Course Chem 343 Lecturer Gellman
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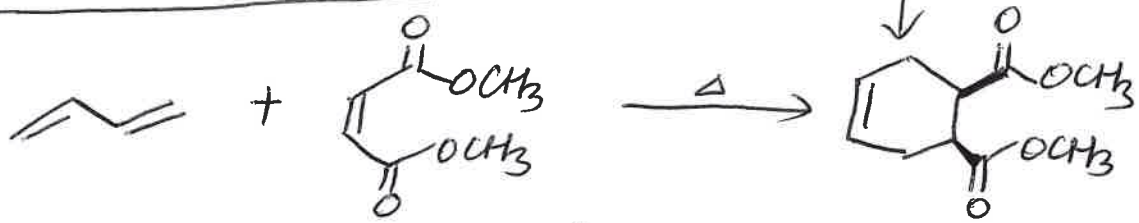
Recall: "conjugated" Dienes — special properties as a result of π e⁻ delocalization "$H_2C=CH-CH=CH_2$" is really "$H_2C=CH\overset{\cdots}{-}CH=CH_2$"

Manifestations —
1) Heats of hydrogenation
2) Planar conformations ~~preffer~~ preferred (s-trans vs. s-cis)
3) New reactions

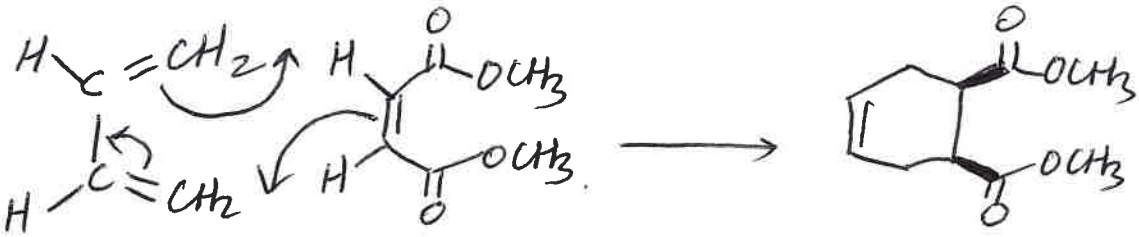
"Diels-Alder Rxn"

6-membered ring!

Ex:



Accepted mechanism (concerted):



(s-cis)

3 π-bonds → 2 σ-bonds
+1 π-bond

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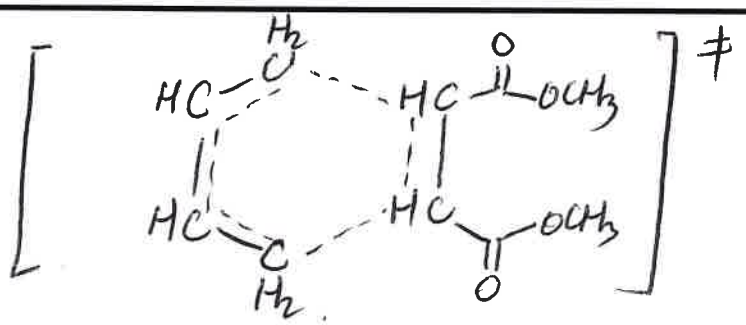
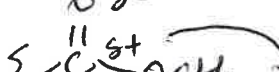
TS: 

New word: Diene
+
"Dienophile"

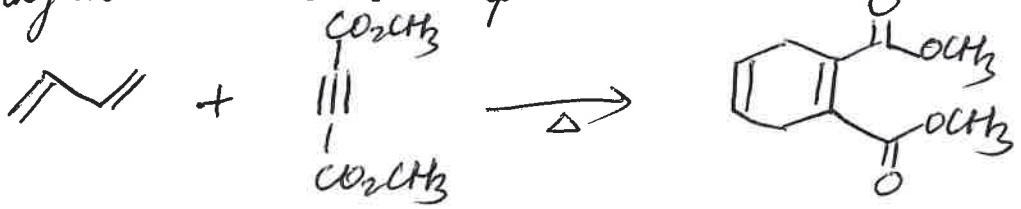
What makes for good dienophile reactivity? ⇒ e⁻-withdrawing substituents.



