

Organic chemistry for
nonmajor students
Chem 233

Chapter 9

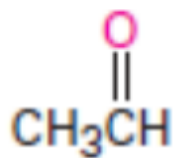
Aldehydes and Ketones



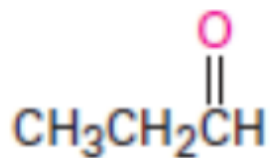
9.1 Naming Aldehydes and Ketones



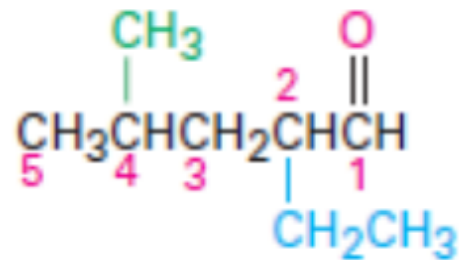
Aldehydes are named by replacing the terminal **-e** of the corresponding alkane name with **-al**.



Ethanal
(acetaldehyde)



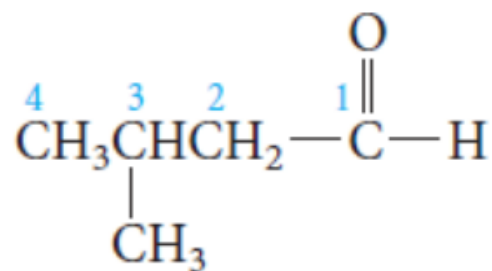
Propanal
(propionaldehyde)



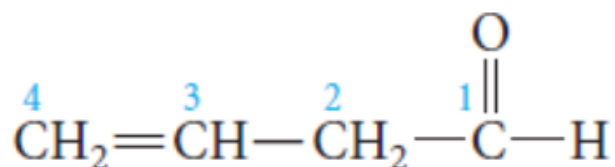
2-Ethyl-4-methylpentanal



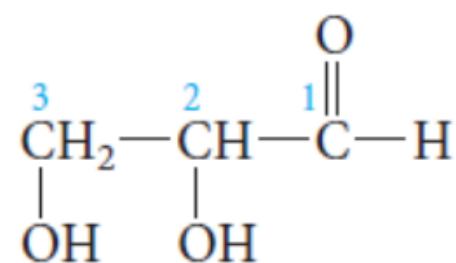
Aldehydes and ketones have priority to have the **suffix** over all functional groups except carboxylic group.



3-methylbutanal



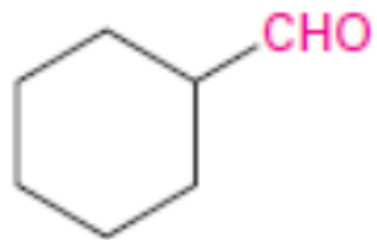
3-butenal



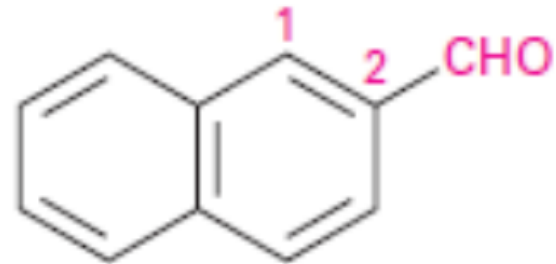
2,3-dihydroxypropanal
(glyceraldehyde)



For cyclic aldehydes in which the -CHO group is directly attached to a ring, the suffix *-carbaldehyde* is used.

