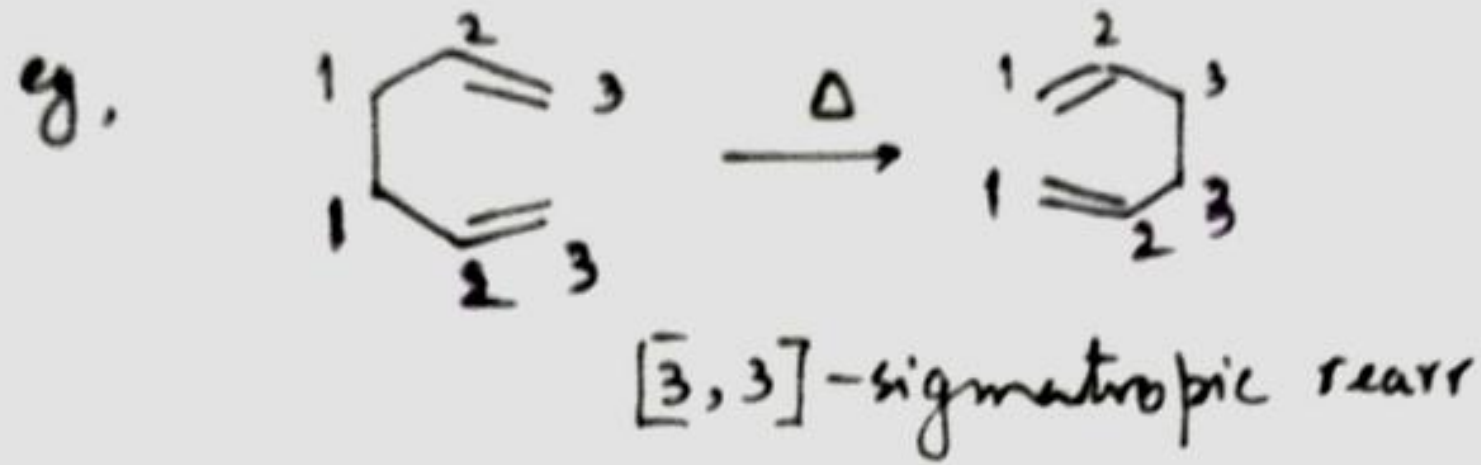


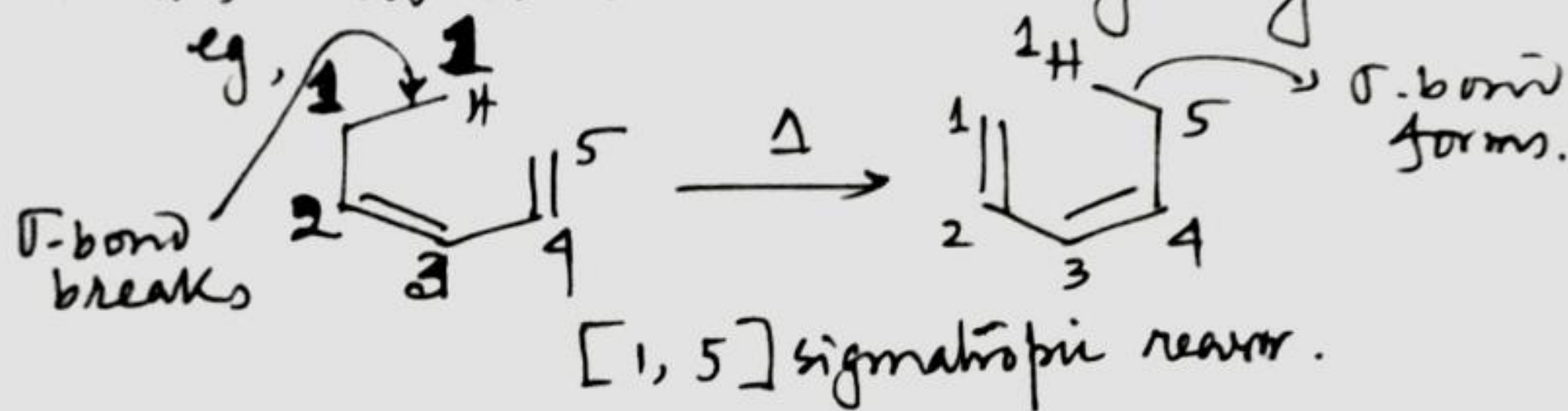
Sigmatropic rearrangement: Pericyclic rxns in which a σ -bonded atom/gr migrates from one end of a π -system to the other or a σ -bond flanked by two π electron systems migrates to a new post within the molecule in an uncatalyzed intramolecular process.

