

59-230
Introductory Organic Chemistry I

Dec. 5, 2008

Carbonyl Chemistry

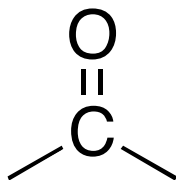
This Lecture:

1. The carbonyl group
2. Nucleophilic addition
3. Nomenclature

Carbonyl Chemistry

The Carbonyl Group

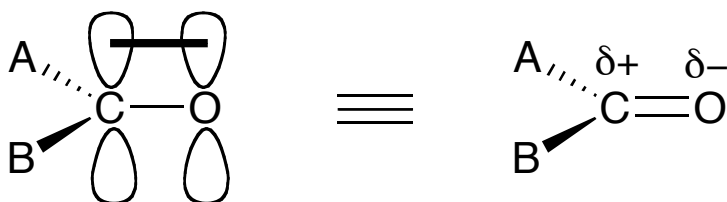
- several different related functional groups
- the key functional group is C=O



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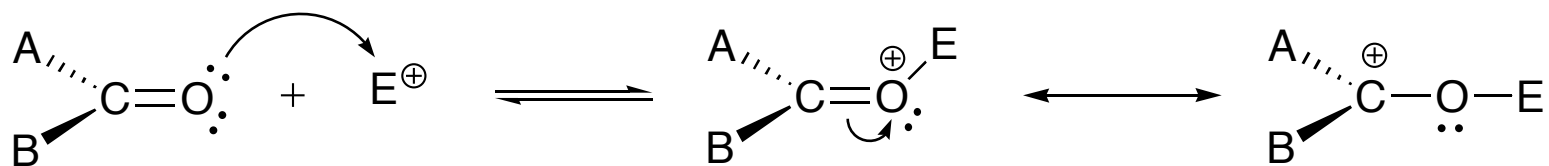
Reactivity of the carbonyl group

- Nucleophilic addition in carbonyls

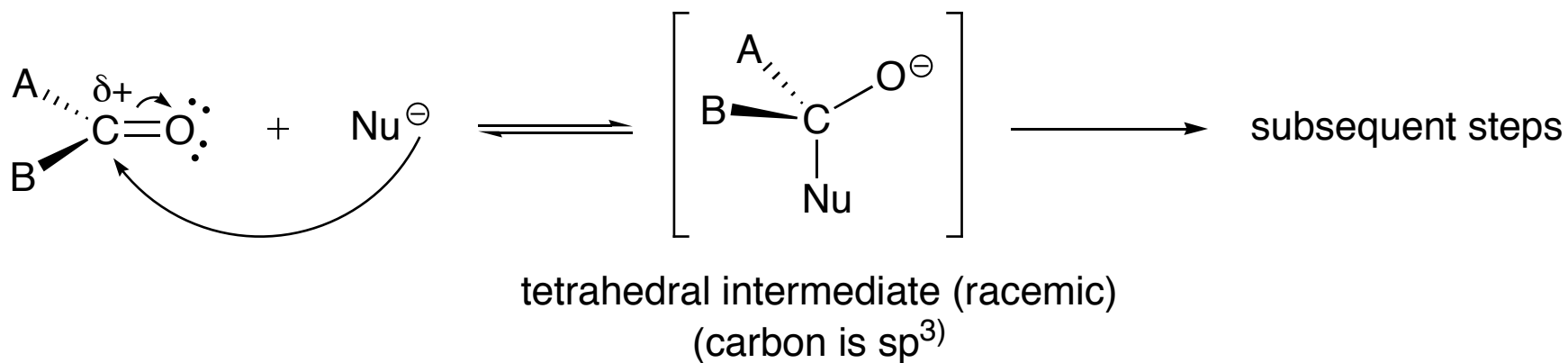


- A, B, C, O are all in the same plane
- both C and O are sp² hybridized
- O is more electronegative than C, therefore C is electrophilic
- electrophiles react at oxygen
- nucleophiles react at carbon

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But more often, and more productively:



- This is called **nucleophilic addition**

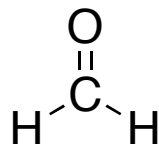
Carbonyl Chemistry

Nomenclature

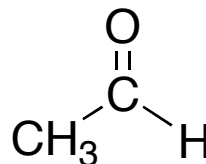
1. Aldehydes

- they have one C atom and one H atom bound to the carbonyl group

e.g.



Methanal
(Formaldehyde)



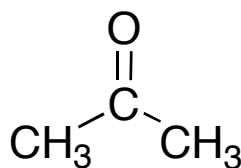
Ethanal
(Acetaldehyde)

Carbonyl Chemistry

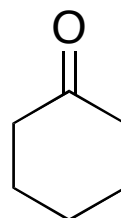
2. Ketones

- they have two C atoms bound to the carbonyl group

e.g.