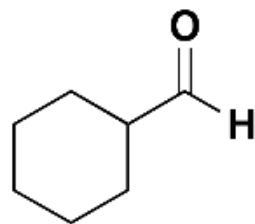


Cyclohexanecarbaldehyde

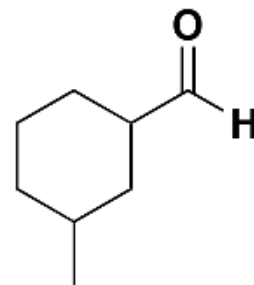


2-Naphthalenecarbaldehyde

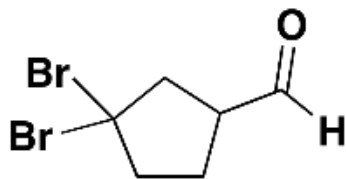




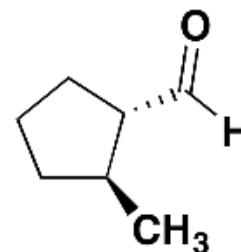
cyclohexanecarbaldehyde



3-methylcyclohexanecarbaldehyde



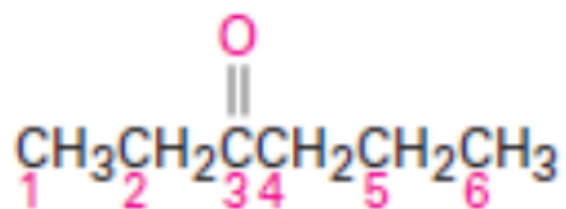
2,2-dibromocyclopentanecarbaldehyde



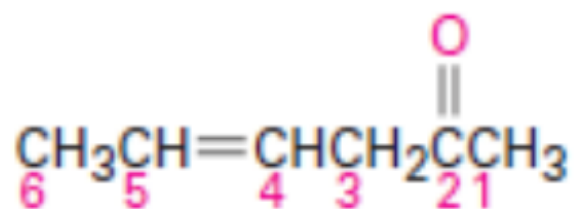
trans-2-methylcyclopentanecarbaldehyde



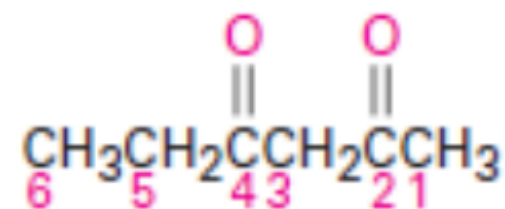
Ketones are named by replacing the terminal *-e* of the corresponding alkane name with *-one*.



3-Hexanone
(New: Hexan-3-one)

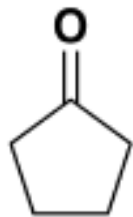


4-Hexen-2-one
(New: Hex-4-en-2-one)

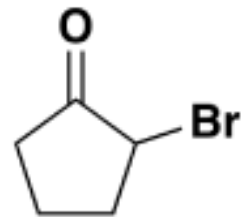


2,4-Hexanedione
(New: Hexane-2,4-dione)

