁻¹) and 3 (33.1 kcal mol⁻¹).



Reaction 1: X = O

Reaction 2: X = CH₂

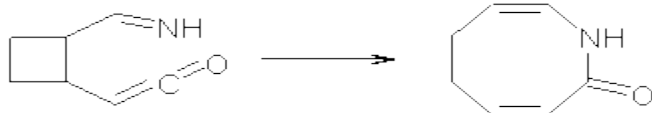
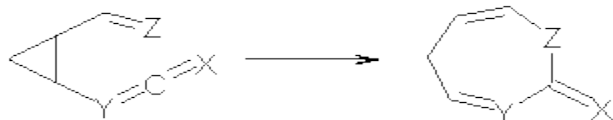
Reaction 3: X = NH

Reaction 4: X = O, Y = CH, Z
= CH₂

Reaction 5: X = NH, Y = CH,
Z = O

Reaction 6: X = CH₂, Y = N, Z
= O

Reaction 7: X = O, Y = CH, Z
= O



Reaction 8



Reaction 9

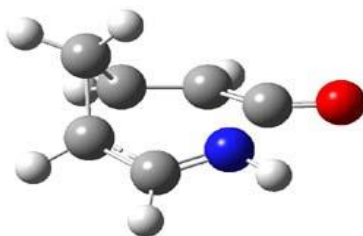


Figure 1. CASSCF/6-31G* optimized TS for Reaction 1.

Source: <http://comporgchem.com/blog/?p=903>