2-Propanone
(Acetone)



Cyclohexanone

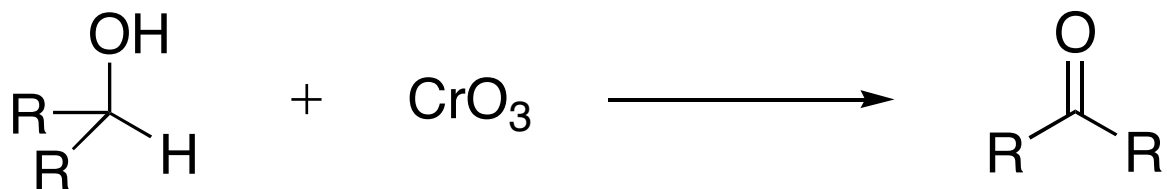
Note: ketones have lower boiling points than alcohols, because they can't self hydrogen bond

Carbonyl Chemistry

Preparation

- we have seen two routes already
 - (i) ozonolysis of alkenes
 - (ii) hydration of alkynes

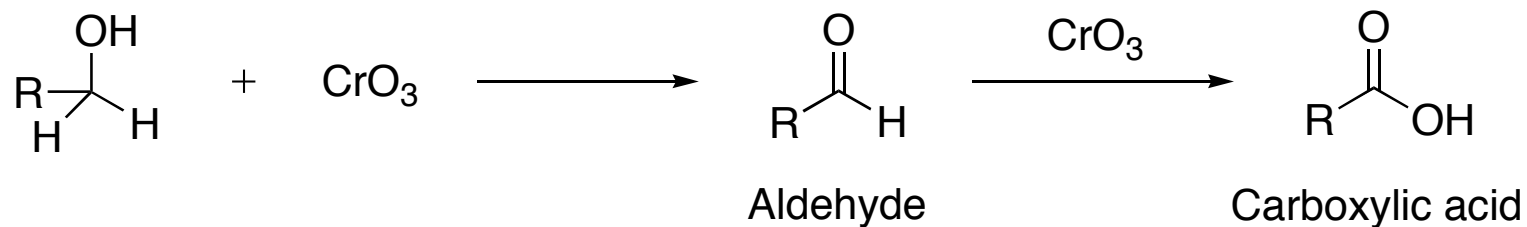
Another route: oxidation of alcohols



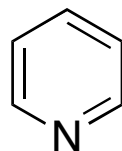
- must have at least 1 H atom on carbinol carbon (1° or 2° alcohol)

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Problem if 1° alcohol is employed:



- Can't stop the oxidation to just get the aldehyde unless the reaction is conducted in the presence of pyridine

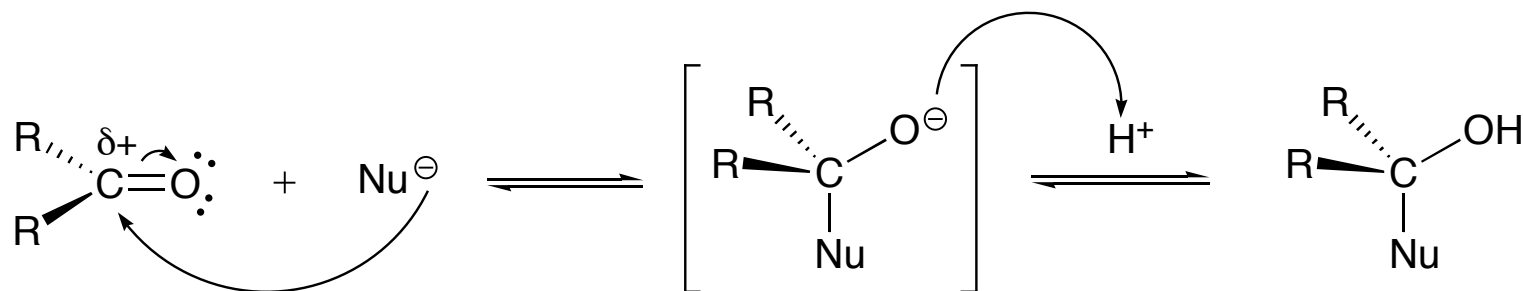


pyridine

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Reactions of Aldehydes and Ketones

Complete mechanism of nucleophilic addition:



- this is in principle an equilibrium
- aldehydes are more reactive than ketones, because aldehydes are less sterically hindered at the carbon atom

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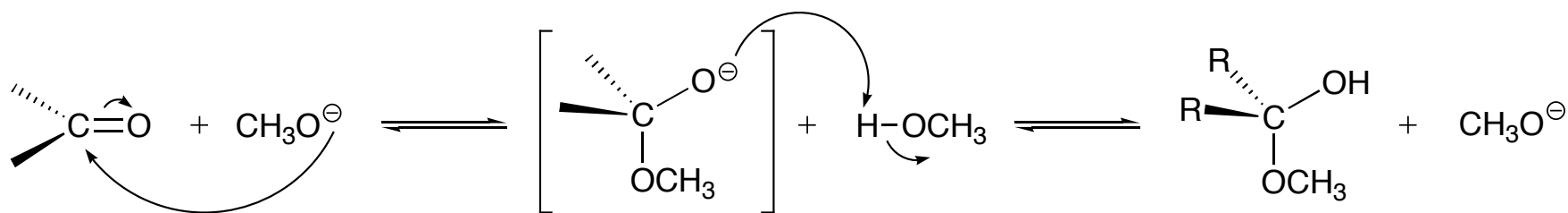
Let's look at some nucleophiles