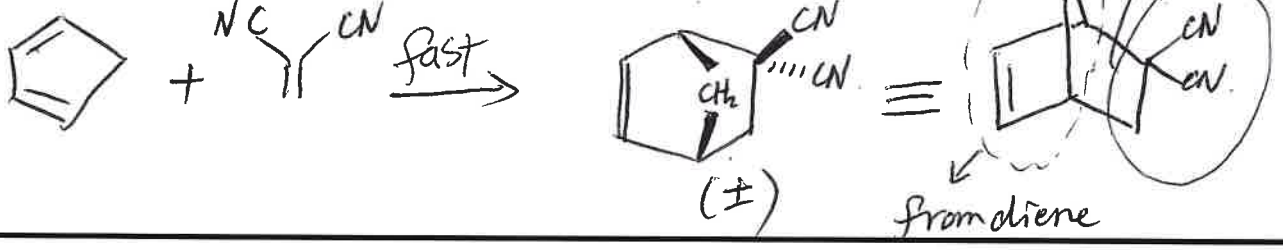
attached to alkene ⇒ good dienophile

Thus, common ~~substit~~ examples are

Alkynes can be dienophiles...



Dienes in a ring are especially DA-reactive.



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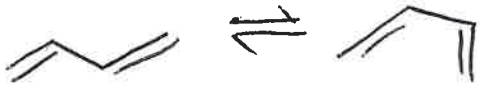
Fast b/c diene "locked" S-cis.

Contrast:



S-trans S-cis.

↑ required for DA.

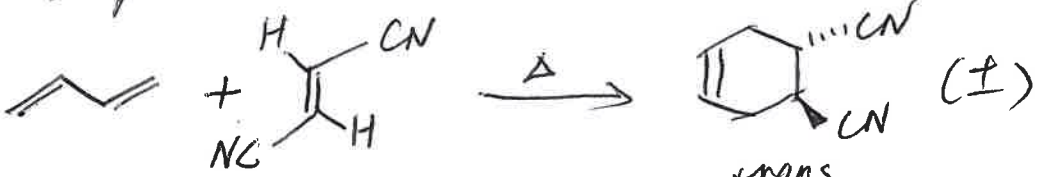
Note:

"locked" S-trans → No DA rxn !

Stereochemical Correlations

SM ---> products.

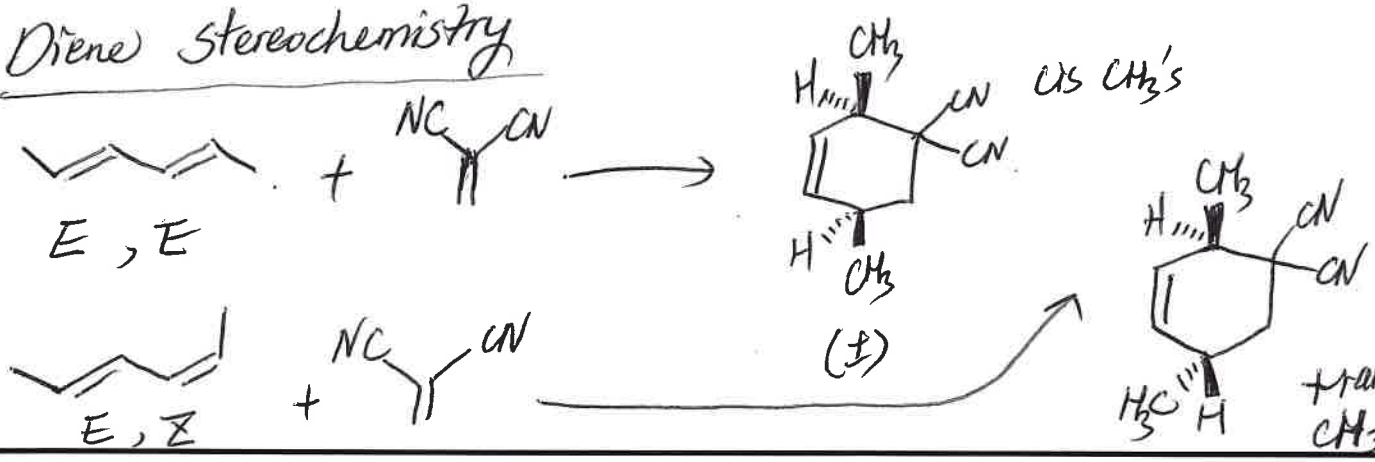
Ex:



trans

(± E dienophile → cis ~~cyclohexene~~ cyclohexene)