[i,j] order: When both the termini of a σ -bond move, ^{say one} from C-1 to C-i and other from C-1 to C-j, it is referred to as [i,j] order of sigmatropic rearr.



Here, a σ -bond migrates from C-1 to C-3 position, so this is [3,3]-sigmatropic rearr.

When an atom/gr migrates unchanged through a π -system, it is referred to as [1,j] order. Because one end of the σ -bond moves from C-1 to a carbon numbered j, but other end remains attached to the migrating atom.

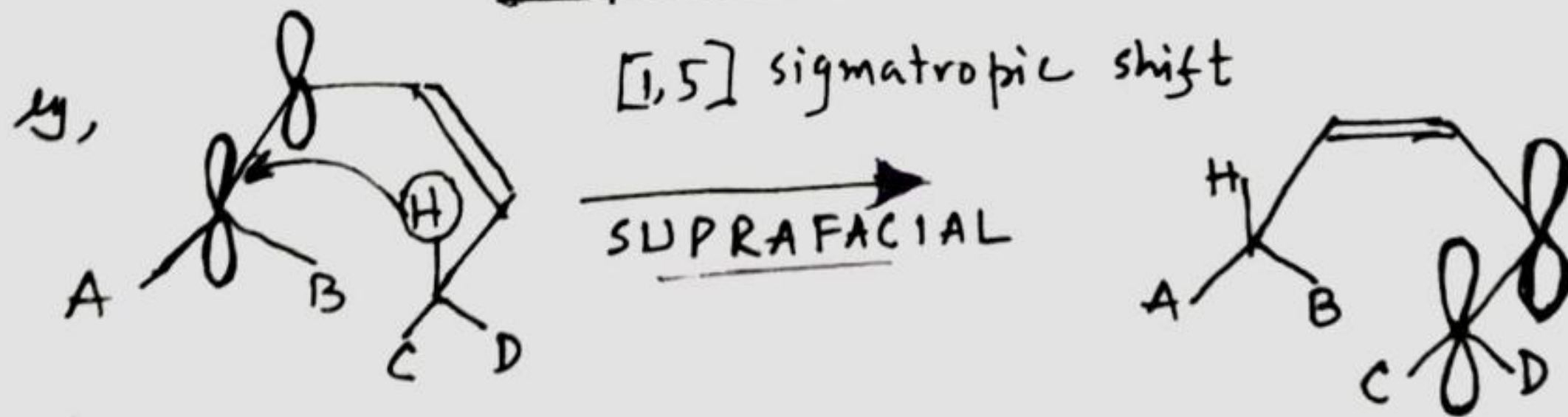


Hydrogen is migrated from C-1 to C-5 (j=5); other end of the σ -bond is still attached to H (i=1). So, [1,5] sigmatropic rearr.

⊛ How many sigmatropic rearr. be classified by its Stereochemistry w.r.t. the migration of σ -bond across the π -electron system?

Two different stereochemical courses by which migration of σ -bond across the π -system may take place.

