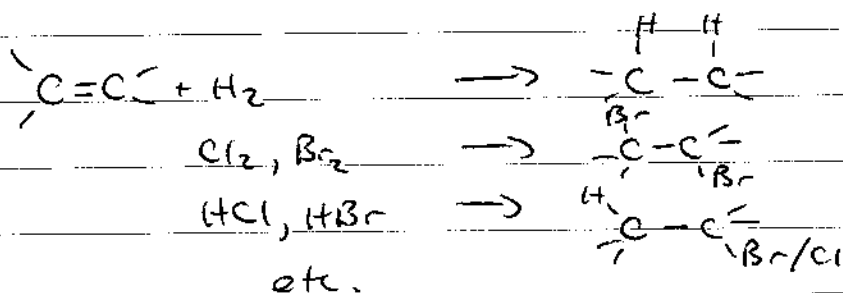


Chapter 15

Skip 15-3, 15-4, 15-7, 15-8, 15-9, 15-10,  
15-12, 15-13

Conjugated Systems

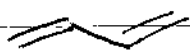
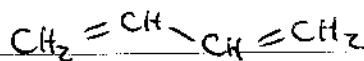
Have discussed  $-C=C-$ ,  $-C\equiv C-$



All are related to ISOLATED DOUBLE BONDS

Now...

Conjugated double bonds

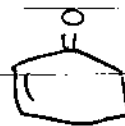
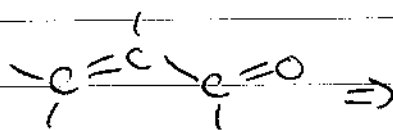


1,3-butadiene



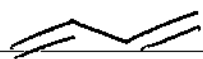
1,3,5-hexatriene

also,

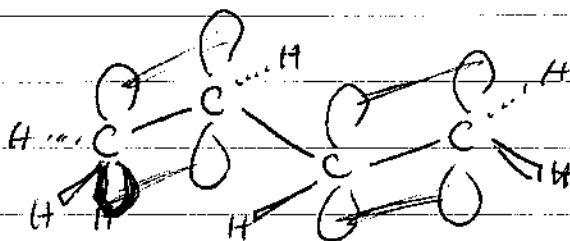


cyclohexenone

# Butadiene

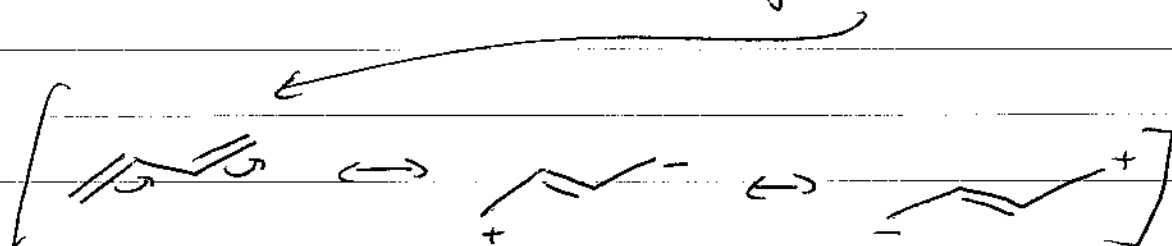


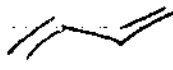
MOs



are ALL in same plane

∴ they interact together

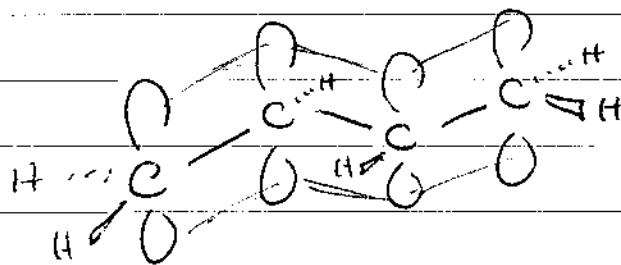


∴ not really 

But rather

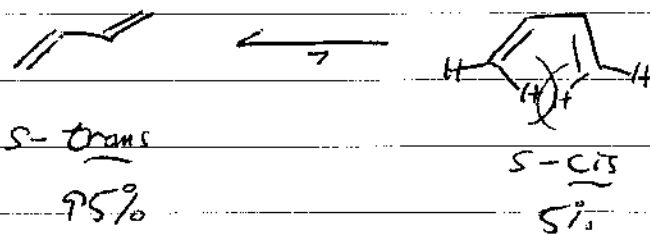


delocalized



1.34 Å      1.48 Å  
(1.32 Å)    (1.54 Å)    C-C  
                  (1.50 Å)    C=C-C

2 possible conformations:

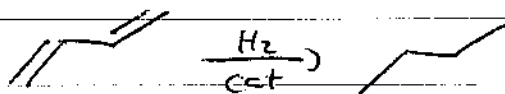


s-trans  
95%

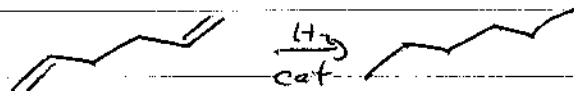
s-cis  
5%

$$\Delta G_r = 1.7 \text{ kcal mol}^{-1}$$

also,



$$\Delta H_r = -57.1 \text{ kcal mol}^{-1}$$



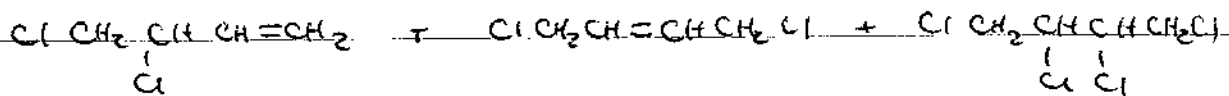
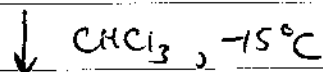
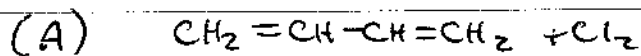
$$\Delta H_r = -61 \text{ kcal mol}^{-1}$$

CC=CC is more stable (less reactive) by  
4 kcal mol<sup>-1</sup>

called resonance energy

## Addition Reactions in conjugated systems

1,2 vs 1,4 addn : Thermo vs. kinetic control



3,4-dichloro-1-butene

1,4-dichloro-2-butene

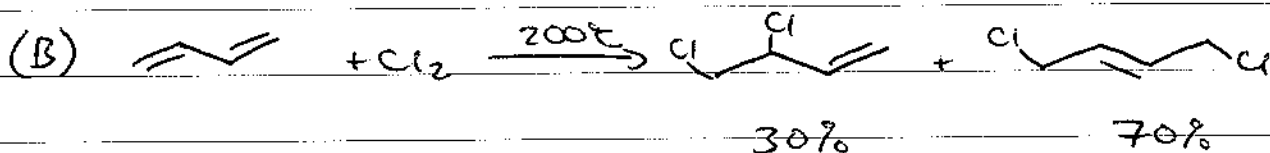
~ 60%

~ 40%

< 1%

1,2 addn. prod.

