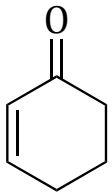
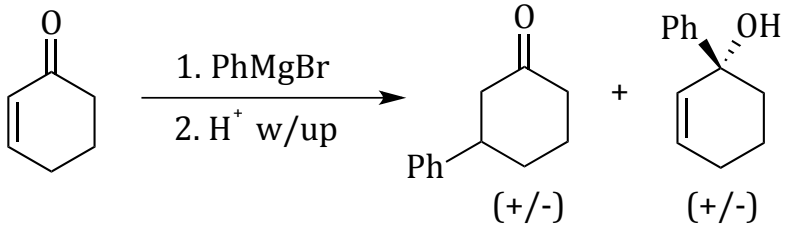
α,β-Unsaturated Carbonyl Compounds:
Not Your Typical Alkenes!

Consider the following compound. What functional groups are present? How can we understand the bonding and reactivity of these types of compounds?



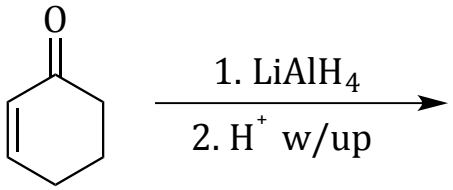
How can we explain the mixture of products observed in the following reaction?

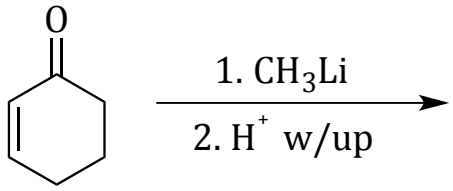


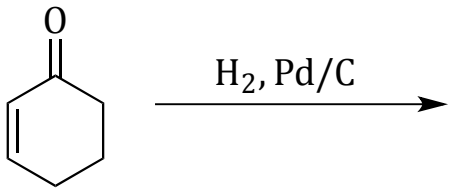
Reading: Section 22.8, 22.10

α,β-Unsaturated Carbonyl Compounds: Reactivity

In each of the following cases, the "usual" products are observed. What are the products and how are they formed?







Reading: Section 22.8-22.10

α,β-Unsaturated Carbonyl Compounds: Hard and Soft Nucleophiles

Different *types* of nucleophiles tend to favor 1,2- or 1,4-addition. *Hard* nucleophiles are small and have high charge density – they favor 1,2-addition. *Soft* nucleophiles are large and have low charge density – they favor 1,4-addition. But why?!

Hard Nucleophiles

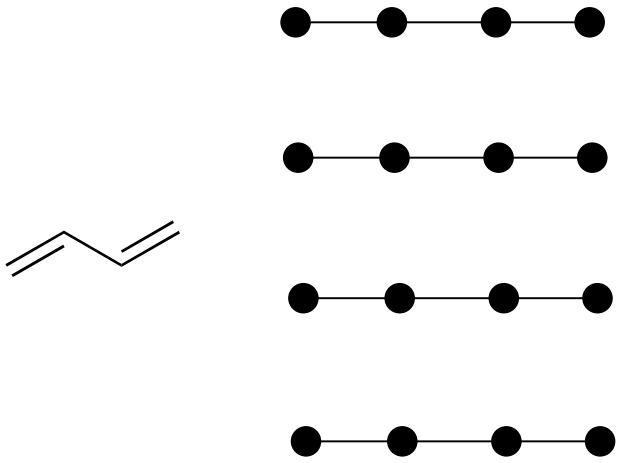
Soft Nucleophiles

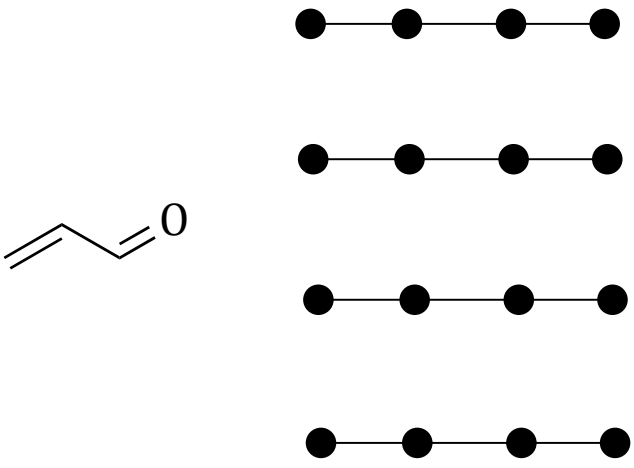
Borderline Nucleophiles

Reading: Section 22.10

α,β-Unsaturated Carbonyl Compounds:
Molecular Orbitals

To understand why both 1,2 and 1,4 addition are possible, let's examine the molecular orbitals of some conjugated systems.



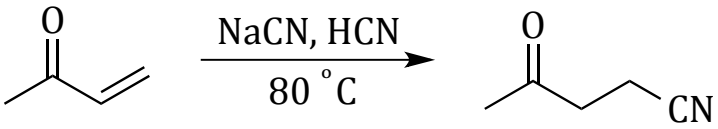


Reading: Section 22.10

α,β-Unsaturated Carbonyl Compounds:
Kinetic vs. Thermodynamic Control

Why do the following sets of reaction conditions yield different products?