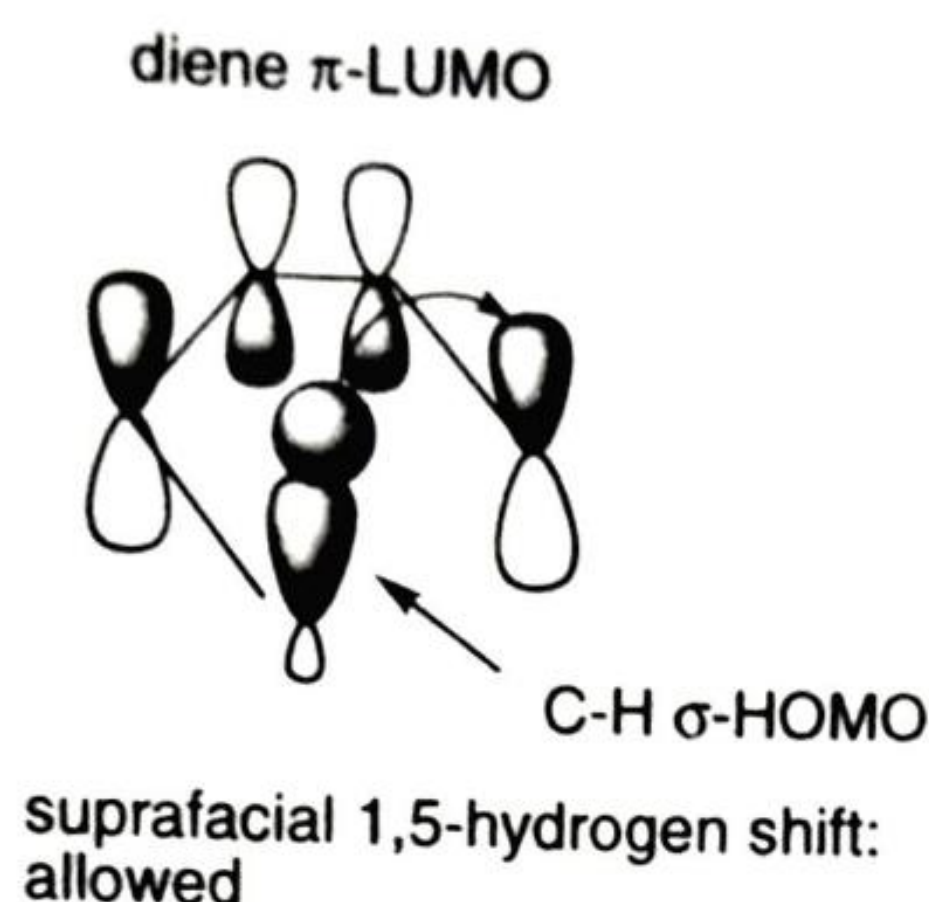
When the migrating σ -bond moves across the same face of the conjugated system, it is called suprafacial process and when it moves across the opposite π -electron face, it is called antarafacial process.



NB: Due to steric reasons, suprafacial migrations are more common than antarafacial shifts. However, with the lengthening of the conjugated system sometimes it is possible for a σ -bond to migrate to the opposite face.

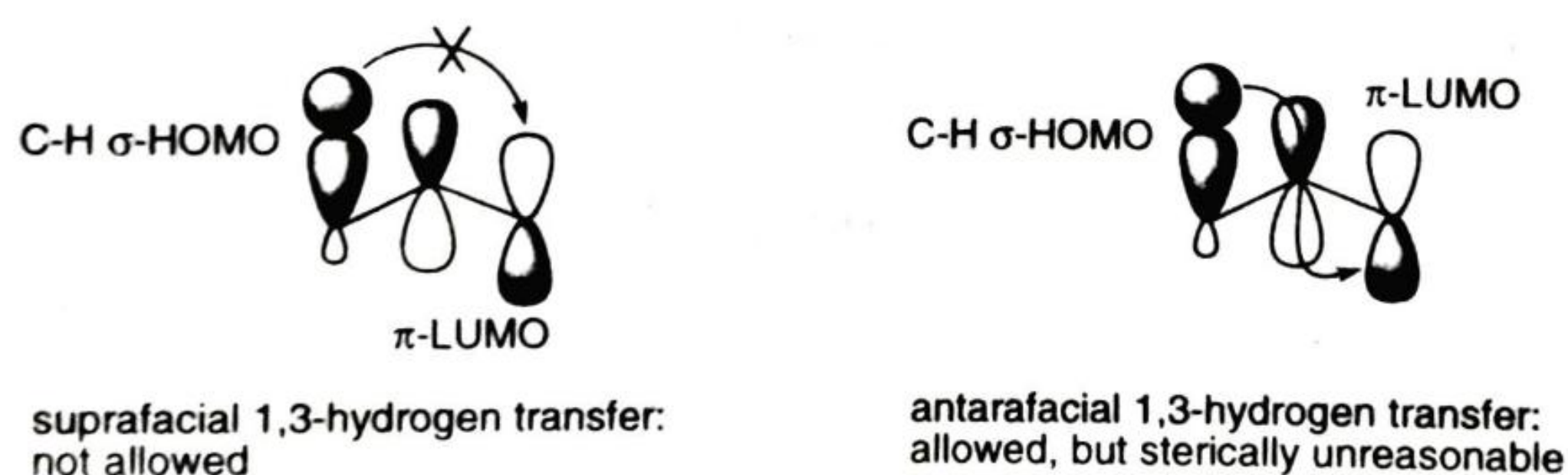
(a) [1,j]-Sigmatropic rearrangements

The occurrence and stereochemistry of sigmatropic rearrangements can be accounted for, like other pericyclic reactions, in terms of the symmetry of frontier orbitals. Consider the [1,5]-shift of hydrogen as in the first example:

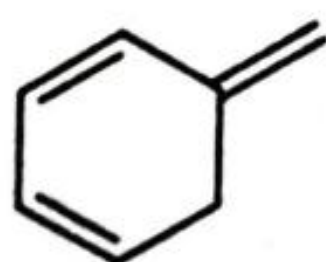


For a maximum of bonding to occur in the transition state when the HOMO (or LUMO) of the C—H σ -bond interacts with the LUMO (or HOMO) of the diene π -system, the hydrogen is transferred suprafacially. Since this arrangement is easily accessible geometrically, the [1,5]-shift of hydrogen in dienes readily occurs thermally.

Owing to the difference in symmetry between the LUMO of a simple alkene and that of a diene, a similar suprafacial [1,3]-transfer of hydrogen in a substituted alkene is symmetry-forbidden. A [1,3]-hydrogen transfer would be allowed if the π -bond were to interact antarafacially,



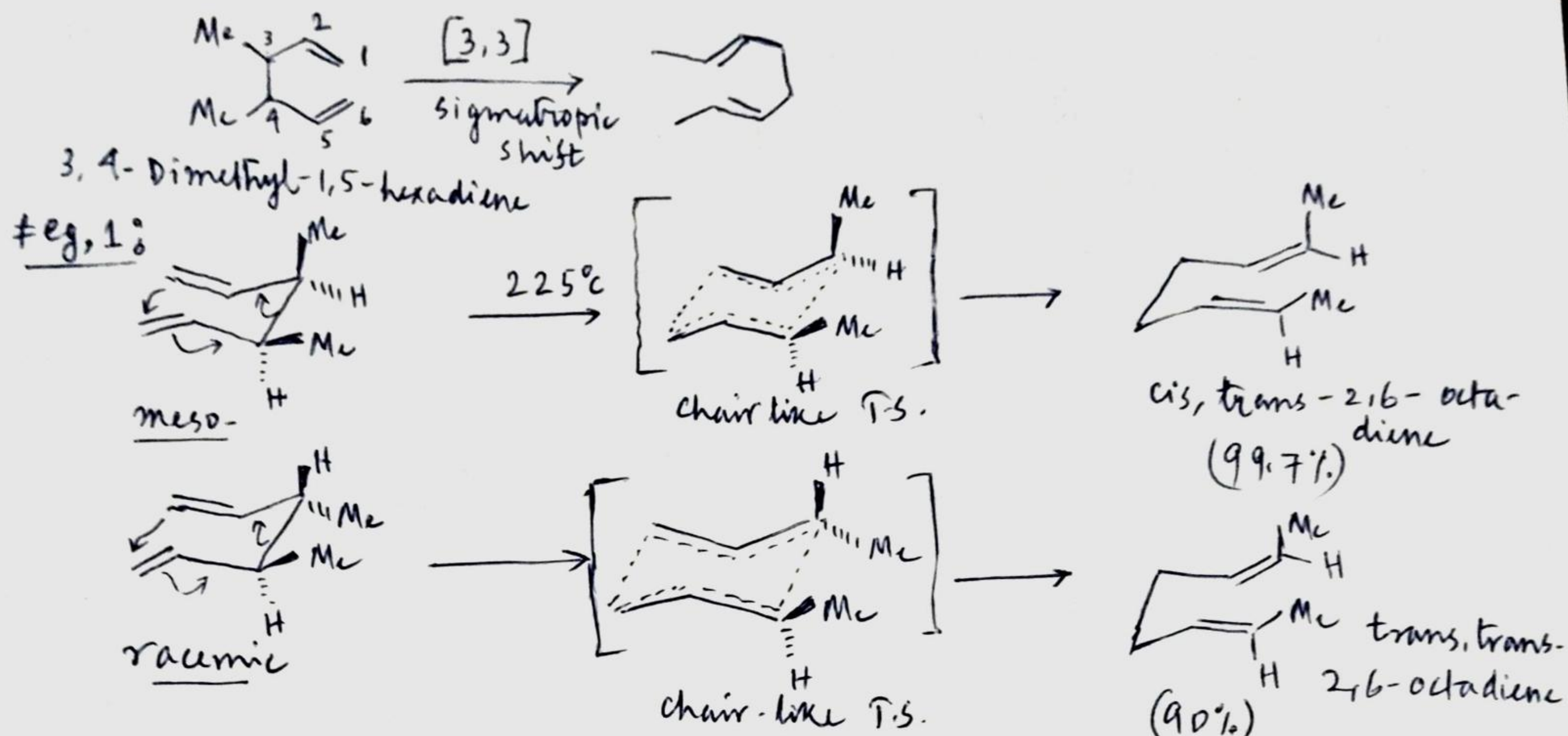
but the geometric constraint that this imposes is too great and concerted [1,3]-transfer of hydrogen is not observed. The stability of the triene,



