

# Lecture 22

## Michael Addition and Diels Alder



Arthur Michael  
1853-1942



Otto Paul Hermann Diels  
1876-1954



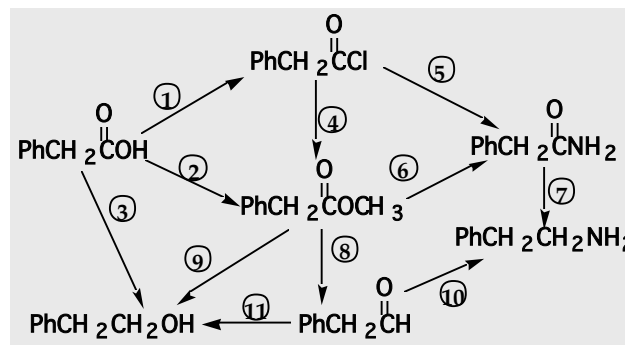
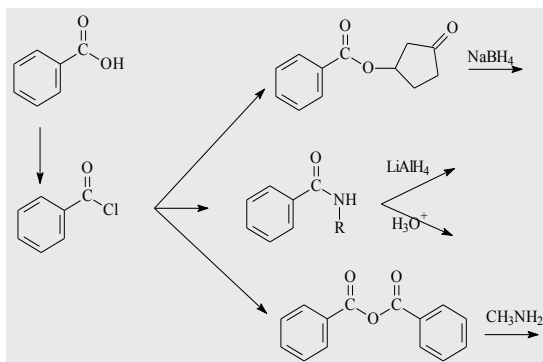
Kurt Alder  
1902-1958

April 7, 2016

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Practice: How far can you expand these web?



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## The Signature Page

**Claisen Condensation:**  $\beta$ -ketoesters

**Dieckmann:** Cyclic  $\beta$ -ketoesters


**Aldol:**  $\alpha$ ,  $\beta$ -unsaturated aldehydes and ketones

**Acetoacetic ester synthesis:** decorated acetones

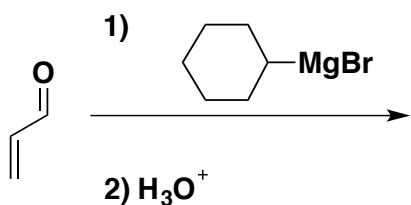
**Malonic ester synthesis:** decorated acetic acids


**Michael Reaction:** 1-5 dicarbonyl compounds

**Grignard Reaction:** Alcohols..., etc.

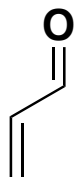
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## $\alpha,\beta$ -unsaturated carbonyl reactivity



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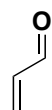
## Direct Addition and Conjugate Addition



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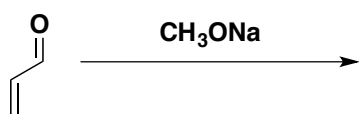
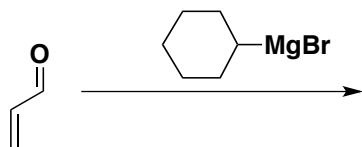
## Energy Landscape



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## Generalization: Direct vs. Conjugate Addition



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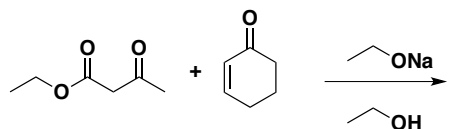
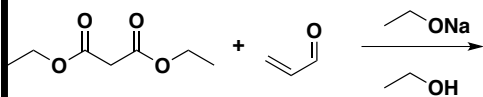
## Michael Reaction