- alcohols (ROH); let's use CH₃-OH as an example:

What happens? Nothing by itself (not reactive enough)

BUT, something can happen under Acidic or Basic Catalysis

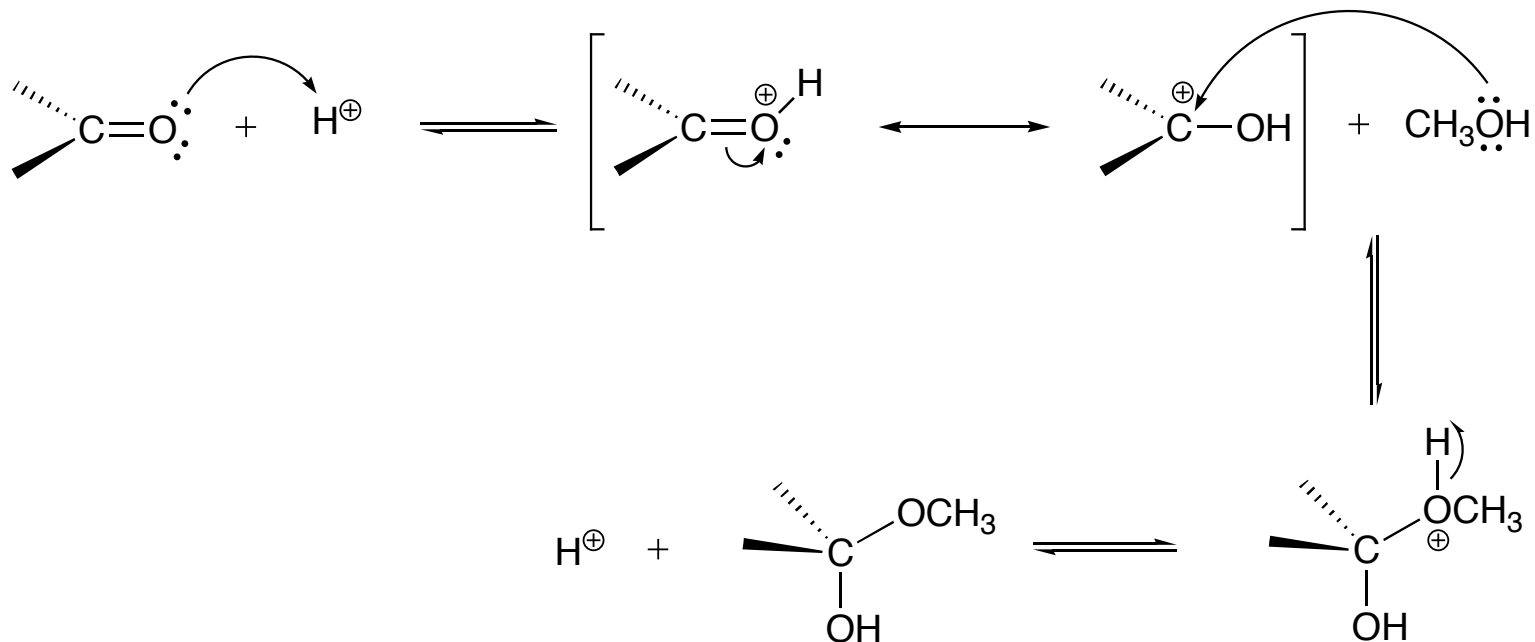
if we add some alkoxide (RO[⊖]) e.g. CH₃O[⊖] in CH₃OH



- for every molecule of CH₃O⁻ used, it is regenerated (*i.e.* true catalyst)
- the product is called a “hemiacetal”

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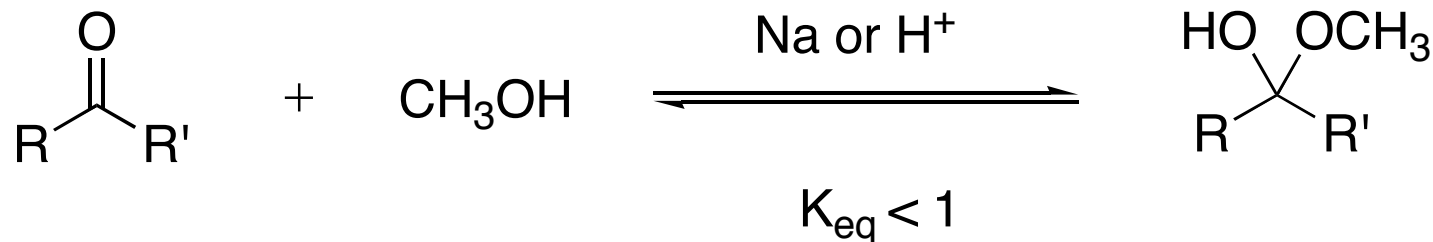
Acid Catalyzed Mechanism:



- again, truly catalytic in H^+
- CH_3OH itself is now the nucleophile

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Problem: the K_{eq} isn't quite favourable (<1)



- Therefore, can't isolate the hemiacetal, except for cyclic cases:

