

CH 318 N

LECTURE 11

Textbook Assignment: Chapter 16

Homework (for credit): POW 5 posted

Today's Topics: Aldehydes & Ketones

Notice & Announcements:

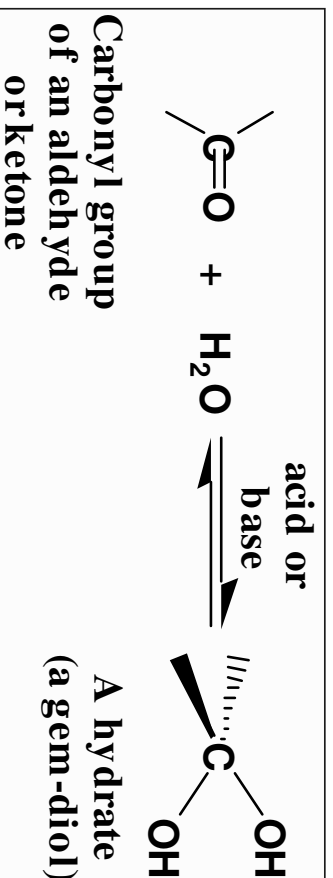
ORGANIC LECTURE SERIES

Aldehydes And Ketones

Addition of H₂O to Carbonyls

Addition of water (**hydration**) to the carbonyl group of an aldehyde or ketone gives a geminal diol, commonly referred to a gem-diol

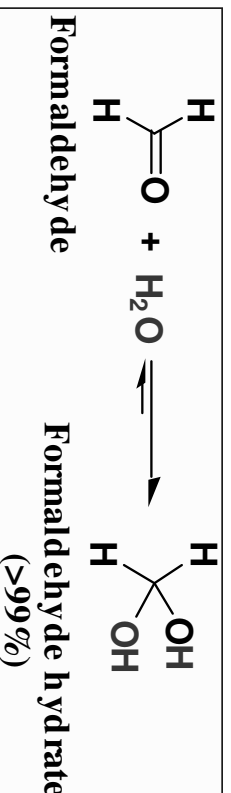
– gem-diols are also referred to as **hydrates**



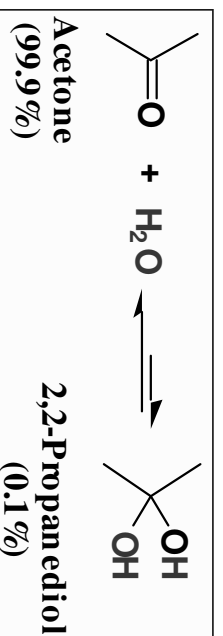
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Addition of H₂O to Carbonyls

– when formaldehyde (*g*) is dissolved in water at 20 °C, the carbonyl group is more than 99% hydrated



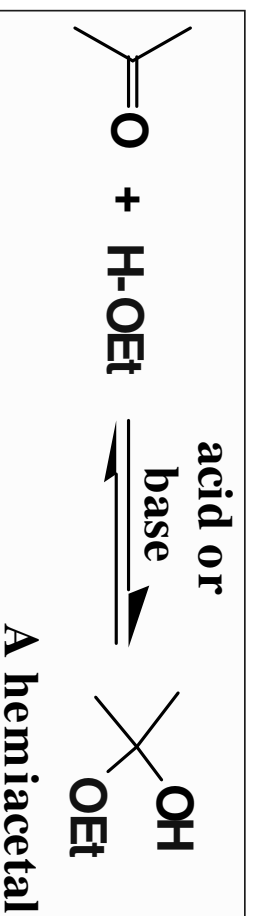
– the equilibrium concentration of a hydrated ketone is considerably smaller



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Addition of Alcohols to Carbonyls

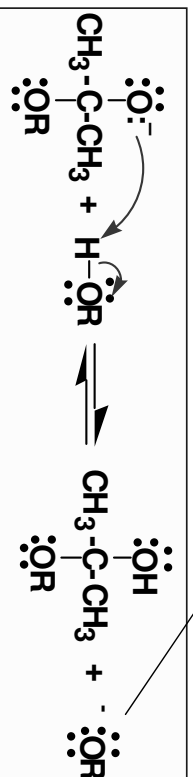
- Addition of one molecule of alcohol to the C=O group of an aldehyde or ketone gives a hemiacetal
- **Hemiacetal:** a molecule containing an -OH and an -OR or -OAr bonded to the same carbon



