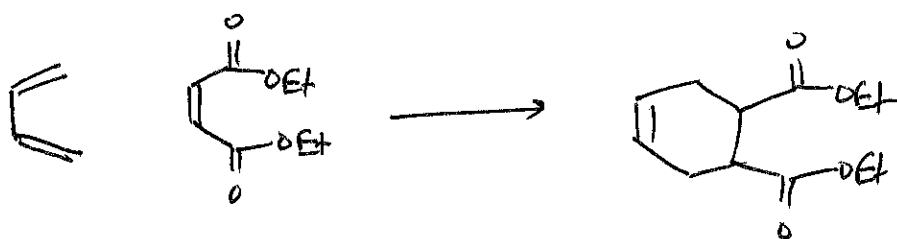


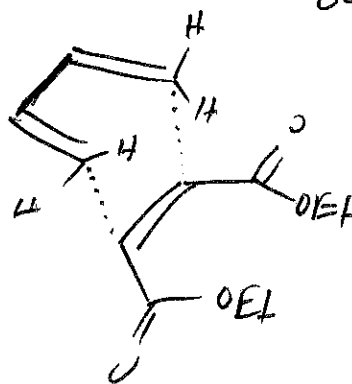
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• Last lecture: conjugated dienes.

- MO's and structural consequences of π -bond delocalization
- Diels Alder reaction



concerted cycloaddition

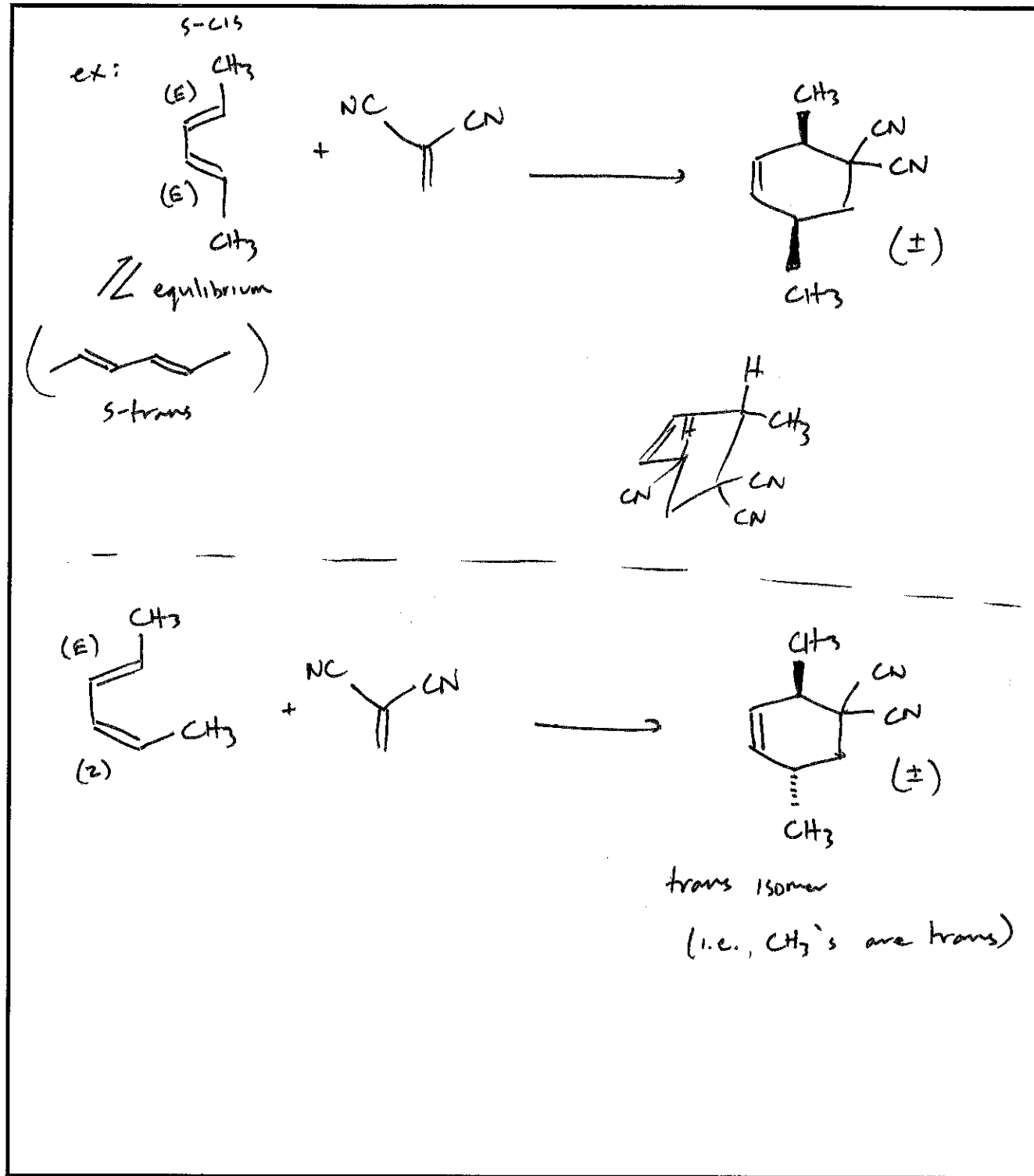


• Stereochemistry of starting material is important and propagates into the product stereochemistry.

