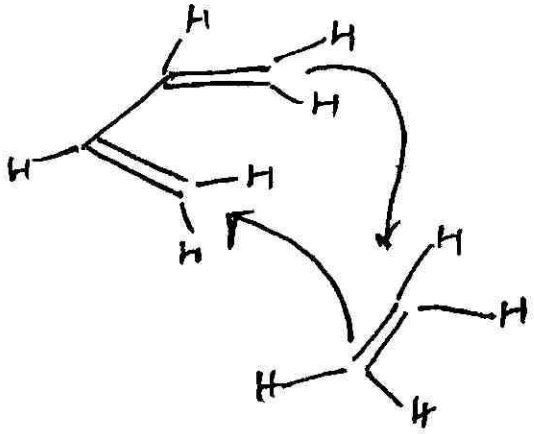
Lecture 31 (skip lecture 30)

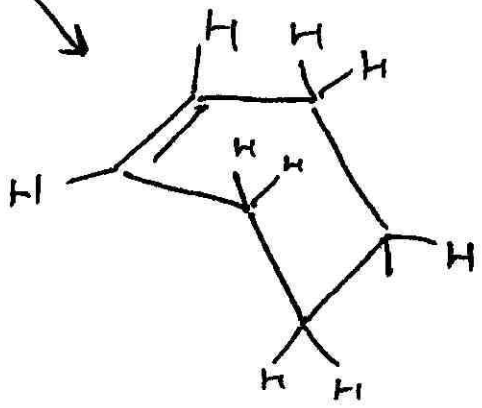
① As our last example from organic chemistry we consider the Diels-Alder reaction, an important reaction in the field.

Prototype

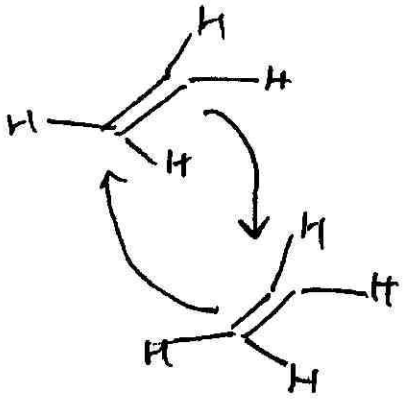


butadiene

ethylene

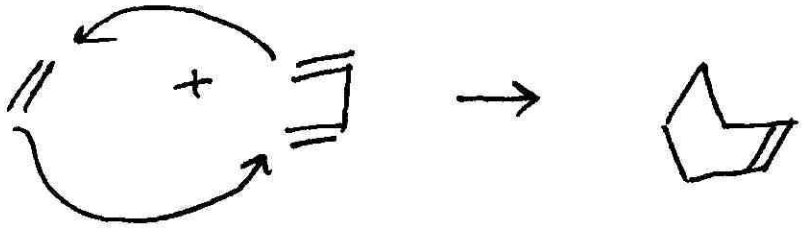


While this reaction is common in organic chemistry, the [2+2] reaction is rare



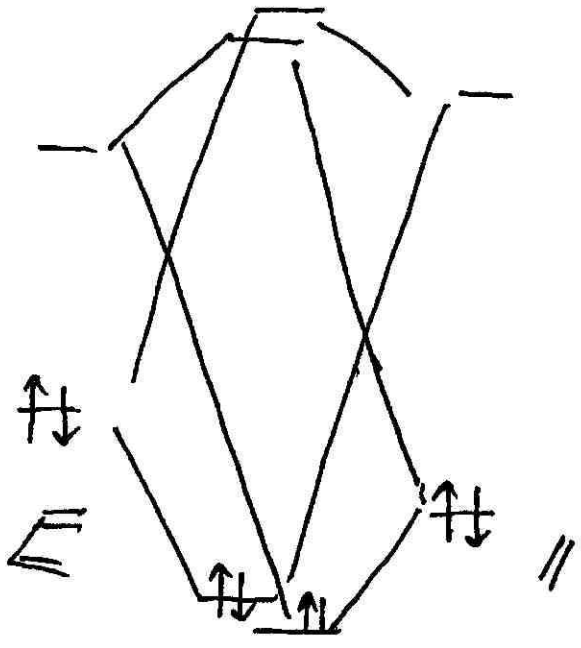
We will explain today why the Diels-Alder reaction is much more facile than the [2+2] addition.