1,4 addn product



ONLY Diff is temp

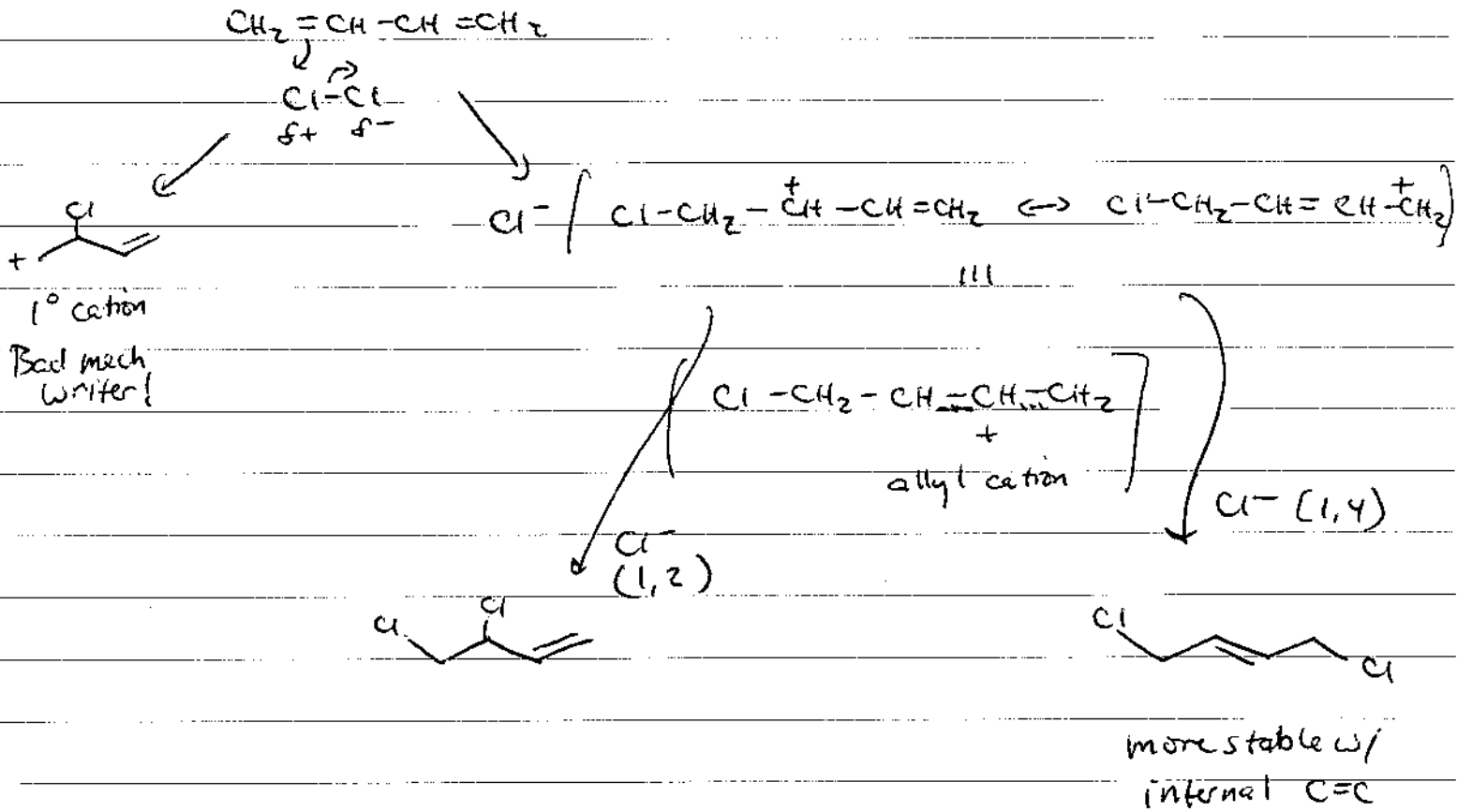
(A)  $\Rightarrow -15^\circ\text{C}$

(B)  $\Rightarrow 200^\circ\text{C} \rightarrow$  allows formation of thermodynamic product (more stable)

kinetic product predominates

faster formed product

Mechanism

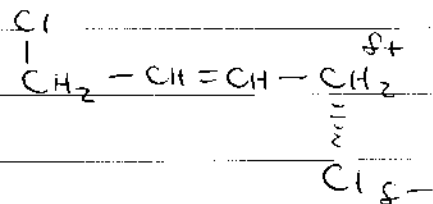
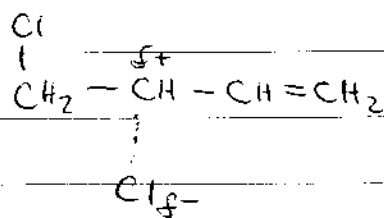


explains why thermo product is formed.

Why is 1,2 kinetically favored?