Diene Stereochemistry



E, E

E, Z

(±) cis CH_3's

trans CH_3's

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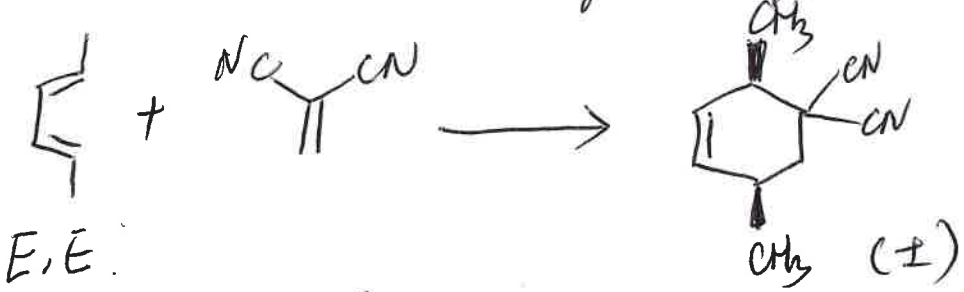
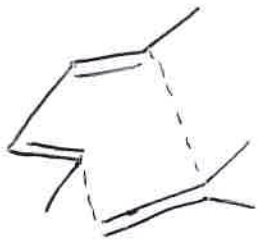
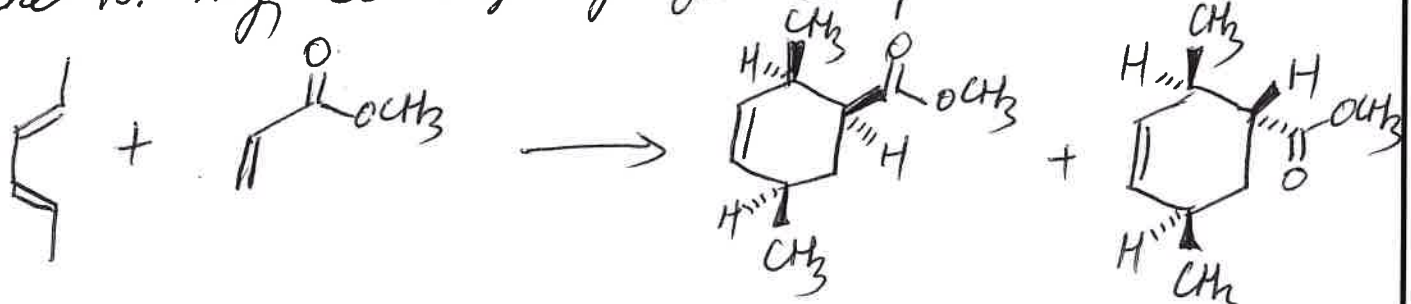
How do diene and dienophile approach one another?



E, E (±)

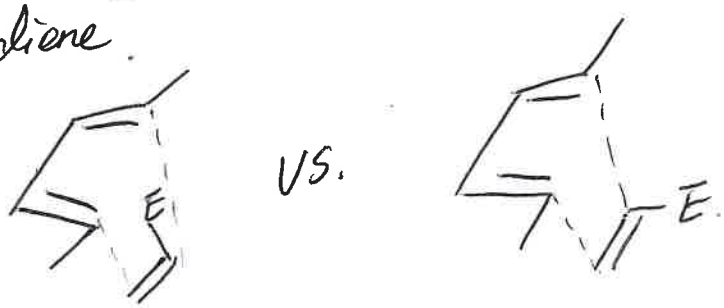


Stereochemical relationships in ring carbons originating from diene vs. ring C's originating from dienophile.



Whence?

Diastereomeric forms arise from different dienophile orientations rel. to diene.



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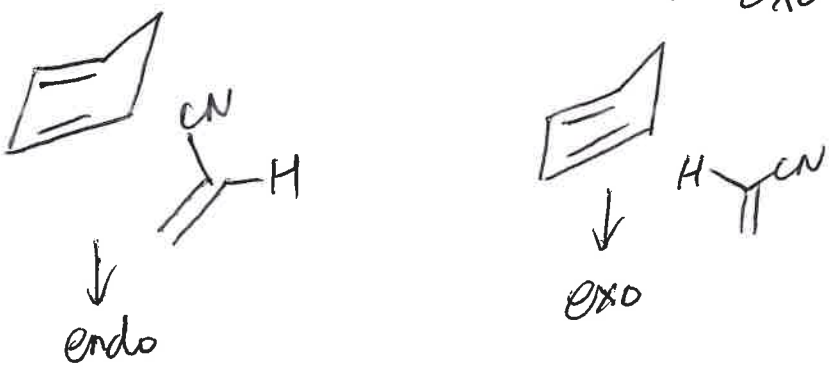
Cyclic diene example

(±) "exo" (±) "endo"



Another distinctive rxn → HX addition