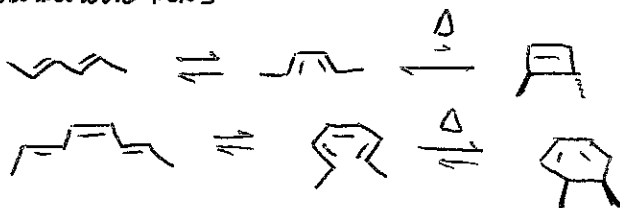


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PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

RECALL: PERICYCLIC REACTIONS

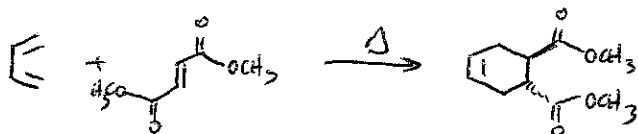
1. ELECTROCYCLIC REACTIONS



STEREOCHEMISTRY CAN BE EXPLAINED
 BASED ON W.O. SYMMETRY CONSIDERATIONS

2. CYCLOADDITION REACTIONS

E.G. DIELS-ALDER REACTION

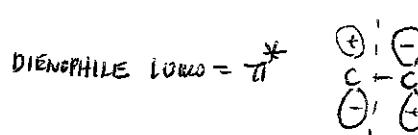
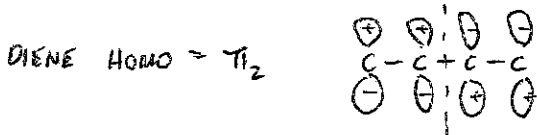


TERMINOLOGY - GENERAL

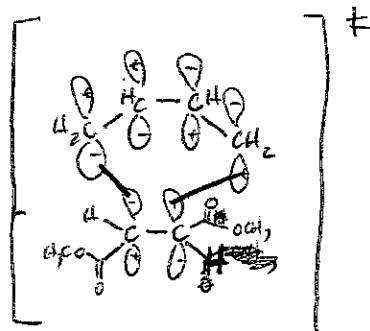
D.A. = [4q2]

OF e⁻S IN
 REACTING π -SYSTEMS
 (DIENE + DIENOPHILE)

BIMOLECULAR - ANALYZE HOMO ON ONE REACTANT & LUMO ON THE OTHER, CHOOSE DIENE FOR HOMO, DIENOPHILE FOR LUMO



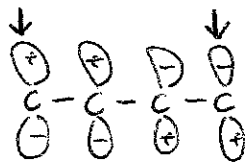
DIELS-ALDER TRANSITION STATE:



\Rightarrow BOTH CONTACTS \Rightarrow THIS REACTION IS "ALLOWED"
 ARE "BONDING"

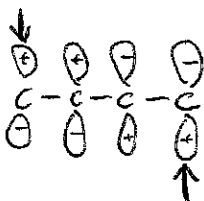
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NEW CONSIDERATION "SIDEDNESS"



SAME SIDE = SUPRAFACIAL

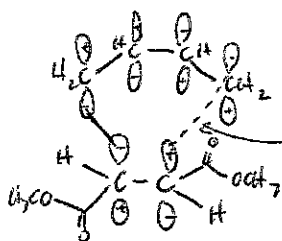
VS.



OPPOSITE SIDES = ANTARAFACIAL

⇒ RE-EVALUATE DIELS-ALDER
 ABOVE $[4+2]$
 ↓ ↓
 SUPRAFACIAL ON
BOTH REACTANTS

CONSIDER $[4_a + 2_s]$ - POSSIBLE?

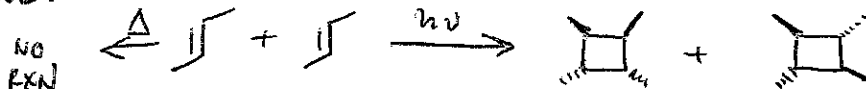


+ Pairs WITH - = UNFAVORABLE ⇒ CONCLUDE $[4_a + 2_s]$ IS
 FORBIDDEN (THERMAL)

CONSIDER $[2+2]$ CYCLOADDITIONS...

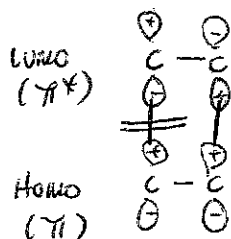


OBSERVE:



RATIONALE FOR PHOTO VS. THERMAL...

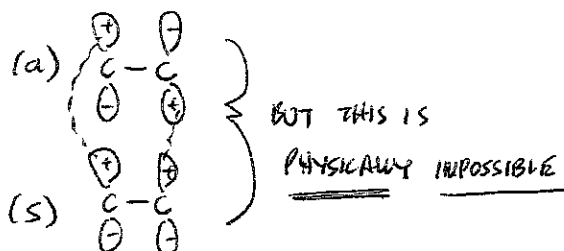
CONSIDER $[2_s + 2_s]$ - THERMAL



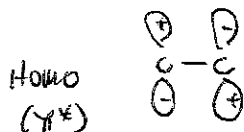
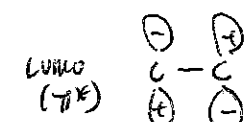
⇒ THERMAL $[2_s + 2_s]$ IS FORBIDDEN

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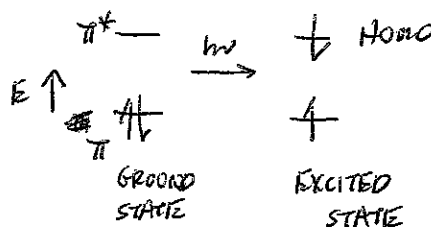
IN PRINCIPLE, $[2s+2a]$ IS ALLOWED, ...



HOWEVER, PHOTO $[2s+2s]$ IS ALLOWED



ONE ALKENE IS IN ELECTRONICALLY-
 EXCITED STATE



FIRST EXAMPLE OF PHOTO- $[2+2]$ WITH ENANTIOSELECTIVITY

→ T. YOON SCIENCE 344, 392 (2014)

KAZ SKOBI