2 Reasons

1) TS's

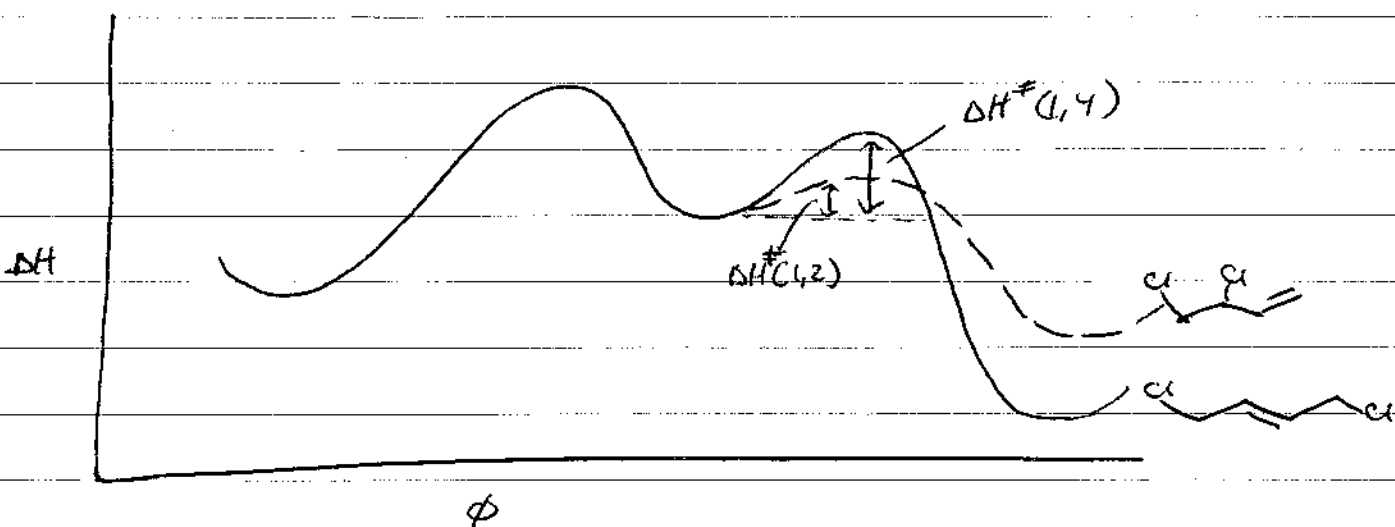


Better

"2° cation-like" TS

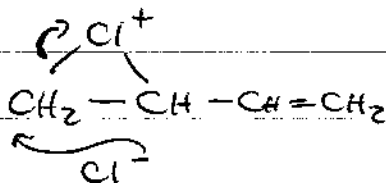
"1° cation-like" TS

# PES

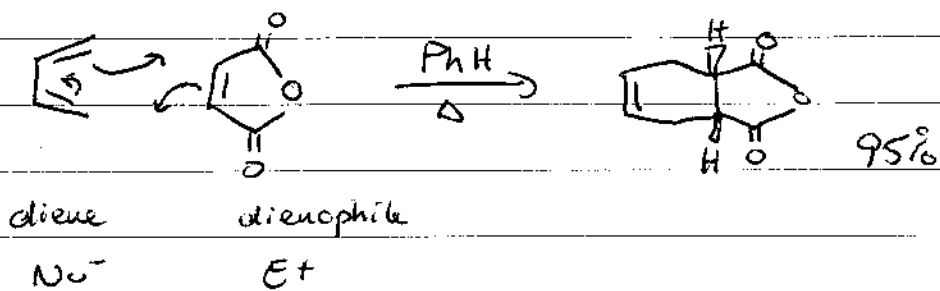


∴ at low temps,  $\Delta H^\ddagger$  controls rxn  
high temps,  $\Delta H_{rxn}$  controls rxn

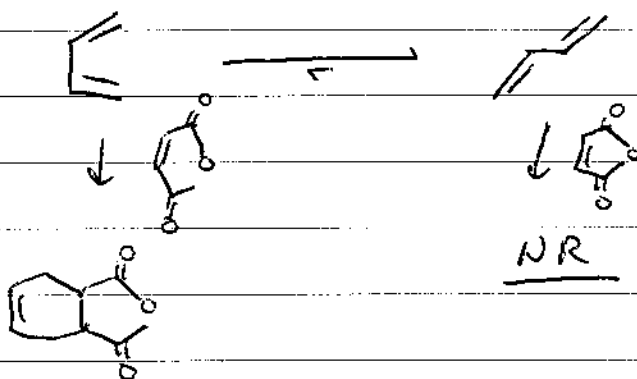
2) Reason why 1,2 addn is ok,



## Diels-Alder Rxn



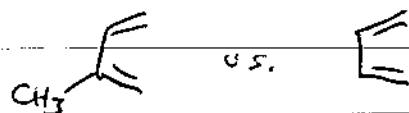
Problem with this rxn:



Would be nice if we could "lock" into s-cis conformation

2 ways to do this:

1) put bulky groups in place of H:  
i.e.,



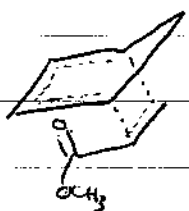
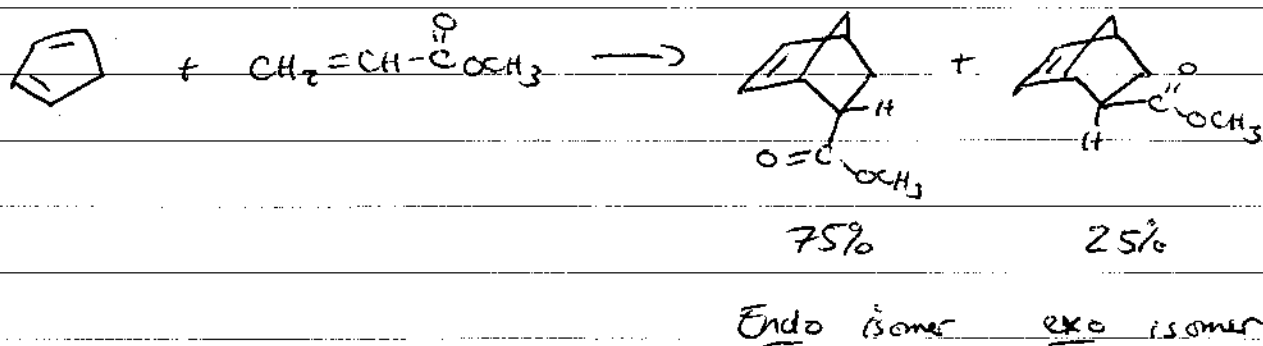
↳ forces s-cis to be favored

2) use diene as part of a ring

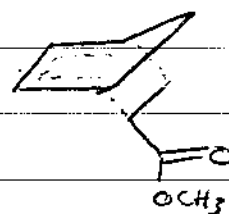




## Endo rule / Alder Rule

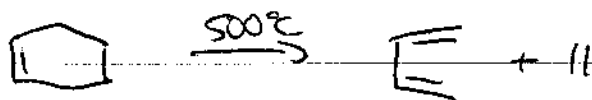


endo product  
allows overlap  
btw pi-orbitals  
- stabilizes TS

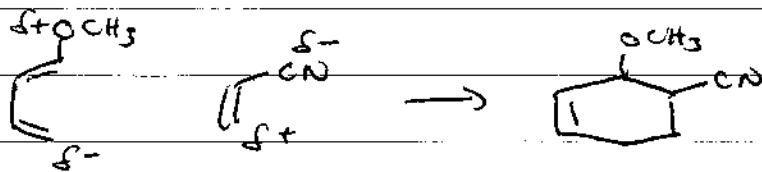
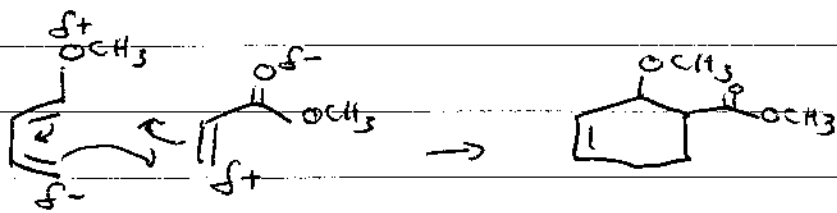


exo product

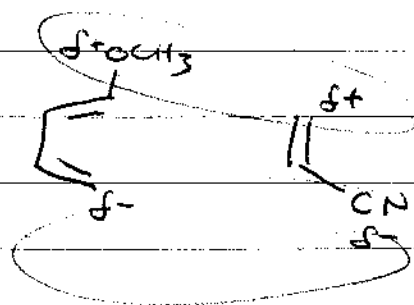
## Retro DA Rxn







otherwise



oops! don't think so...