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Formation of a hemiacetal-- base catalyzed

- **Step 1:** proton transfer from HOR gives an alkoxide
- $$\text{B:}^- + \text{H-}\ddot{\text{O}}\text{R} \xrightleftharpoons{\text{fast and reversible}} \text{B-H} + \text{:}\ddot{\text{O}}\text{R}^-$$
- **Step 2:** attack of RO⁻ on the carbonyl carbon
- $$\text{CH}_3\text{-C(=O)-CH}_3 + \text{:}\ddot{\text{O}}\text{-R}^- \rightleftharpoons \text{CH}_3\text{-C(O}^-\text{)(OR)-CH}_3$$
- **Step 3:** proton transfer from the alcohol to O⁻ gives the hemiacetal and generates a new base catalyst



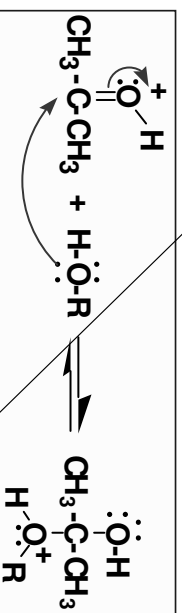
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Formation of a hemiacetal --acid catalyzed

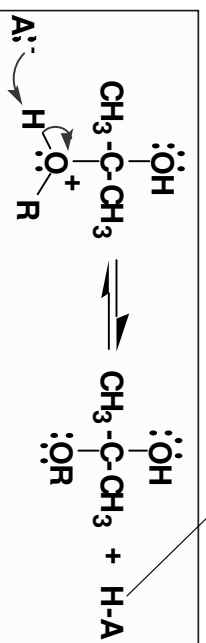
Step 1: proton transfer to the carbonyl oxygen



Step 2: attack of ROH on the carbonyl carbon



Step 3: proton transfer from the oxonium ion to A⁻ gives the hemiacetal and generates a new acid catalyst

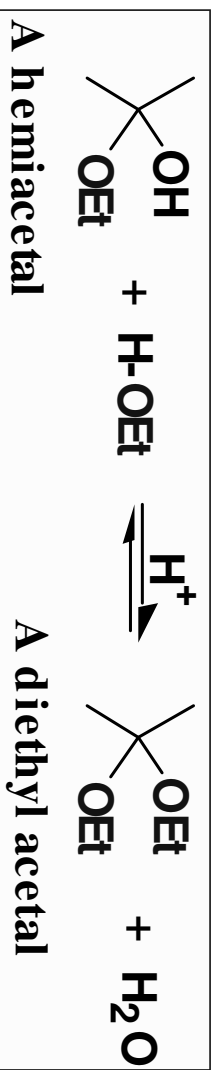


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Addition of Alcohols to Carbonyls

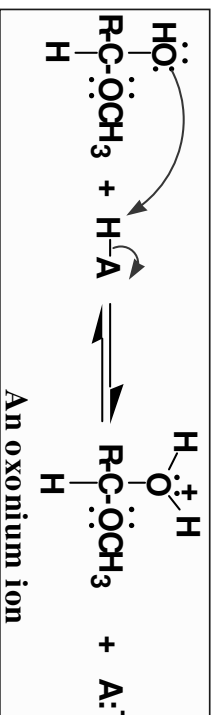
- Hemiacetals react with alcohols to form acetals

Acetal: a molecule containing two -OR or -OAr groups bonded to the same carbon

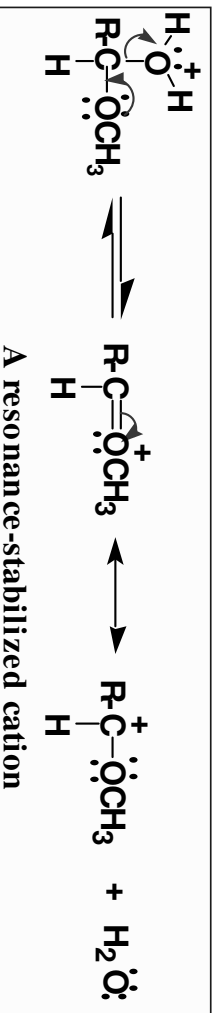


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Step 1: proton transfer from HA gives an oxonium ion