- i.e., Diels-Alder rxn is stereospecific

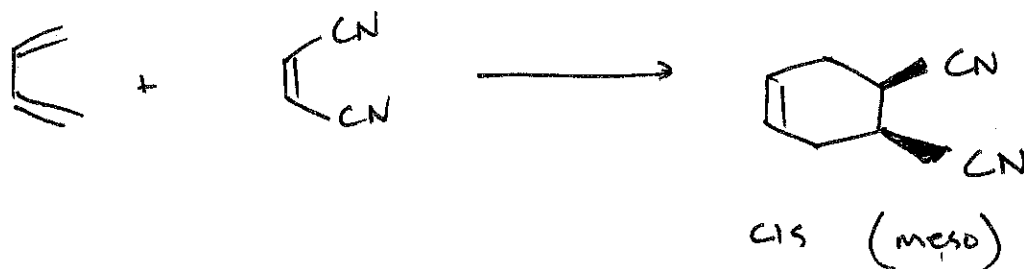
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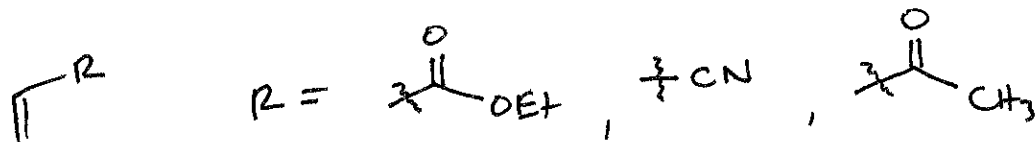
• Now looking at dienophile:



• Many pairs of dienes and dienophiles



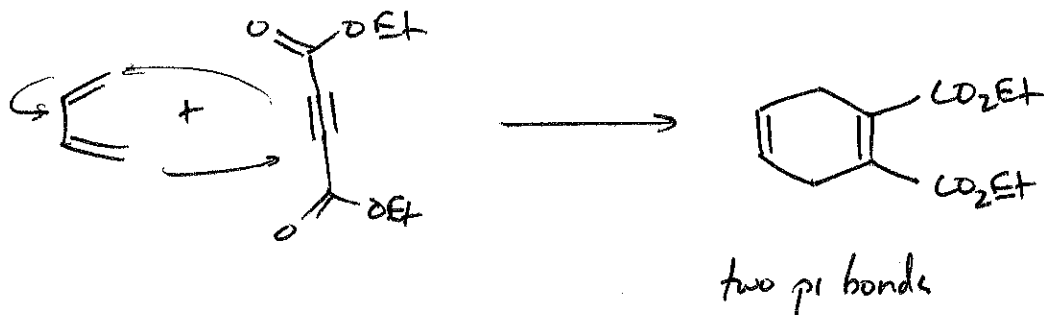
- electron-deficient dienophiles are more reactive



• All of these R groups are electron-withdrawing groups.

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• Electron-deficient alkynes also react well



• Requirements for diene:

- need a conjugated diene in the s-cis conformation

* Good diene: cyclopentadiene



locked in s-cis conformation, so good for Diels-Alder rxn



|||



Norbornene

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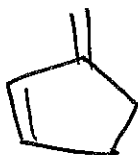
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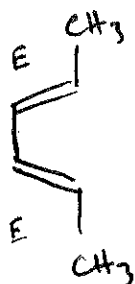
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• Unreactive diene

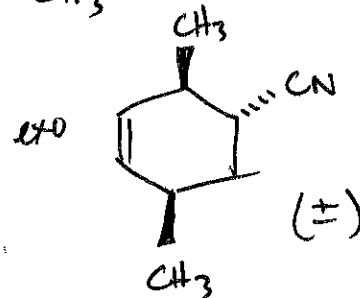
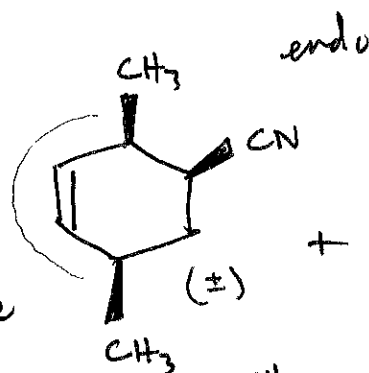