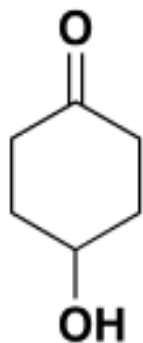




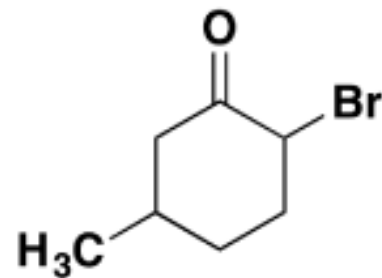
cyclopentanone



2-bromocyclopentanone

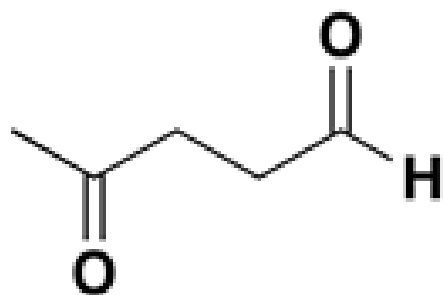


4-hydroxycyclohexanone

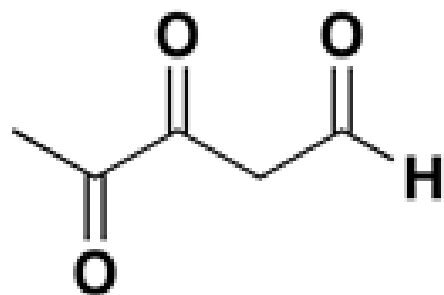


2-bromo-5-methylcyclohexanone

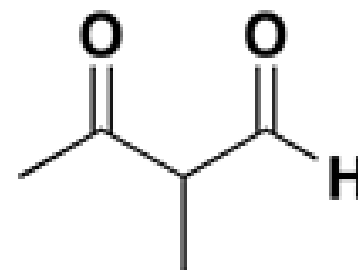




4-oxopentanal



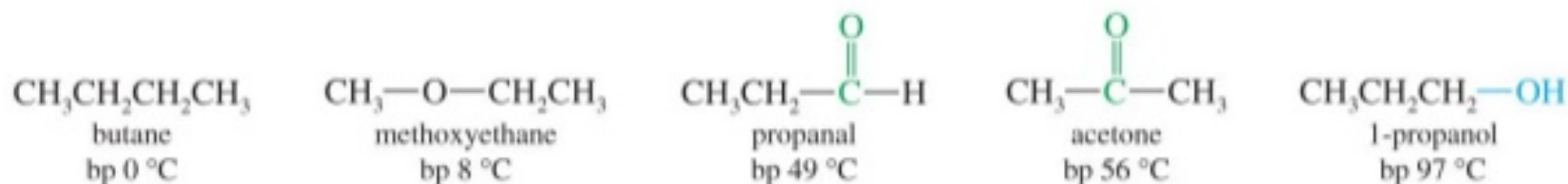
3,4-dioxopentanal



2-methyl-3-oxo-butanal



Boiling Points



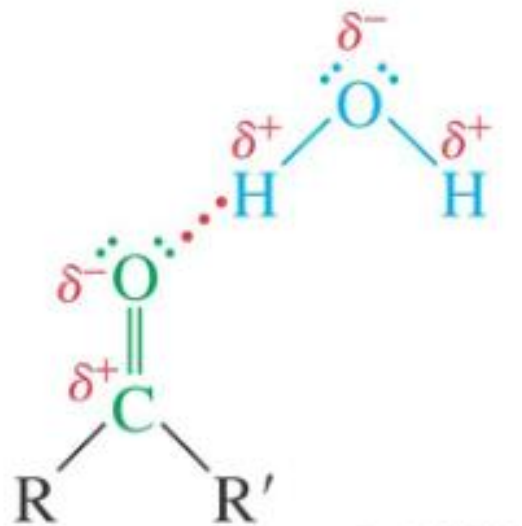
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- Ketones and aldehydes are more polar, so they have a higher boiling point than comparable alkanes or ethers.
- They cannot hydrogen-bond to each other, so their boiling point is lower than comparable alcohol.



Solubility in water

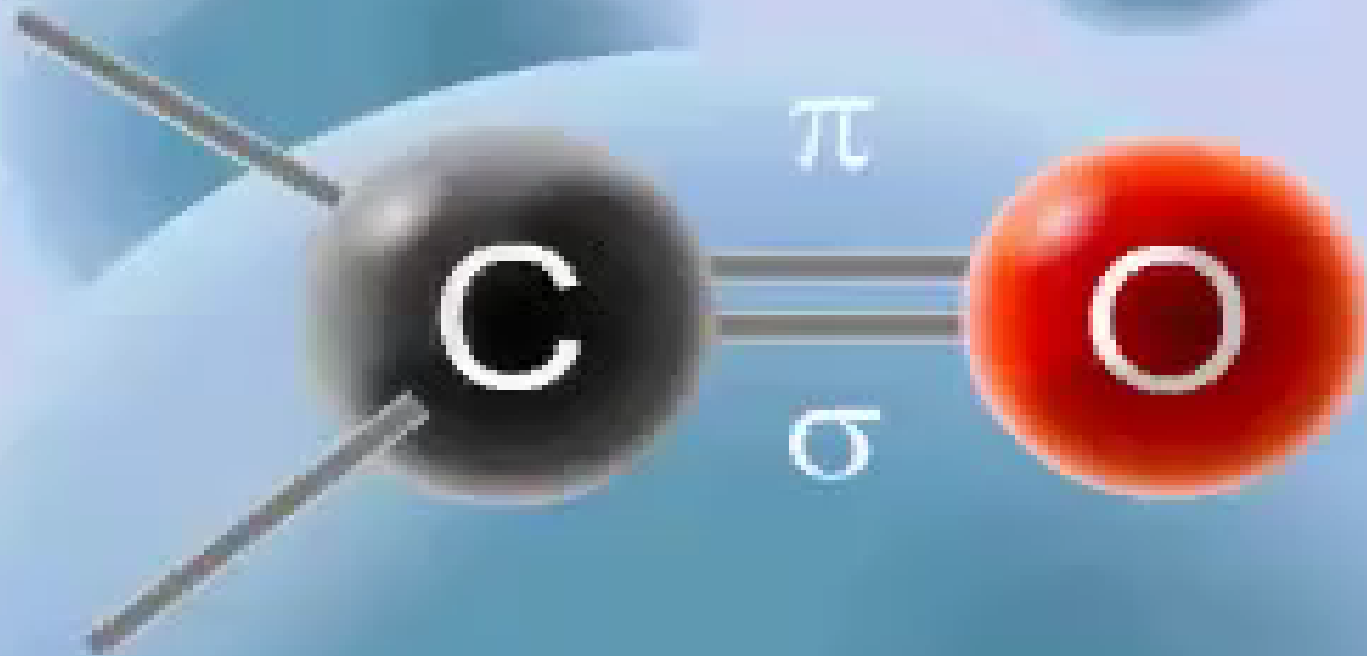
Ketones and aldehydes have similar solubility in water as alcohols because they can make hydrogen bonding with water.