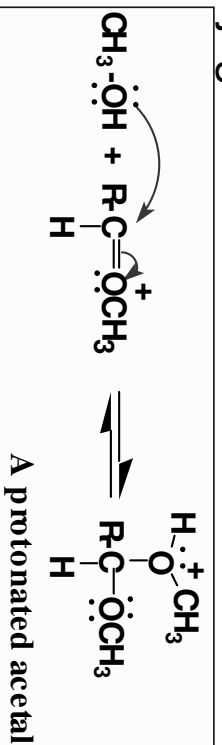


Step 2: loss of water gives a resonance-stabilized cation

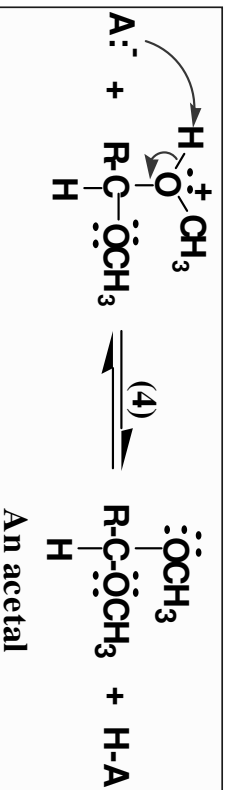


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Step 3: reaction of the cation (an electrophile) with methanol (a nucleophile) gives the conjugate acid of the acetal



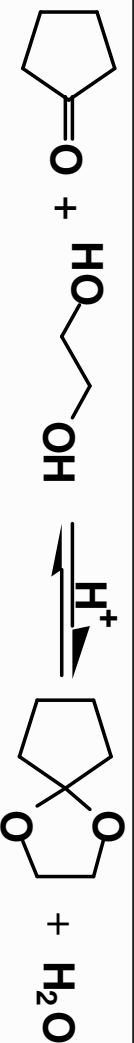
Step 4: proton transfer to A⁻ gives the acetal and generates a new acid catalyst



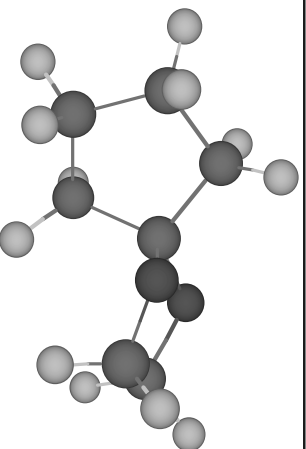
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Addition of Alcohols to Carbonyls

- with ethylene glycol and other glycols, the product is a five-membered cyclic acetal
- this a method of “protecting” ketones



Cyclic acetal



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Dean-Stark Trap

ORGANIC LECTURE SERIES

$$\text{C}-\text{O} + 2 \text{ROH} \rightleftharpoons \text{C} \begin{matrix} \text{OR} \\ \text{OR} \end{matrix} + \text{H}_2\text{O} \quad \xrightarrow{\text{H}^+}$$

Aldehyde Alcohol or ketone

Acetal

Vapor rising toward condenser contains 91% benzene and 9% water

Reaction takes place in the benzene layer

Heat source

Water-jacket condenser

Condensing vapor

Cold H₂O

Dean-Stark trap

Upper layer contains 99.94% benzene and 0.06% water

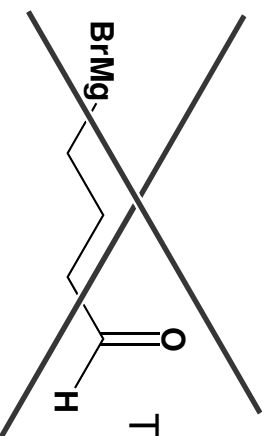
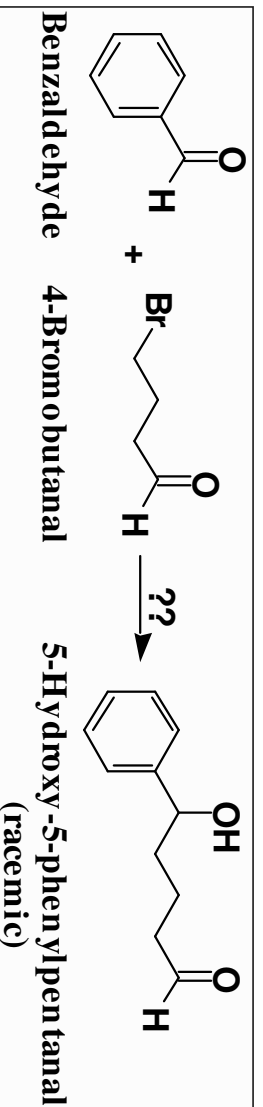
Lower layer contains 0.07% benzene and 99.93% water

