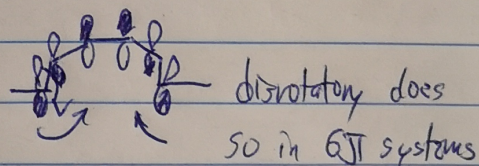
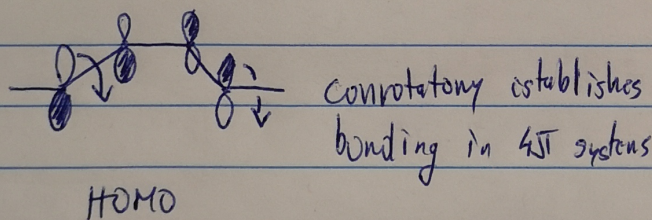
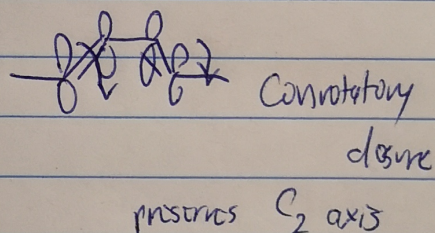
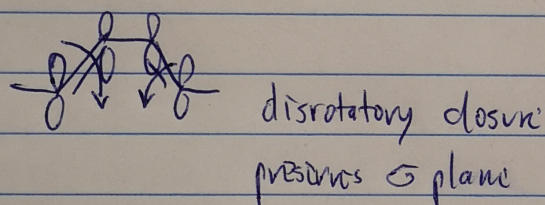
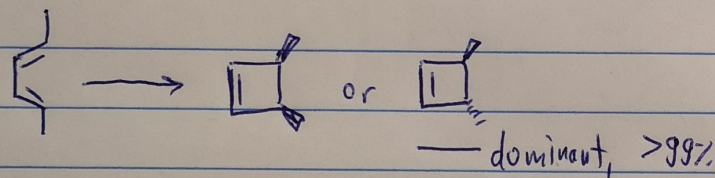
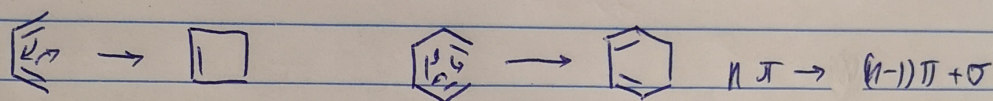


Lecture XXX: Stereochemistry of Pericyclic Reactions 2

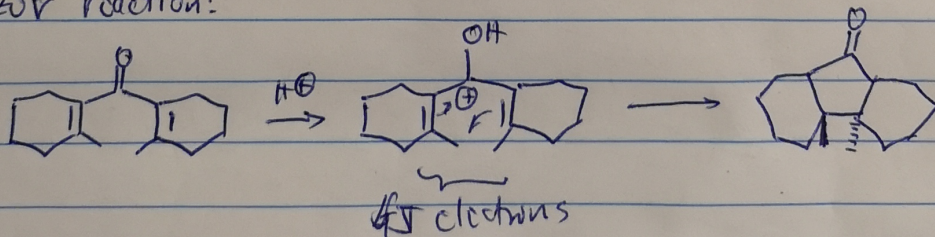
04-15-2020

Today, we will discuss the other two big classes of pericyclic reactions: electrocyclizations and sigmatropic rearrangements.

Electrocyclizations

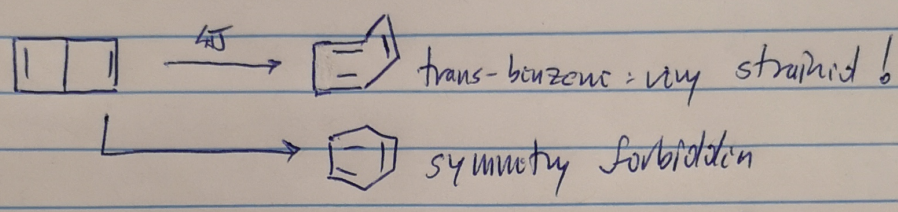


Arbuzov reaction:

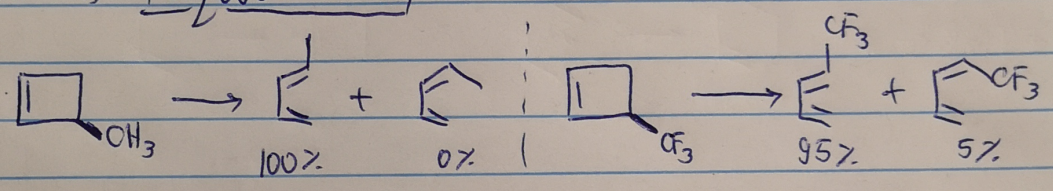


This stereochemistry is also behind the unusual stability of

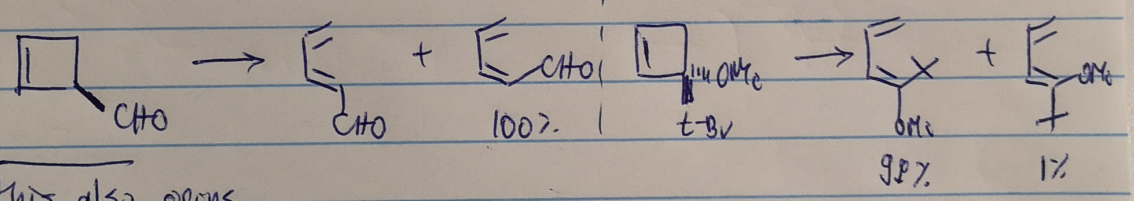
Denard's benzene:



Electrocyclizations show an additional level of stereoselectivity known as torquoselectivity:

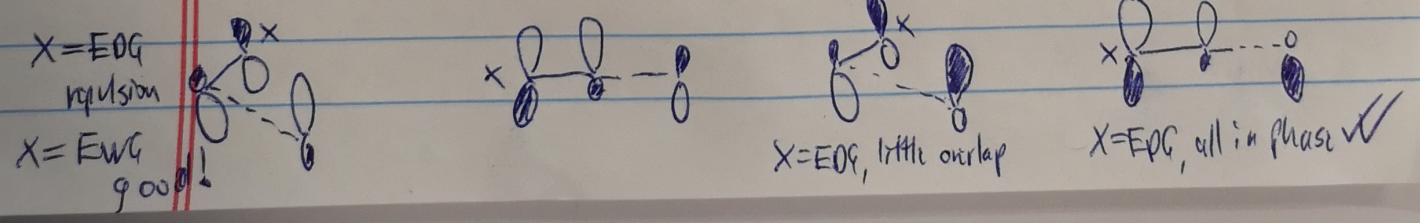
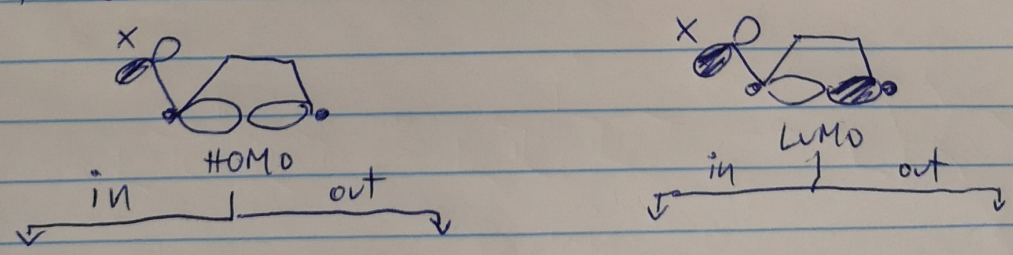


These examples could be explained by steric bulk, but the bottom ones... not so much:

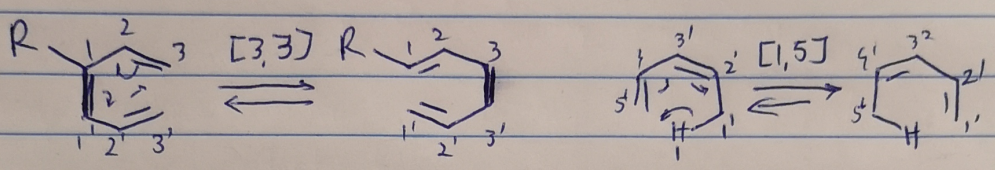


This also opens up much faster!