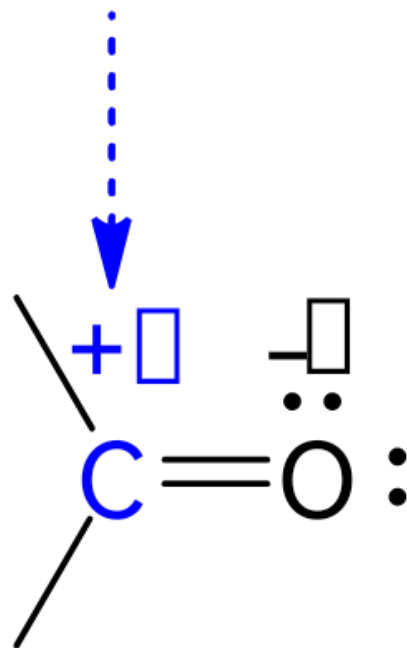
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9.5 The Carbonyl Group





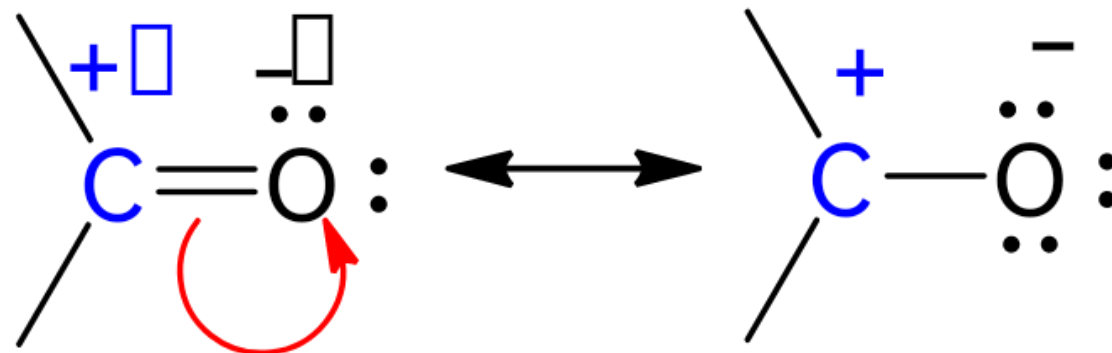
Electrophilic center



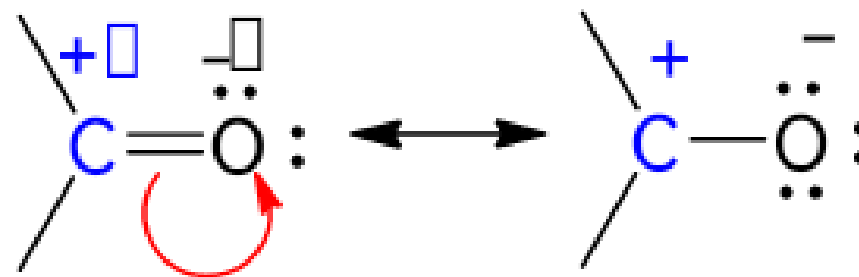
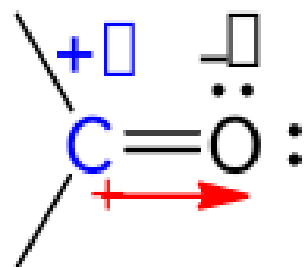
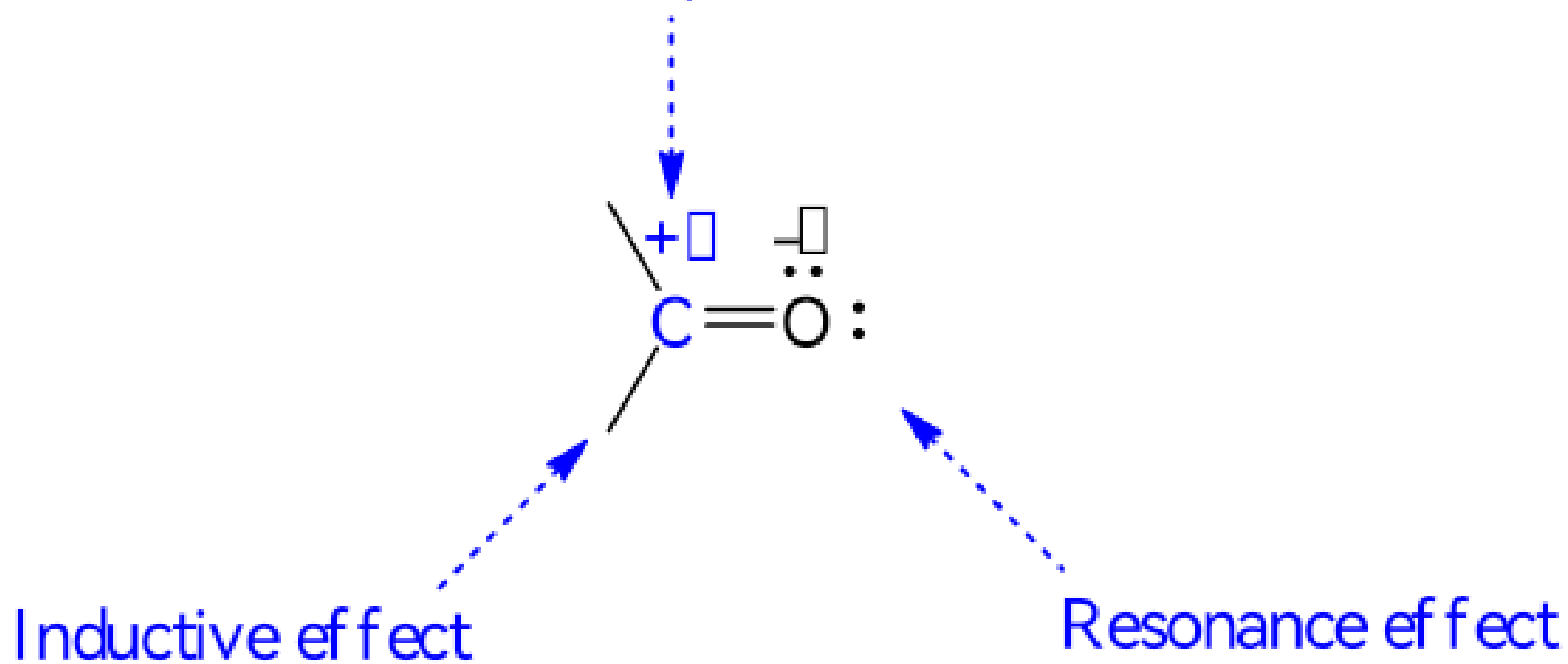
Inductive effect