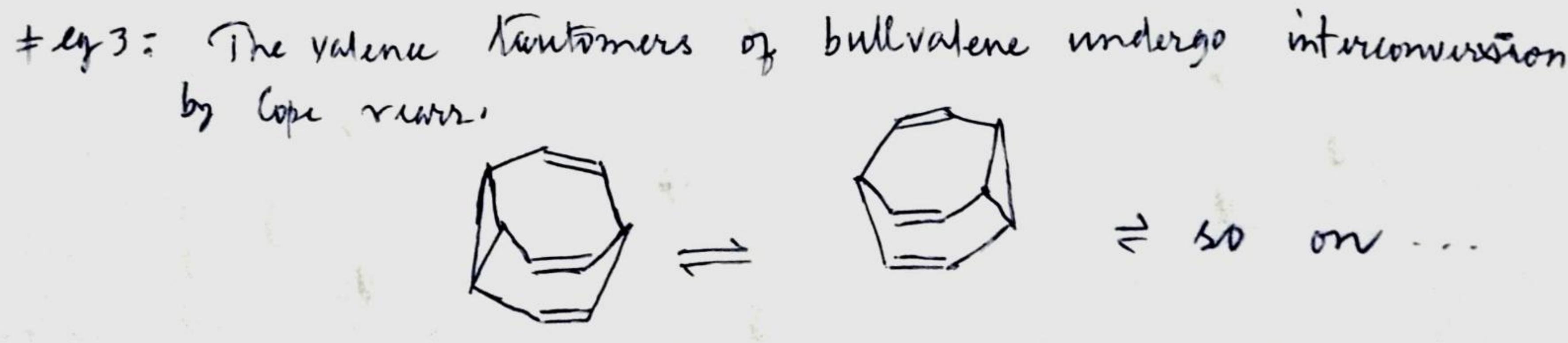
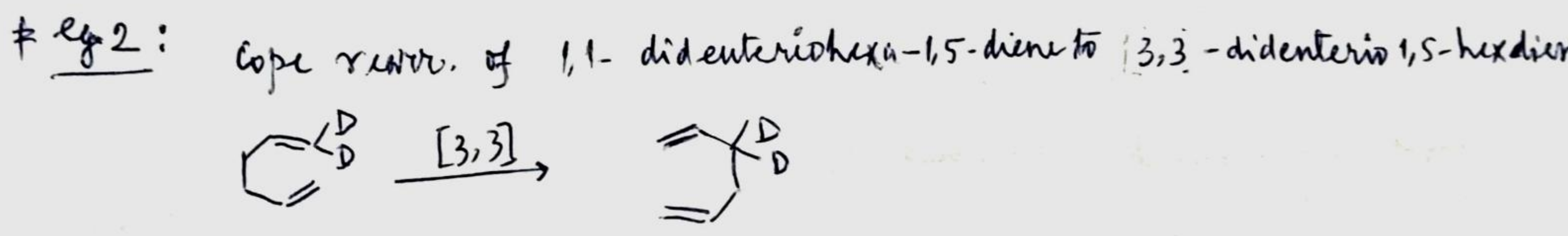
derives from the fact that concerted thermal isomerization to toluene, which is thermodynamically much the more stable, is a symmetry-forbidden process.

On the other hand, the [1,5]-hydrogen shift in 1,3-butadiene is allowed.

① Cope rearrangement: This is a [3,3] sigmatropic shift in a 1,5-diene system. The reaction is an intramolecular concerted rxn proceeding through a cyclic T.S.