All of these reactions are conrotatory, but CH_3 , CF_3 , OMe prefer to rotate outwards, and CHO and $t-Bu$ inwards. Let's look at the orbitals:

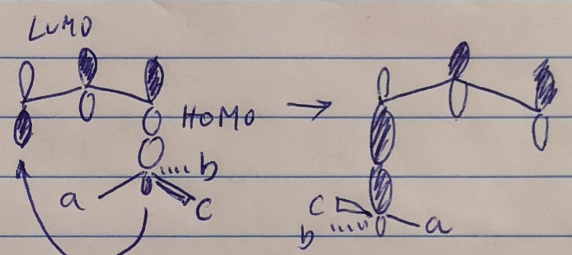
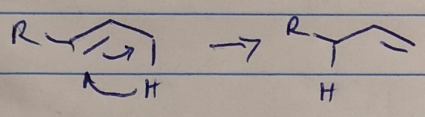


Sigmatropic Rearrangements are a broad class of reactions in which a σ -bond formally migrates over an emerging π -system.

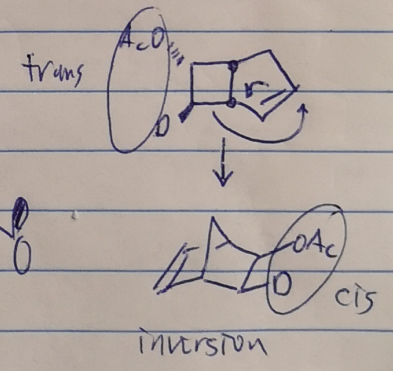
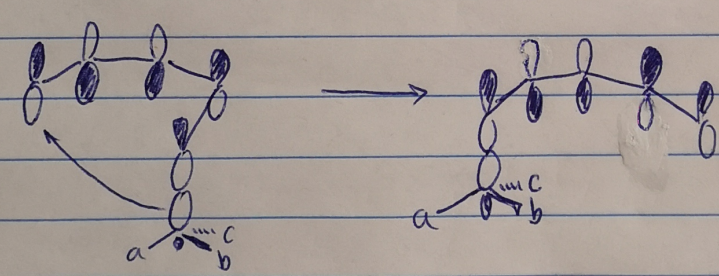


Cope rearrangement

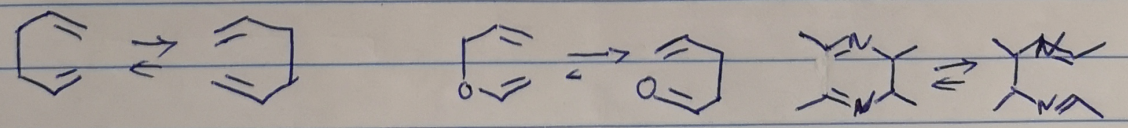
The simplest one is [1,3]-shift.



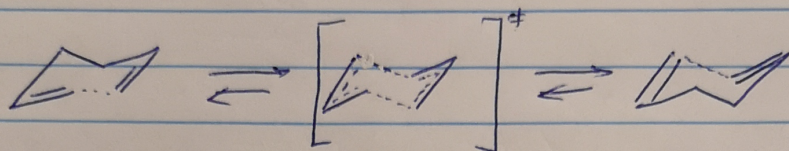
In 1,5-shifts, retention is observed:



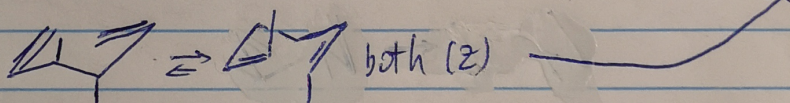
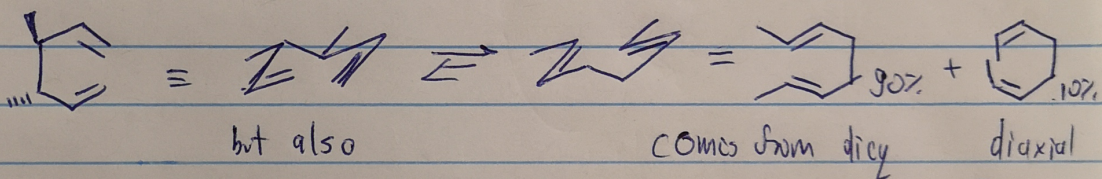
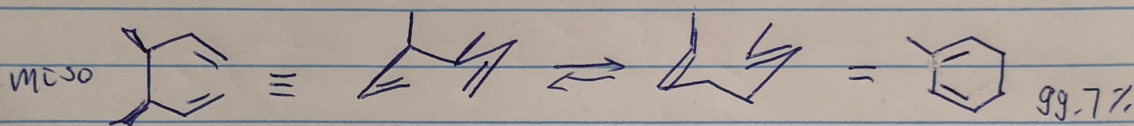
In recent decades, Cope rearrangement and its heteroatomic versions have dramatically increased in importance.



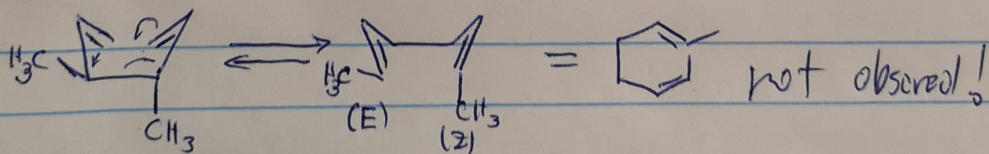
These [3,3] rearrangements proceed through chair-like transition states:



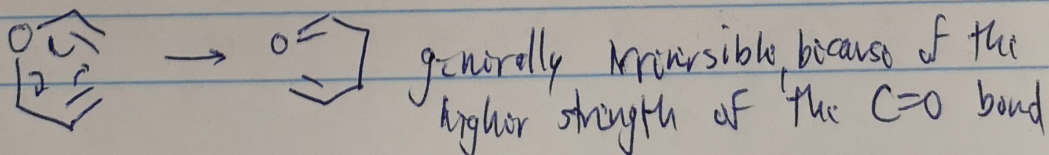
Substituents orient themselves to minimize axial interactions and the reaction is completely stereospecific:



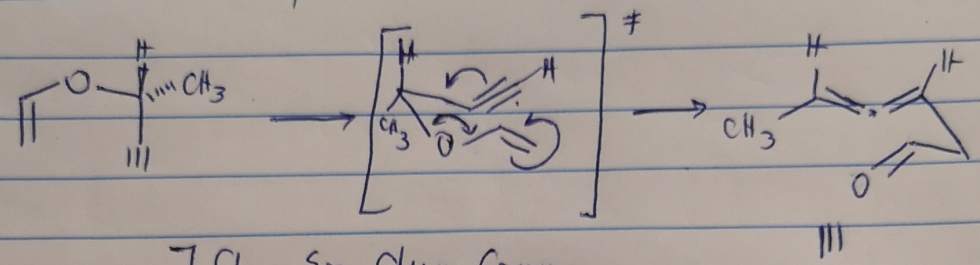
Notably, diequatorial and diaxial both happen - but the boat conformation does not:



Many heteroatomic versions of Cope rearrangement exist. The most widely known one is probably Claisen rearrangement:



An interesting example of translation of point chirality into axial chirality:



J Chem Soc Chem Commun
1965, 397