② One hint in the electron behavior of the Diels-Alder reaction is the classical organic chemistry arrow picture:



There are 2 arrows in the classical picture. If we associate the $\xrightarrow[\text{(left)}]{\text{(right)}}$ left side of the arrow drawn here with the nucleophile & the right side w/ the electrophile, then the mechanism seems to be saying the Diels-Alder reaction seems to involve two molecules which are both simultaneously acting as an electrophile & a nucleophile.

③ Associating electrophiles with LUMO's and nucleophiles w/ HOMO's the MO picture is:



2 sets of HOMO-LUMO interactions.

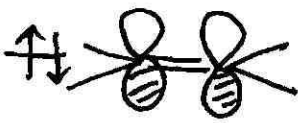
④ We need to derive the MO diagram of the two component pieces

Review

LUMO

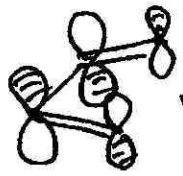
$\begin{pmatrix} \alpha & \beta \\ \beta & \alpha \end{pmatrix}$

E↑



HOMO

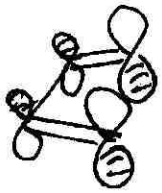
| $\psi_j$ | $E_j$ |
|---|---|
| $\begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix}$ HOMO | $\alpha+\beta$ HOMO |
| $\begin{pmatrix} 1/\sqrt{2} \\ -1/\sqrt{2} \end{pmatrix}$ LUMO | $\alpha-\beta$ LUMO |



$\begin{pmatrix} 1 \\ -\frac{1+\sqrt{5}}{2} \\ \frac{1+\sqrt{5}}{2} \\ -1 \end{pmatrix}$ $\alpha - \left(\frac{1+\sqrt{5}}{2}\right)\beta$

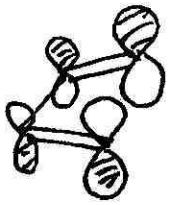
LUMO

ET

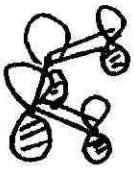


$\begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ -1 \\ -1 \\ \frac{1+\sqrt{5}}{2} \end{pmatrix}$ $\alpha - \left(\frac{-1+\sqrt{5}}{2}\right)\beta$

Homo



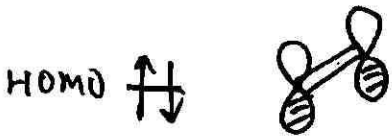
$\begin{pmatrix} \frac{1+\sqrt{5}}{2} \\ 1 \\ -1 \\ \frac{-1-\sqrt{5}}{2} \end{pmatrix}$ $\alpha + \left(\frac{-1+\sqrt{5}}{2}\right)\beta$



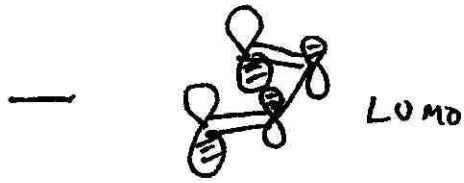
$\begin{pmatrix} 1 \\ \frac{1+\sqrt{5}}{2} \\ \frac{1+\sqrt{5}}{2} \\ 1 \end{pmatrix}$ $\alpha + \left(\frac{1+\sqrt{5}}{2}\right)\beta$

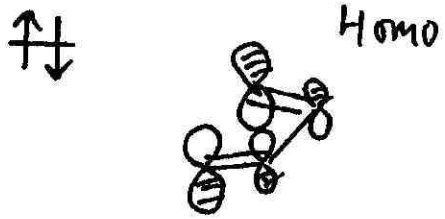
Summary

ethylene

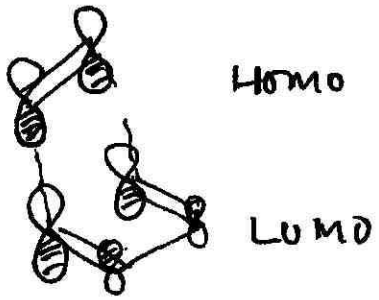




butadiene



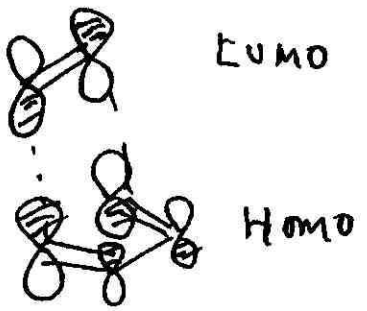




The Homo of ethylene can interact with the Lumo of butadiene:



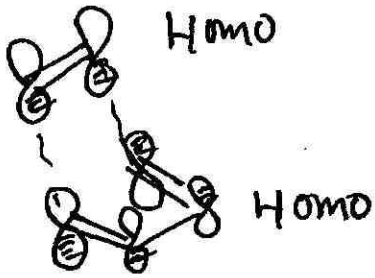

Interaction

The LUMO of ethylene can interact with the HOMO of butadiene:



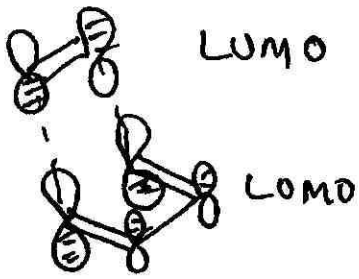

Interaction

But neither the HOMO of butadiene & HOMO of ethylene can interact,



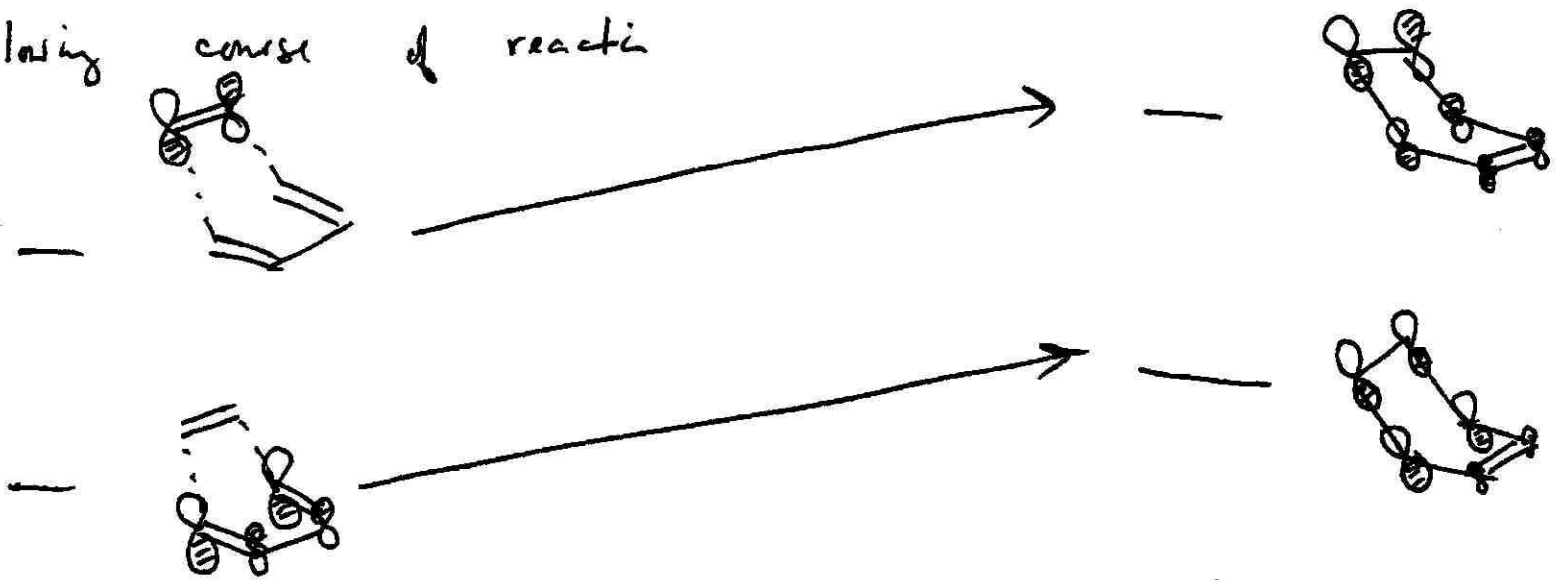

No interaction

Nor can the LUMO of butadiene & LUMO of ethylene interact



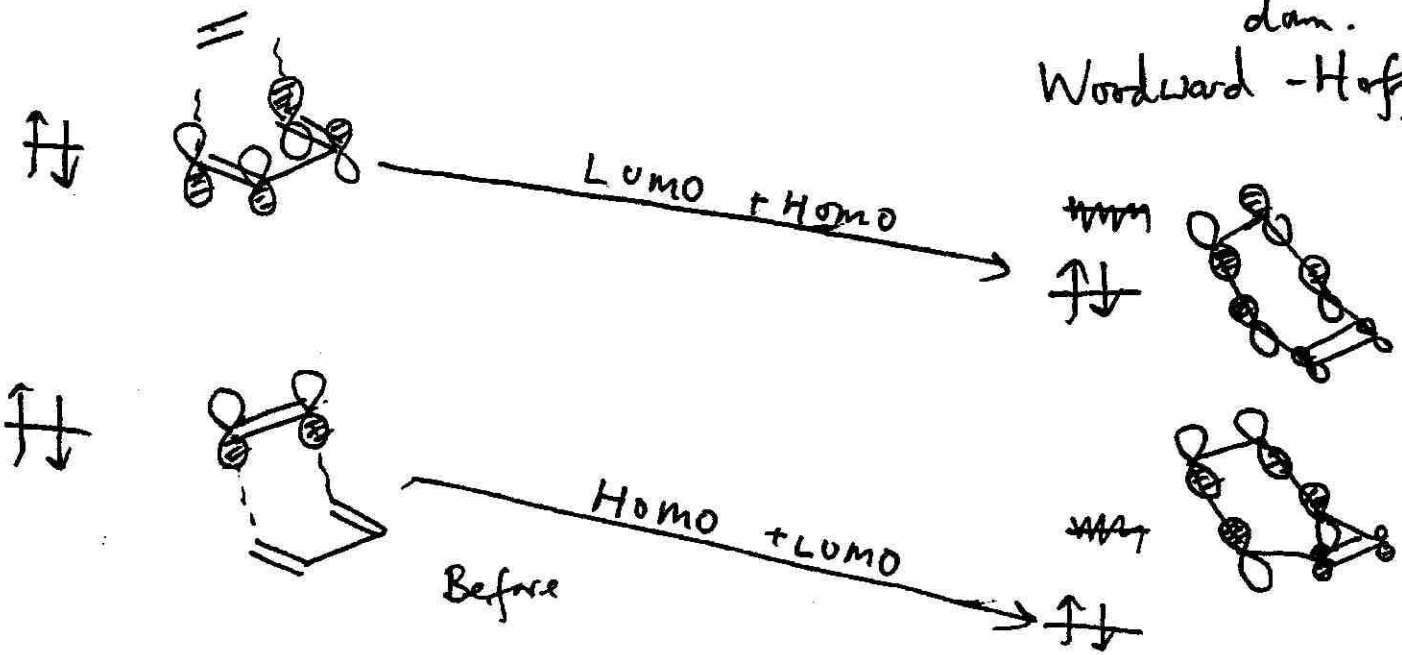

No interaction

Following course of reacti

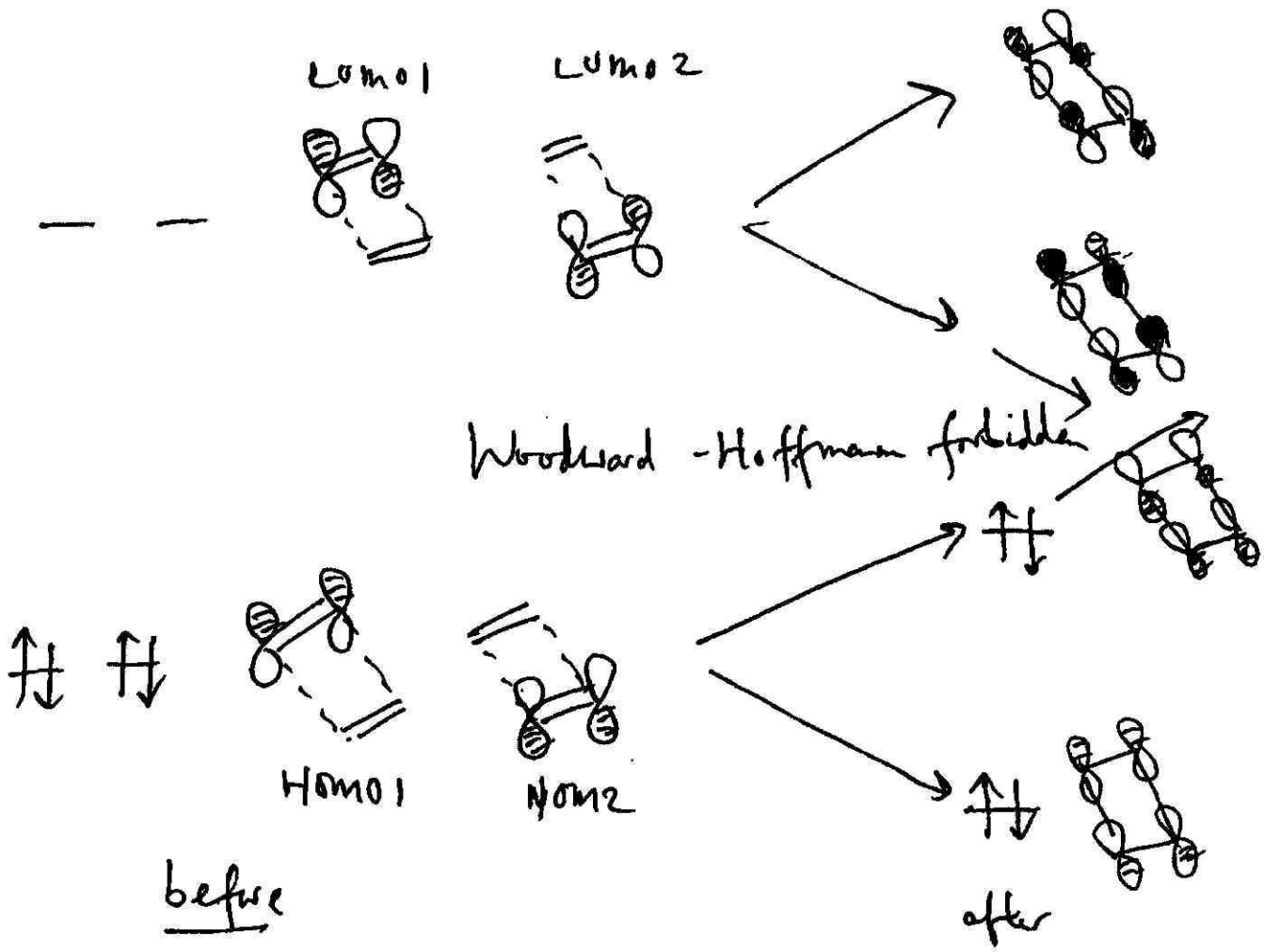


In course of reactio energy of orbitals goes down.

Woodward-Hoffmann Moved



Now compare this result with [2+2] addition




Note here HOMO1 interacts only with HOMO2

& " LUMO1 " " " LUMO2

No stabilization in course of reaction.

Hence [2+2] addition does not really occur