Stopcock to withdraw lower layer

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Acetals as Protecting Groups

- How to bring about a Grignard reaction between these compounds:

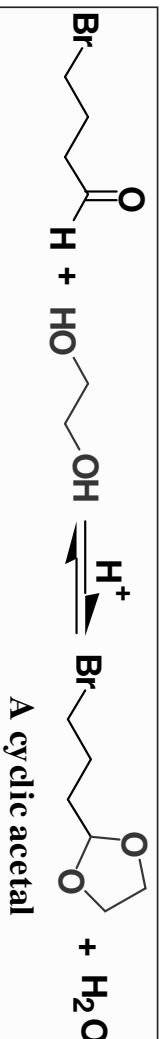


This Grignard cannot be made!!

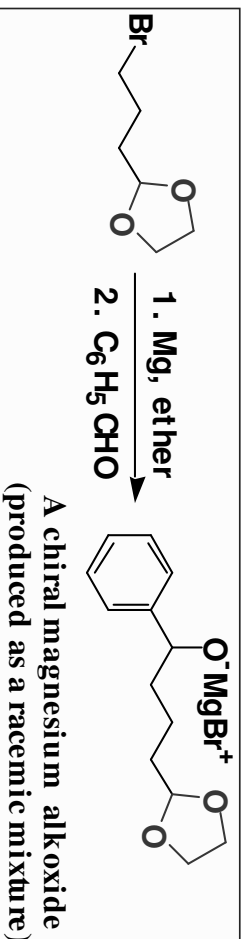
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Acetals as Protecting Groups

- a Grignard reagent prepared from 4-bromobutanal will self-destruct (**decompose**).
 - first protect the -CHO group as an acetal:



- then prepare the Grignard reagent:



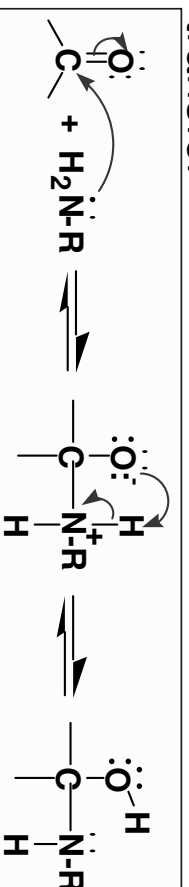
- hydrolysis (not shown) gives the target molecule

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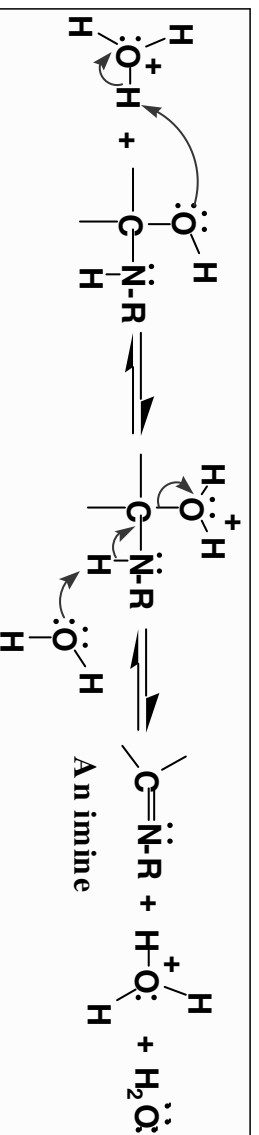
Addition of Nitrogen Nucleophiles

Formation of an imine occurs in two steps

Step 1: carbonyl addition followed by proton transfer



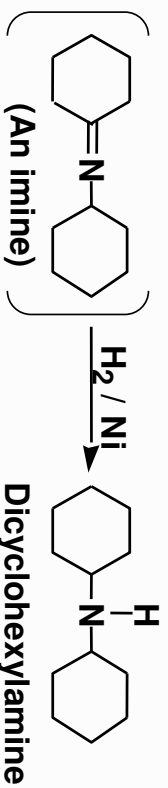
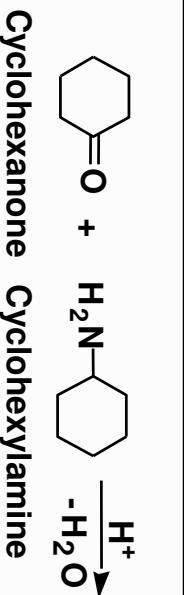
Step 2: loss of H₂O and proton transfer to solvent



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Addition of Nitrogen Nucleophiles

– a value of imines is that the carbon-nitrogen double bond can be reduced to a carbon-nitrogen single bond

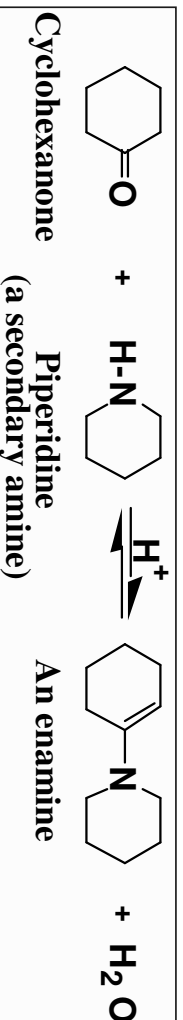


Does not have to be isolated

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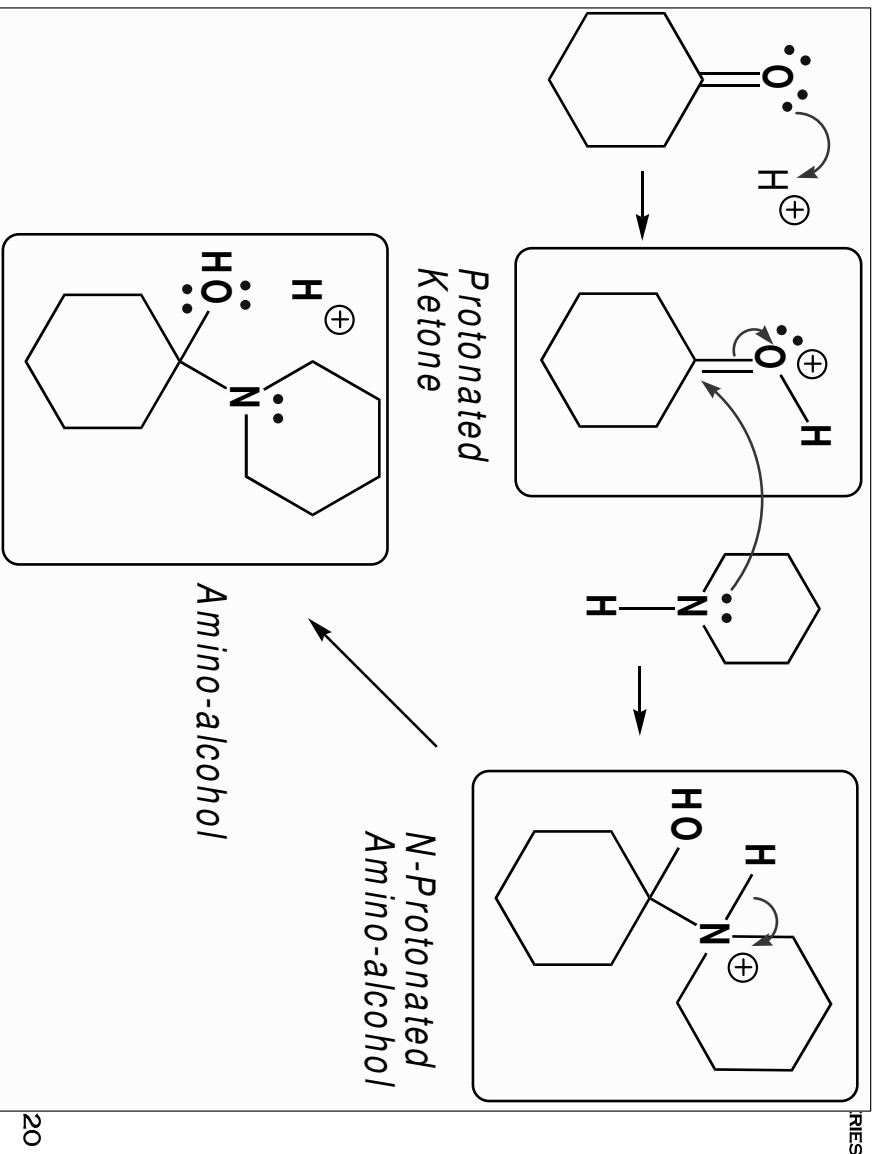
Addition of Nitrogen Nucleophiles