Conjugate addition of an enolate to an  $\alpha,\beta$ -unsaturated carbonyl

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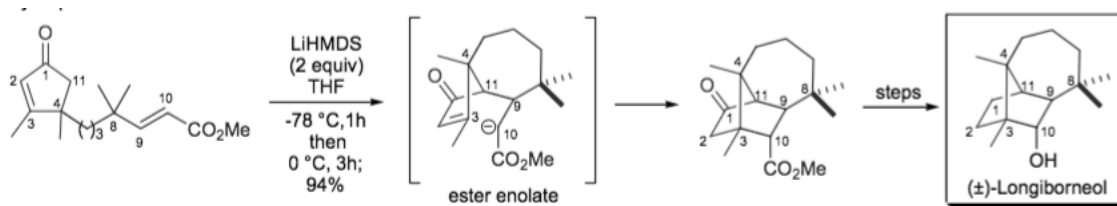
## Two Examples: Predict the Product



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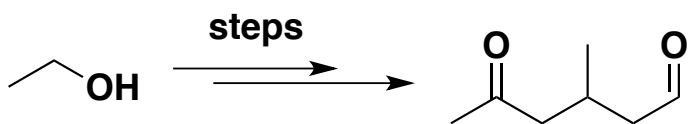
## Example in the Literature



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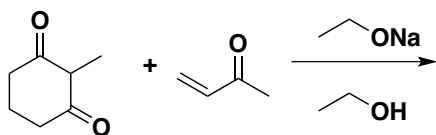
## Practice Problem