(+/-)

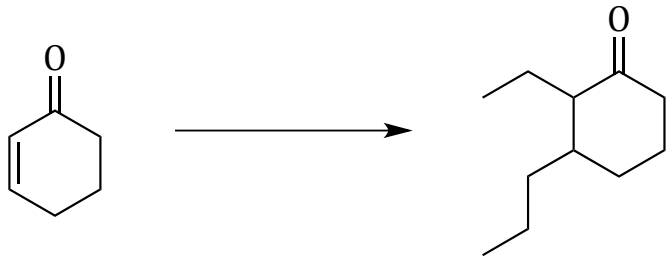


Kinetic control favors 1,2-addition; thermodynamic control favors 1,4-addition.

Reading: Section 22.10

α,β-Unsaturated Carbonyl Compounds:
Tandem Addition/Alkylation

How can we carry out the following transformation?

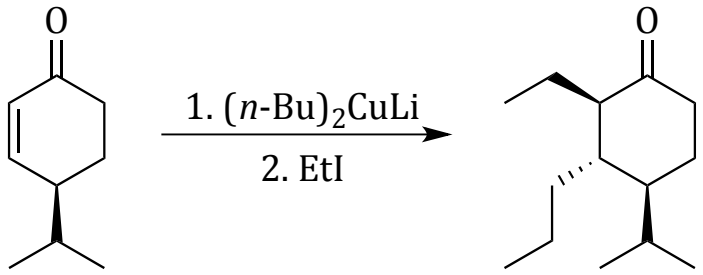


This is an example of a *tandem* reaction. Why are such reactions useful?

What *stereochemistry* do you expect for the product?

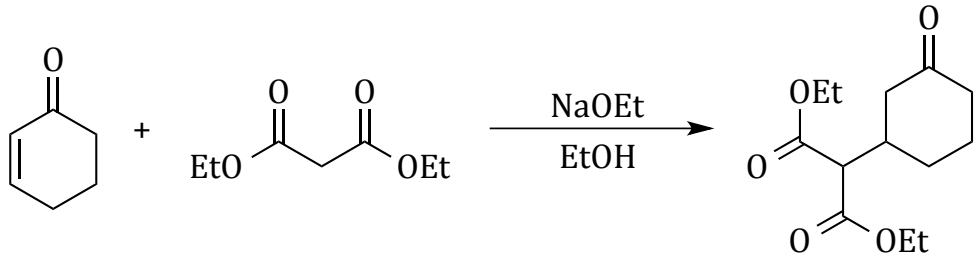
α,β-Unsaturated Carbonyl Compounds:
Stereochemistry of Conjugate Addition

Dialkyl cuprates (and most other soft nucleophiles) are very bulky (why?!). Their bulk makes them very sensitive to steric effects in 1,4-addition. How is that fact being used in the following synthesis?



α,β-Unsaturated Carbonyl Compounds:
The Michael Reaction

Propose a complete curved-arrow mechanism for the following reaction. What's going on here?



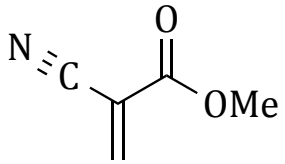
What kinds of enolates can be used in the Michael reaction?

How can you recognize the Michael reaction?

Reading: Section 22.8C

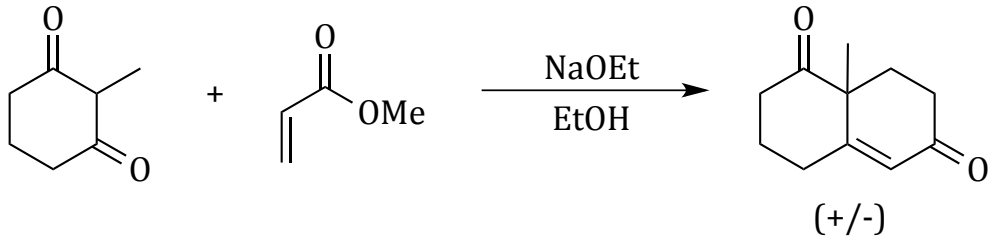
α,β-Unsaturated Carbonyl Compounds:
Krazy Glue

Krazy Glue is methyl cyanoacrylate. How does Krazy Glue work?



Tandem Reactions:
The Robinson Annulation

A remarkable tandem reaction is the *Robinson Annulation*, which is incredibly useful for making 6-membered rings. Provide a complete curved-arrow mechanism:

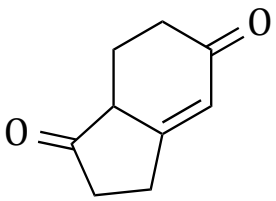


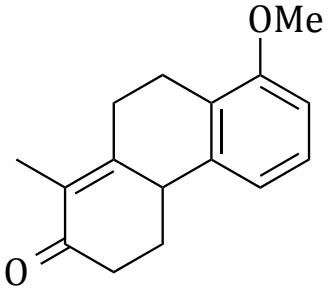
(+/-)

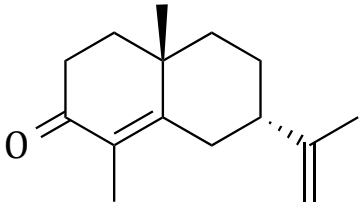
Reading: Section 22.8C

Retrosynthetic Analysis:
The Robinson Annulation

For each of the following *products*, show how it could be formed by the Robinson annulation:







Reading: Section 22.8C