• locked in s-trans
∴ cannot react

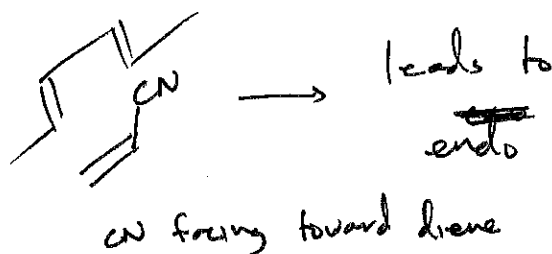
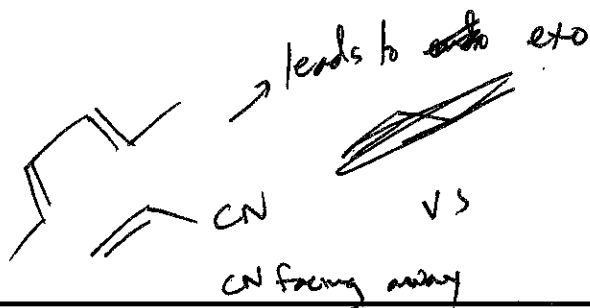
• If both the diene and dienophile bear substituents, the Diels-Alder rxn generates isomeric products



Must be cis due to diene geometry



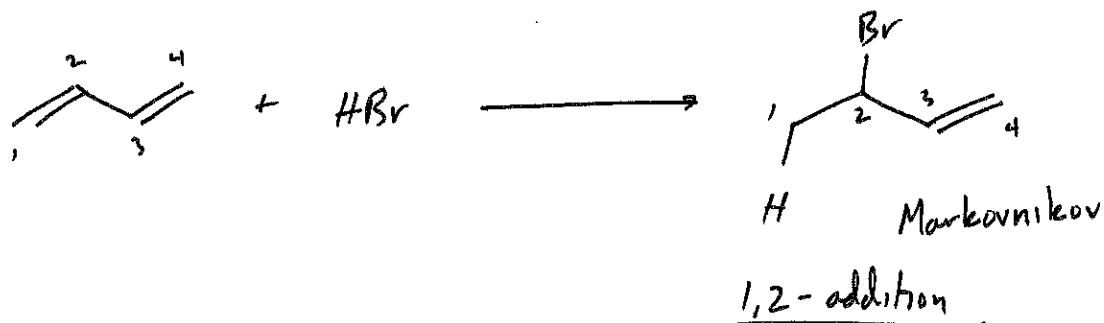
The two diastereomeric products are formed by different approaches of the diene to the dienophile



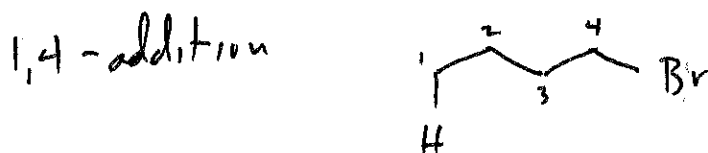
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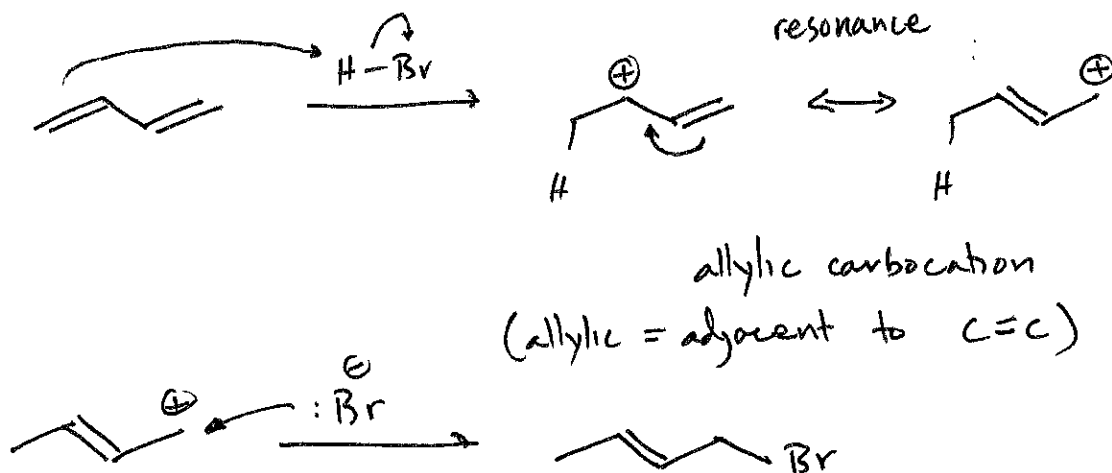
Next reaction: HX addition to diene:



with dienes, an additional product is observed:



Mechanism:



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Allylic carbocation:



Allylic carbocations are similar in stability to 3° carbocations

2° allylic = 3° > 2° > 1° (carbocation stability)