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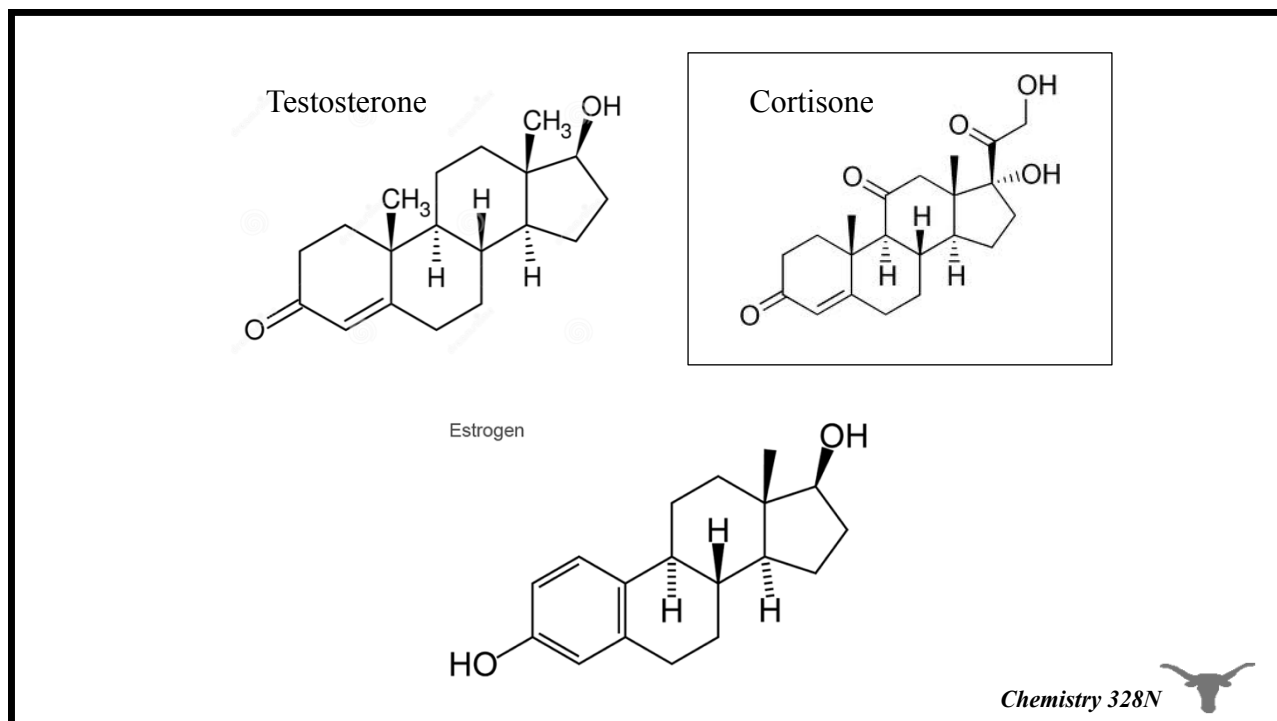
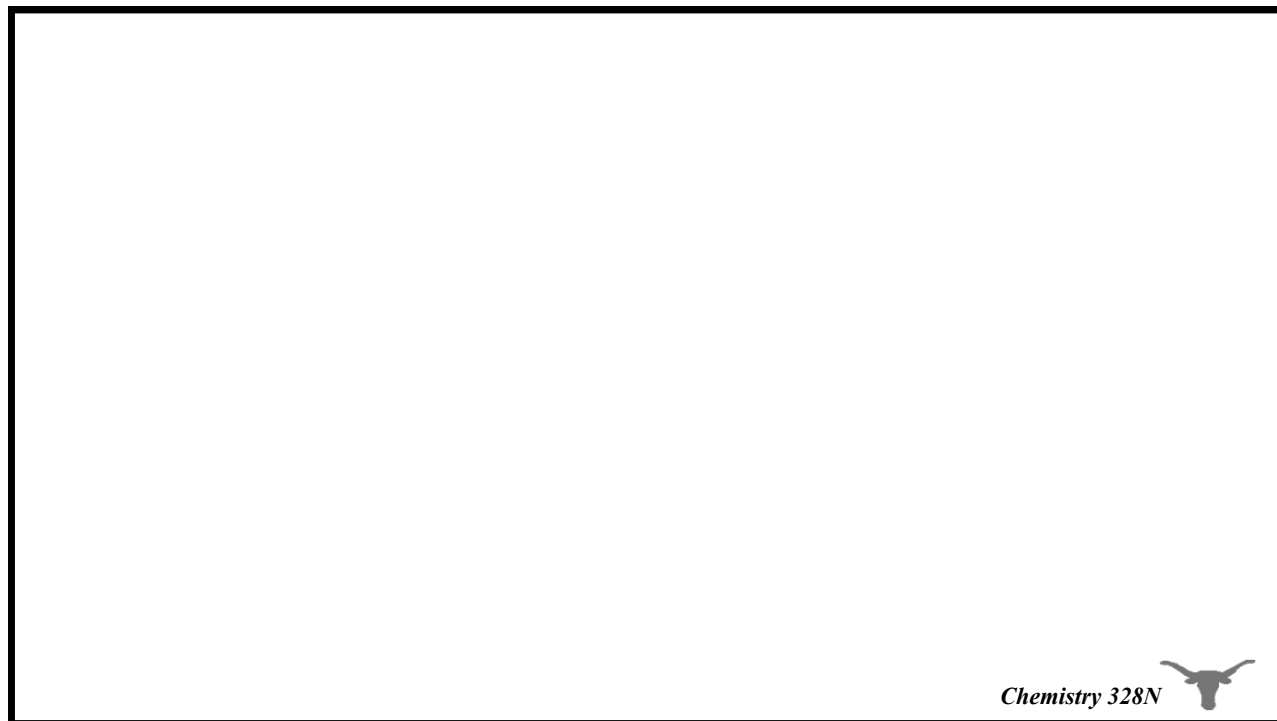


## Robinson Annulation



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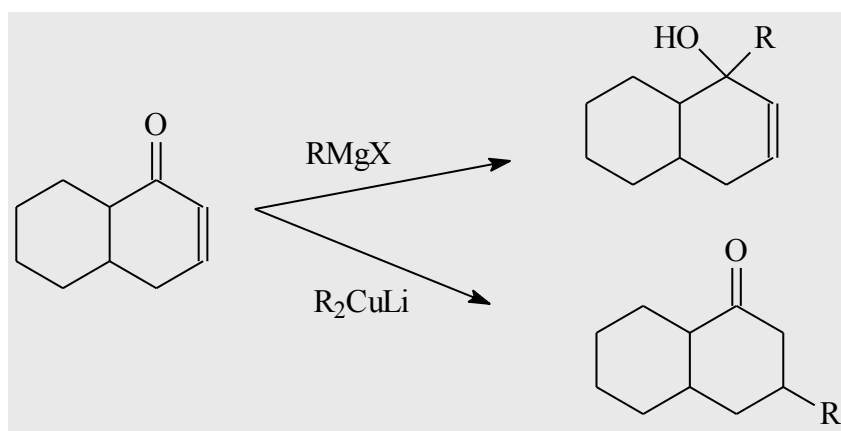
## Gilman Reagents

Gilman reagents undergo conjugate addition to  $\alpha, \beta$ -unsaturated aldehydes/ketones

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## Selectivity!



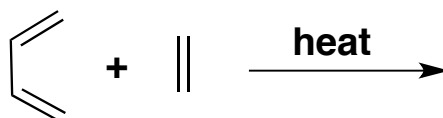
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## Diels-Alder Reaction

- The Diels-Alder reaction is an addition reaction between a 1,3-diene and an alkene (called a dienophile), that forms a new six-membered ring.

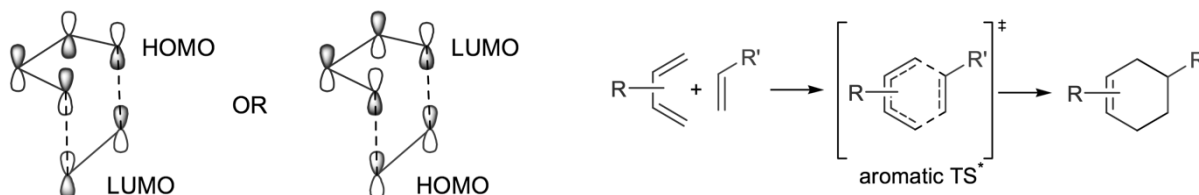


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## All Diels-Alder Reactions

- are initiated by heat; that is, the Diels-Alder reaction is a thermal reaction.
- form new six-membered rings.
- involve breaking three  $\pi$  bonds and making two new  $\sigma$  bonds and one new  $\pi$  bond.
- are concerted; that is, all bonds are broken and new bonds formed in a single step.



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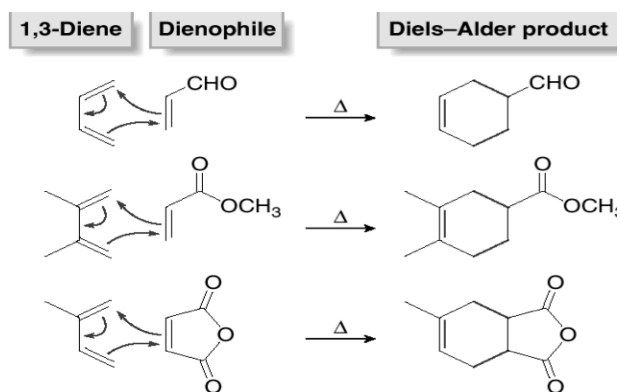


## More Diels-Alder Examples

Diels-Alder works well when:

Dienes are

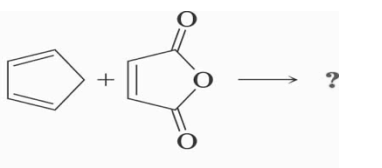
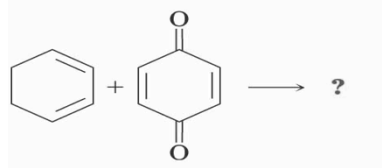
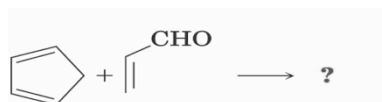
Dienophiles are



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## Predict the Products



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