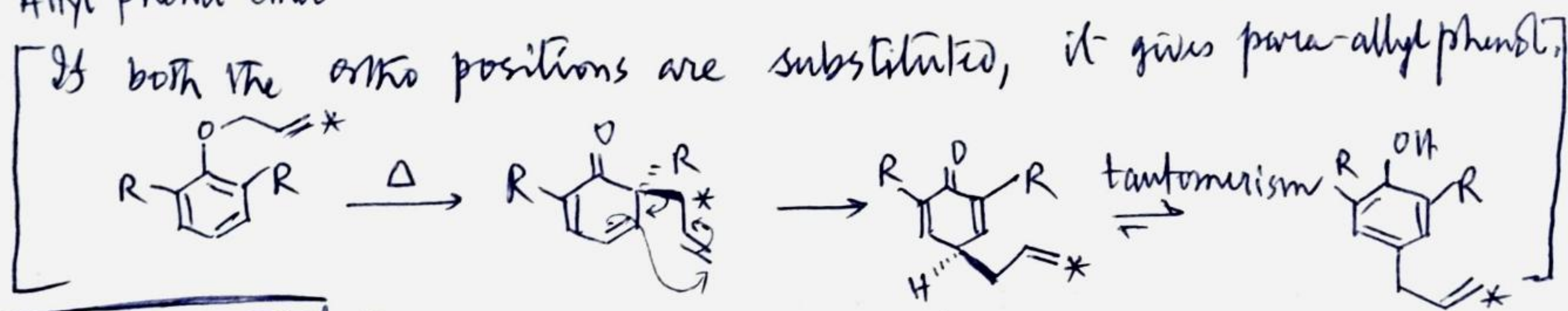
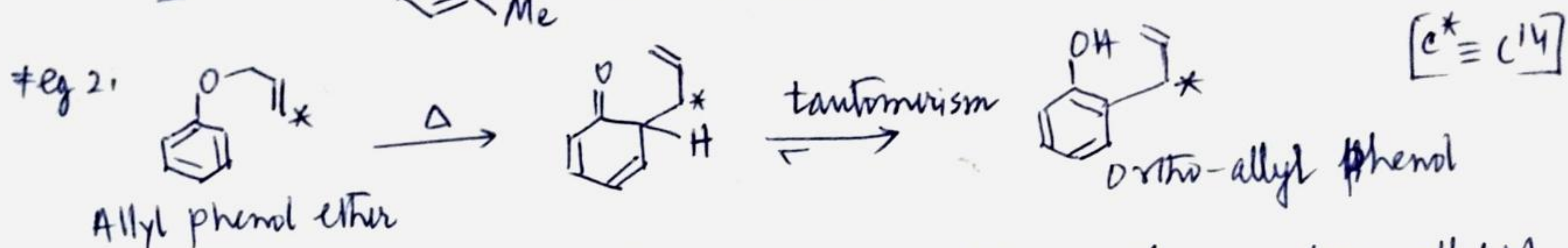


This result can be explained on the basis of the preference for chair-like T.S which is energetically preferred to a boat-like T.S



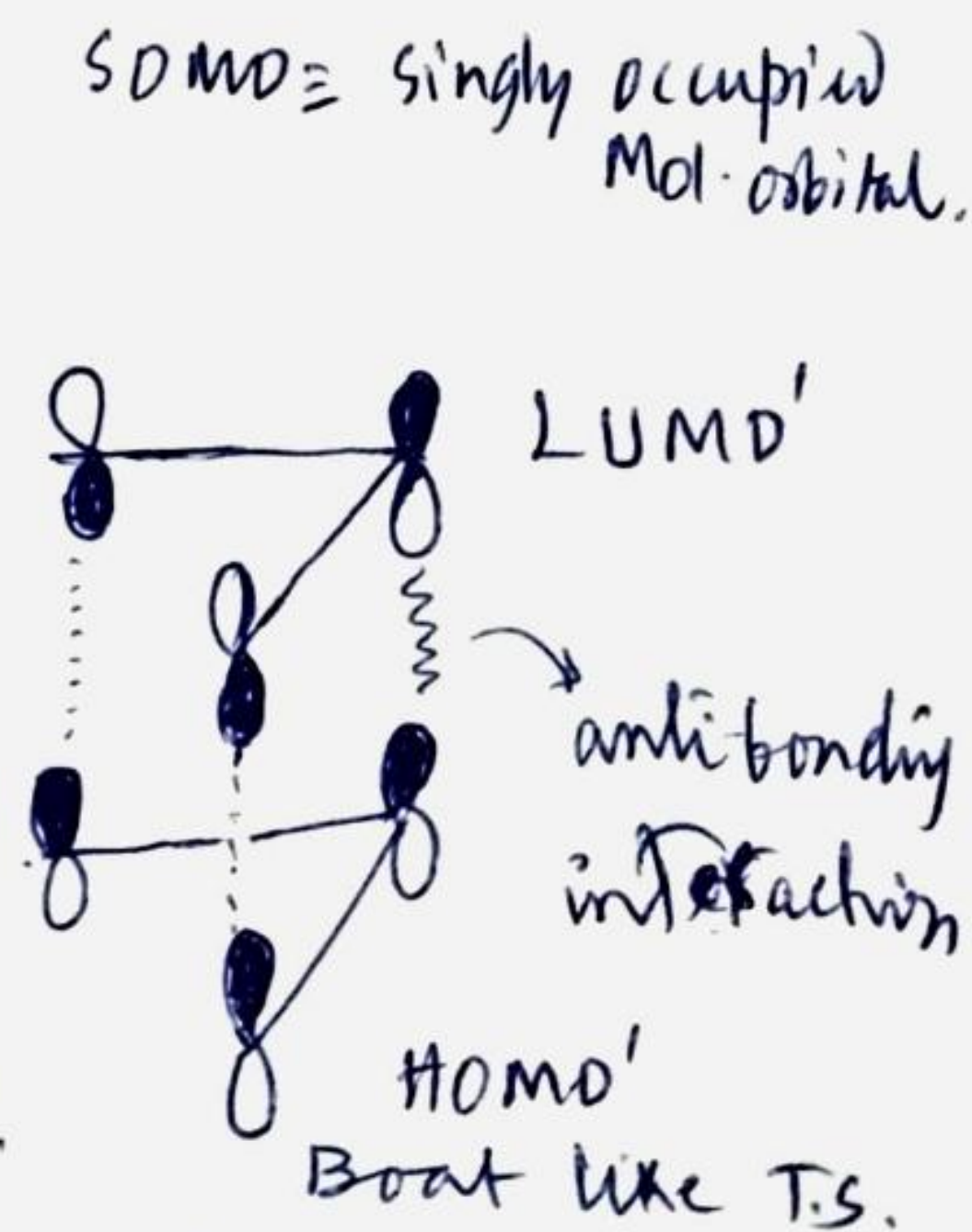
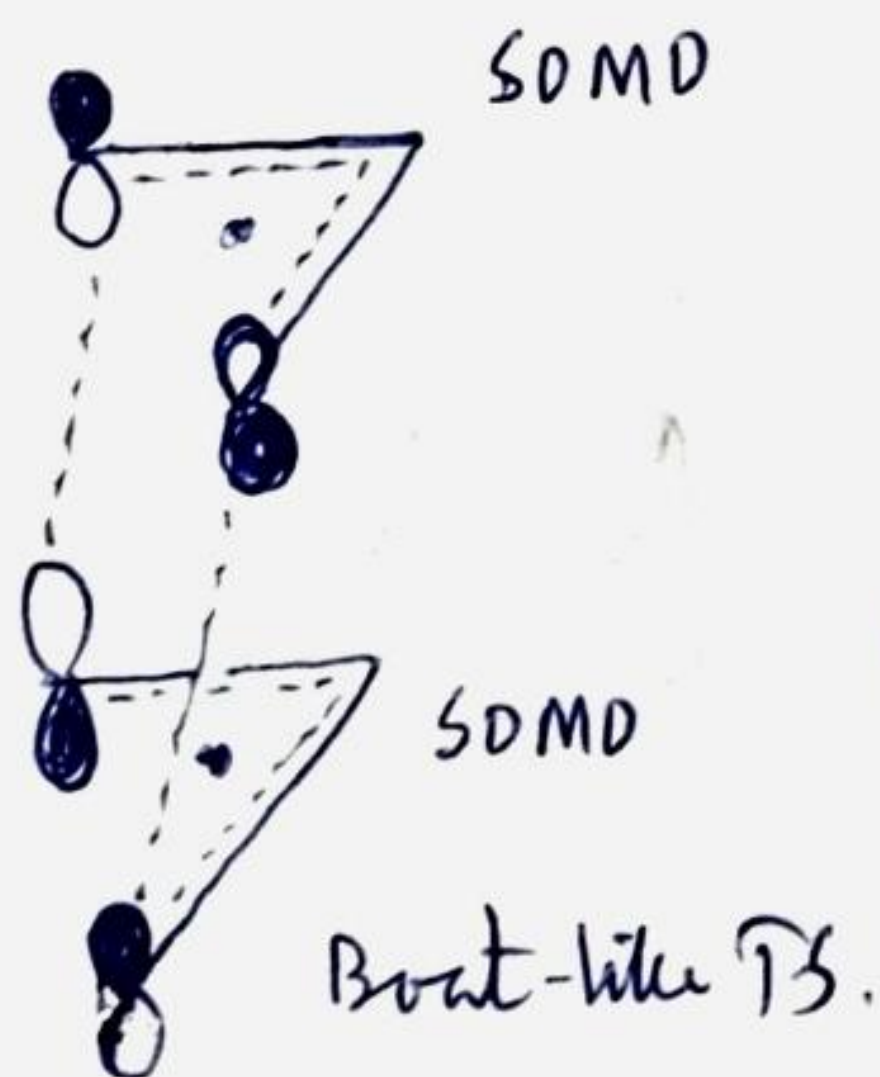
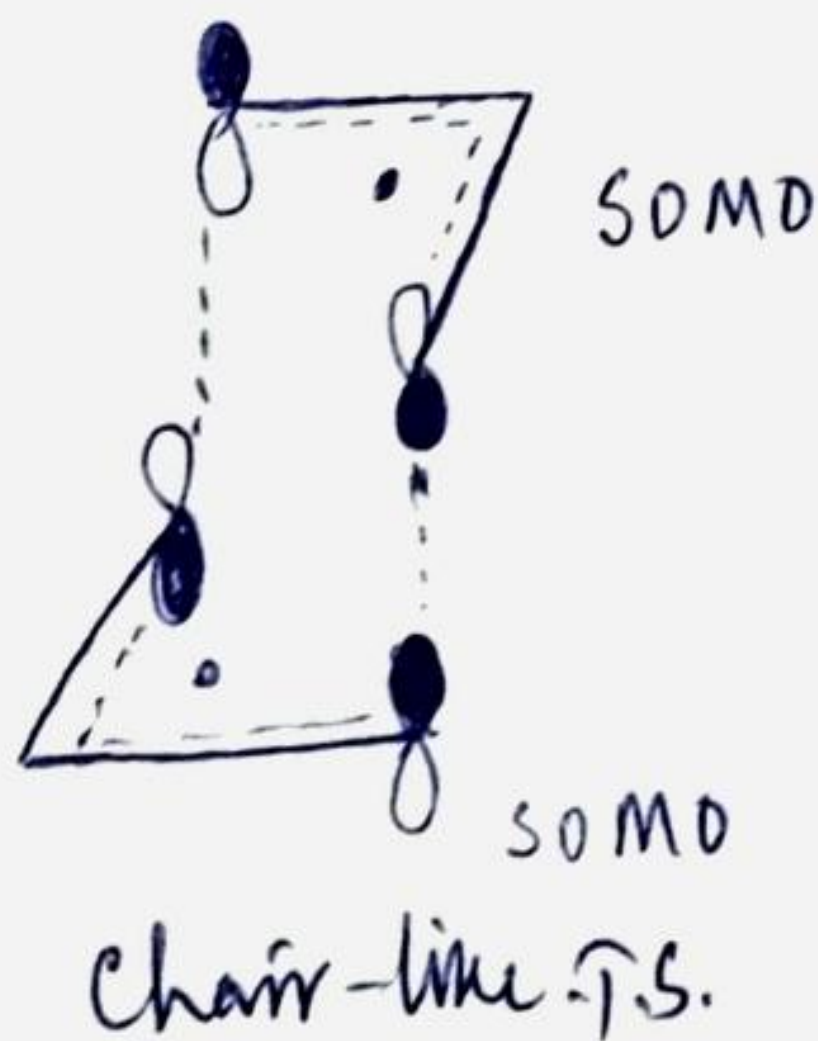
Claisen rearrangement:

The Claisen rearr. of allyl alkyl ethers is another example of [3,3] sigmatropic rearr., differing from the Cope rearr. in the replacement of a CHR fragment by oxygen but having the same stereochemical outcome.



FMO approach:

We can understand the formation of the chair-like T.S. in Cope and Claisen rearr. - the orbitals with their symmetries of the two radicaloid moieties of the T.S.



The consideration of SOMO-SOMO interaction does not help us in determining which form - chair or boat T.S. is preferred.

Preference for the chair-like T.S. is evident from the antibonding interaction at the central atom in the HOMO' of one of radicaloid moieties and LUMO' of the other in the boat conformation of the T.S. So, chair-like T.S. is preferred.