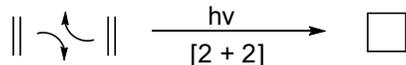


1: [2+2] Photocycloadditions in Organic Chemistry

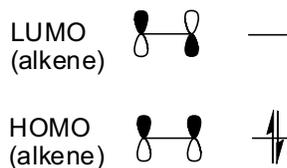
1. Basics

- addition of two alkenes (2 pi electrons + 2 pi electrons) to yield a four-membered ring.

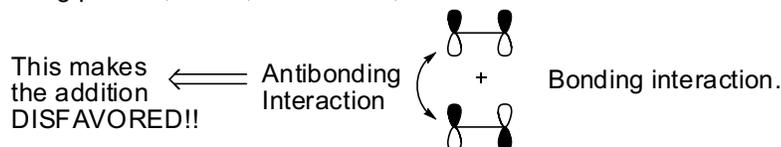


- **light** required for the reaction; nothing happens if only heat is applied.

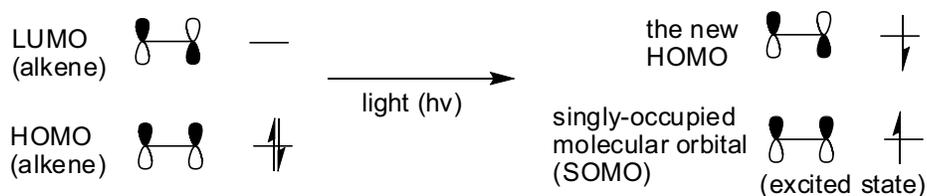
> Since two molecules are reacting to form new chemical bonds, we need interaction between filled and unfilled orbitals. For the thermal case (heat stimulus), the molecular orbitals of the alkene looks like this:



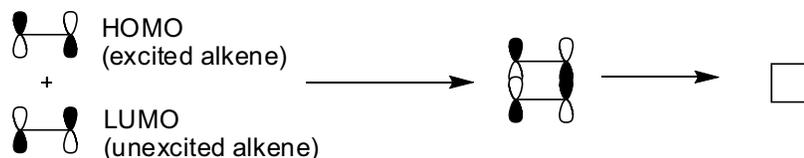
> Therefore, we need the electrons in the HOMO of one alkene entering the LUMO of its reacting partner, which, in this case, is disfavored due to a antibonding interaction:



> When **light** is used as the energy source instead of the heat, the electronic configuration of the alkene changes, as one electron from HOMO jumps to the LUMO:



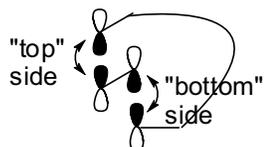
> Now, this "new HOMO", which contains a single electron, can interact with the empty LUMO of an unexcited alkene (there's plenty of this around because, after all, it's more stable than the excited state).



> This type of approach, where one both orbitals of one molecule approach its reacting partner from the same side of the molecule, is called **suprafacial**. [2+2] addition reactions are always suprafacial.

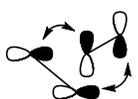
- why is the **antarafacial** approach disfavored?

> anatarafacial approach is when the orbitals from one molecule add to different sides of the reacting partner.



(antarafacial approach)

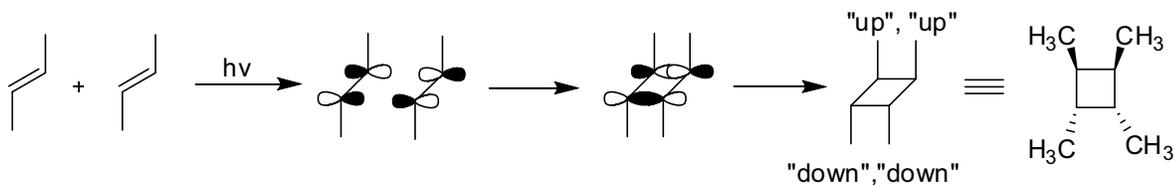
> anatarafacial approach is (almost) impossible for a [2+2]



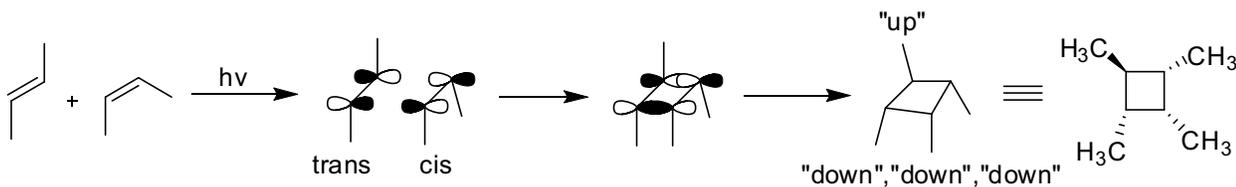
(if such antarafacial approach were possible, heat-induced [2+2] would be feasible. But this "criss-cross" approach is heavily disfavored since orthogonal orbitals cannot interact.)

2. Structural Relationship between the Reactant and Product

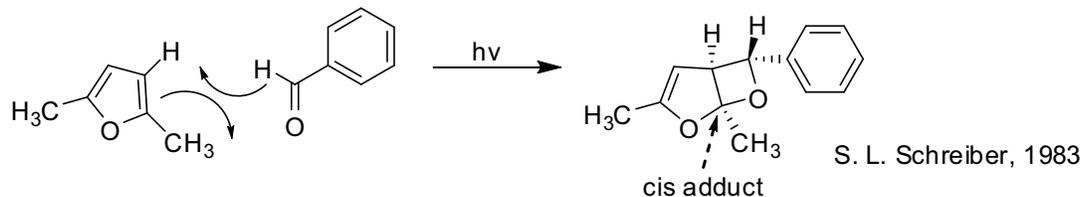
- let's take a look at the dimerization of *trans*-butene:



- lets look at the reaction between *trans*- and *cis*- butenes:



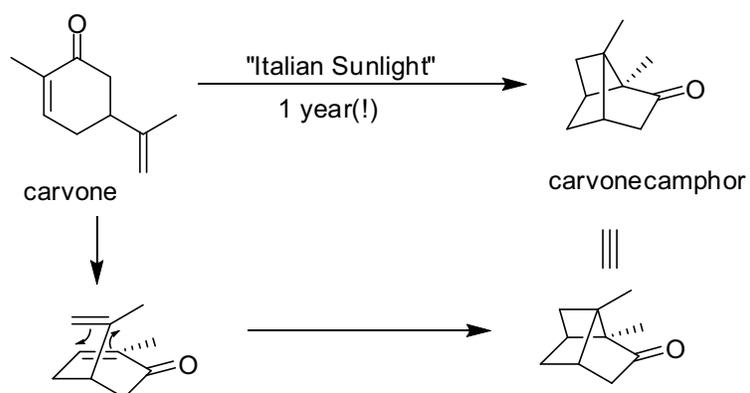
- when one of the two alkenes is in a ring, addition is **cis**.



3. Examples!!!

- first reported [2+2] photocycloaddition

G. Ciamician, P. Silber (1908):



- Paterno-Buchi Reaction

E. Paterno, G. Chieffi (1909):