- Secondary amines react with the C=O group of aldehydes and ketones to form **enamines (alkene and amine)**

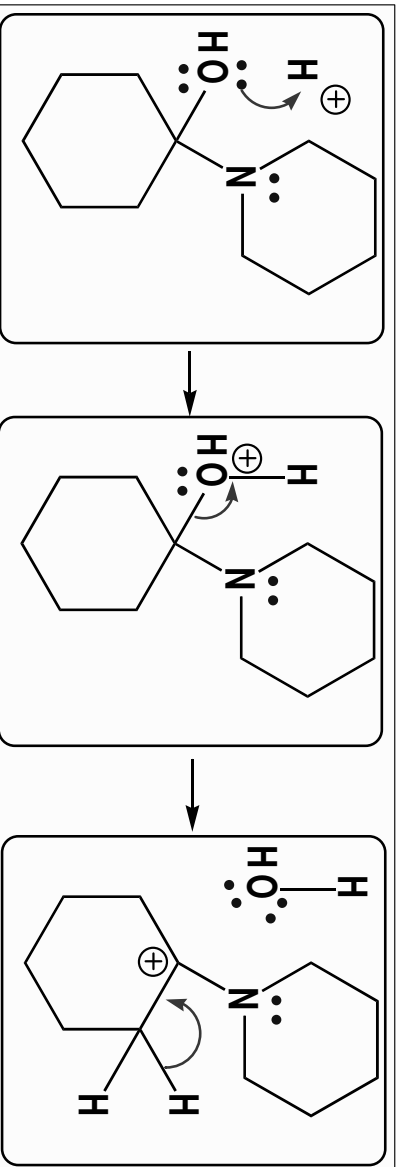


– the mechanism of enamine formation involves formation of a tetrahedral carbonyl addition compound followed by its acid-catalyzed dehydration

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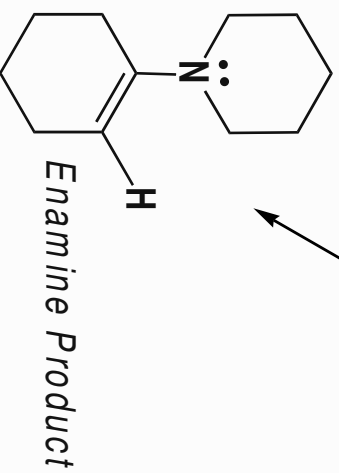
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Amino-alcohol

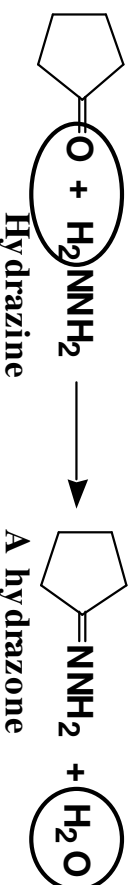
*O-Protonated
Amino-alcohol*

2° Carbocation



Addition of Nitrogen Nucleophiles

– the carbonyl group of aldehydes and ketones reacts with hydrazine and its derivatives in a manner similar to its reactions with 1° amines



Reagent, $\text{H}_2\text{N}\cdot\text{N}\cdot\text{R}$ Name of Reagent Name of Derivative Formed

$\text{H}_2\text{N}\cdot\text{N}\cdot\text{OH}$ Hydroxylamine Oxime

$\text{H}_2\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ Phenylhydrazine Phenylhydrazone

$\text{H}_2\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ 2,4-Dinitrophenyl-
hydrazine 2,4-Dinitrophenylhydrazone

$\text{H}_2\text{N}\cdot\text{N}\cdot\text{NHCNH}_2$ Semicarbazide Semicarbazone

Acidity of α -Hydrogens

Hydrogens alpha to a carbonyl group are more acidic than hydrogens of other hydrocarbons (e.g. alkanes, alkenes, aromatic). The acidity is measured as K_a