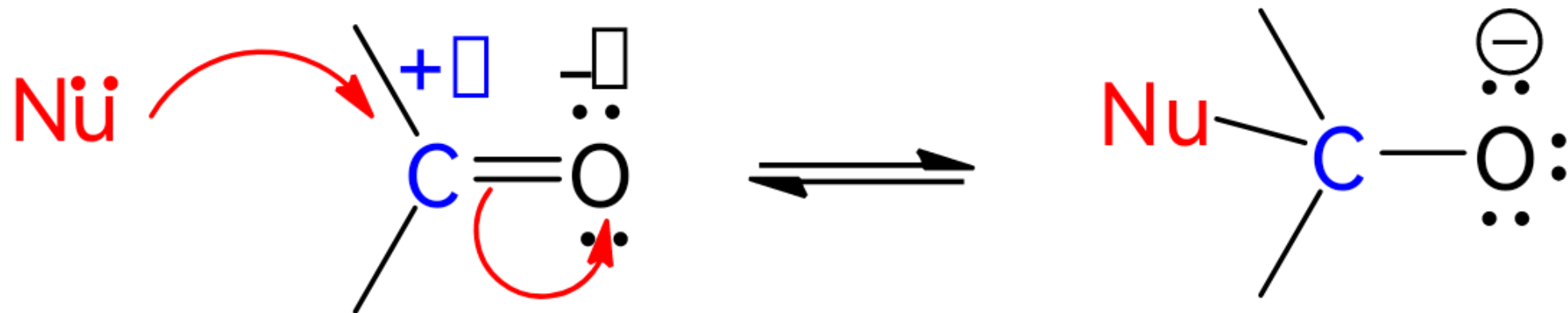
Resonance effect



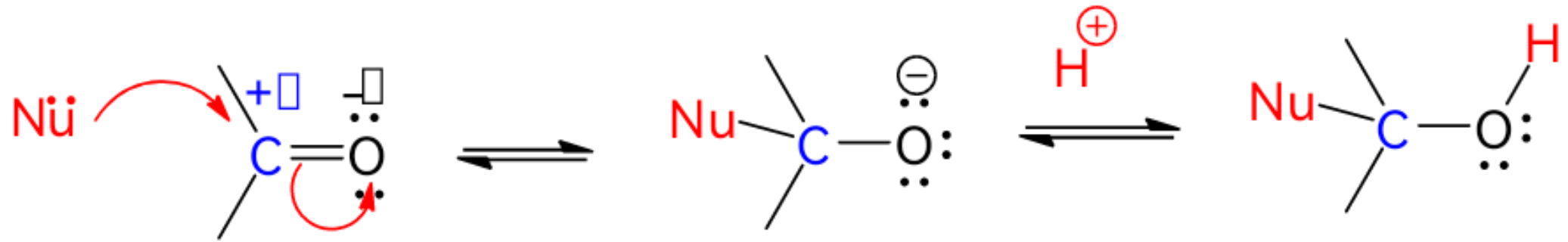
Electrophilic center

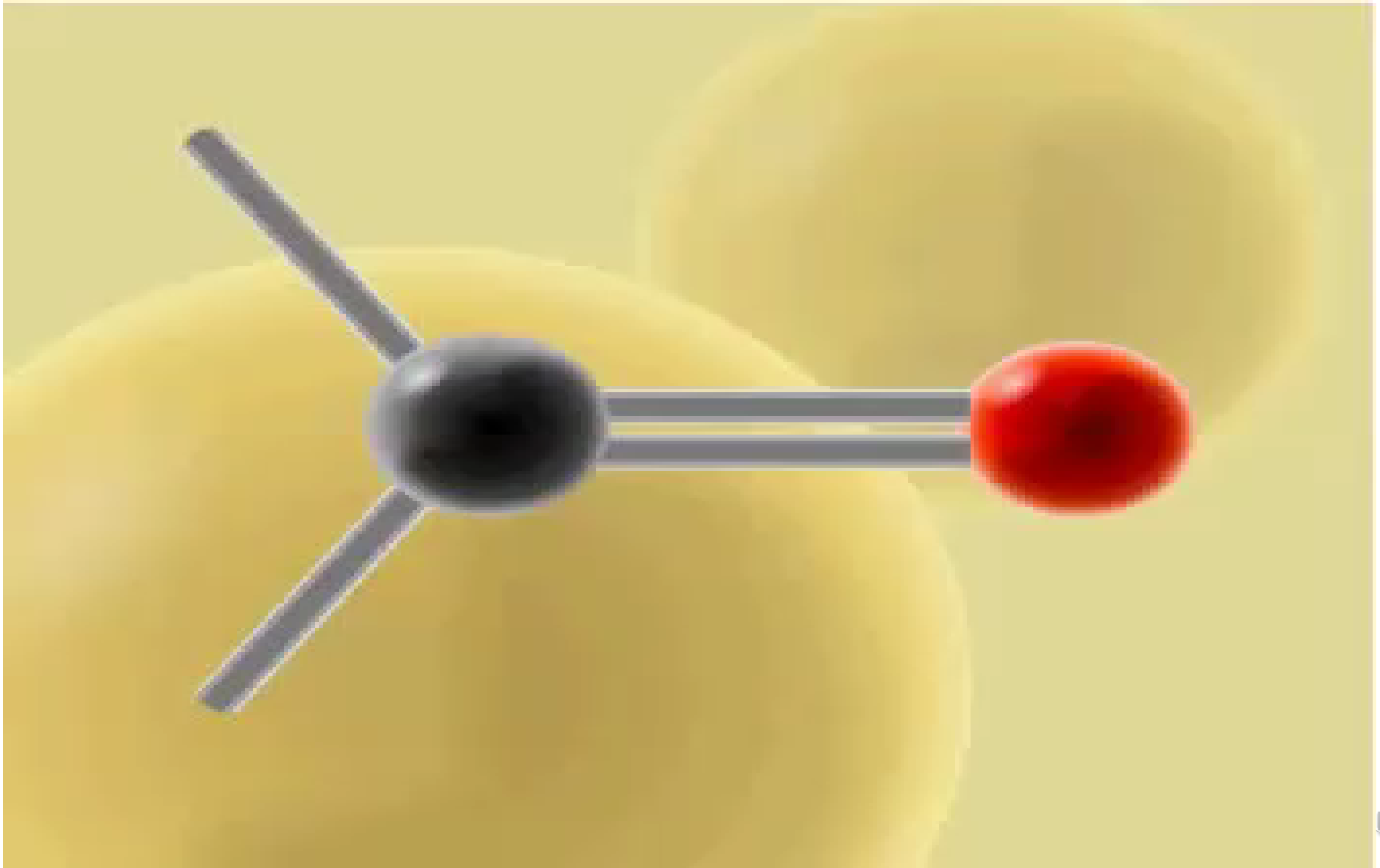


9.6 Nucleophilic Addition Reactions of Aldehydes and Ketones

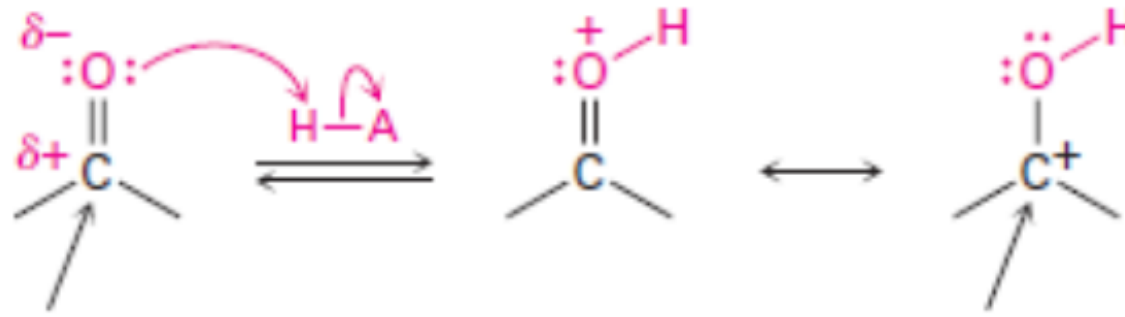


Nucleophilic addition in ketone and aldehyde



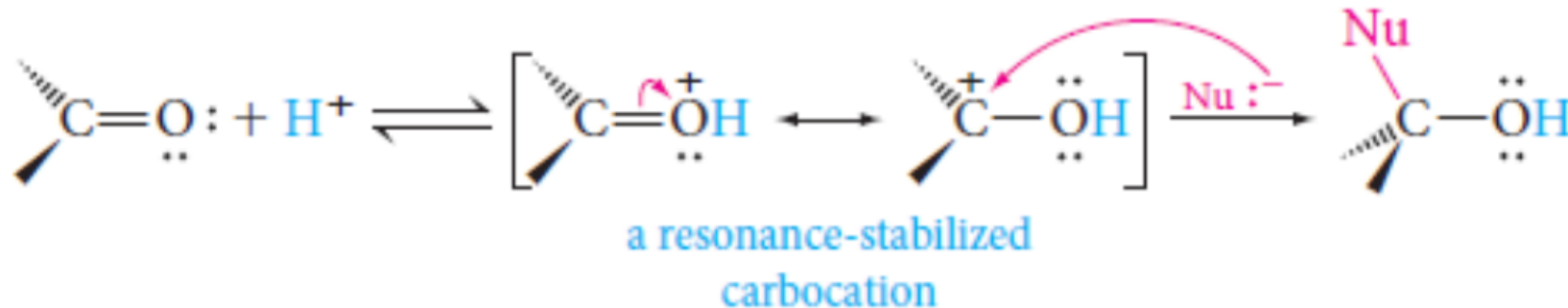


The addition of weak nucleophiles



A neutral carbonyl group is moderately electrophilic because of the polarity of the C-O bond.

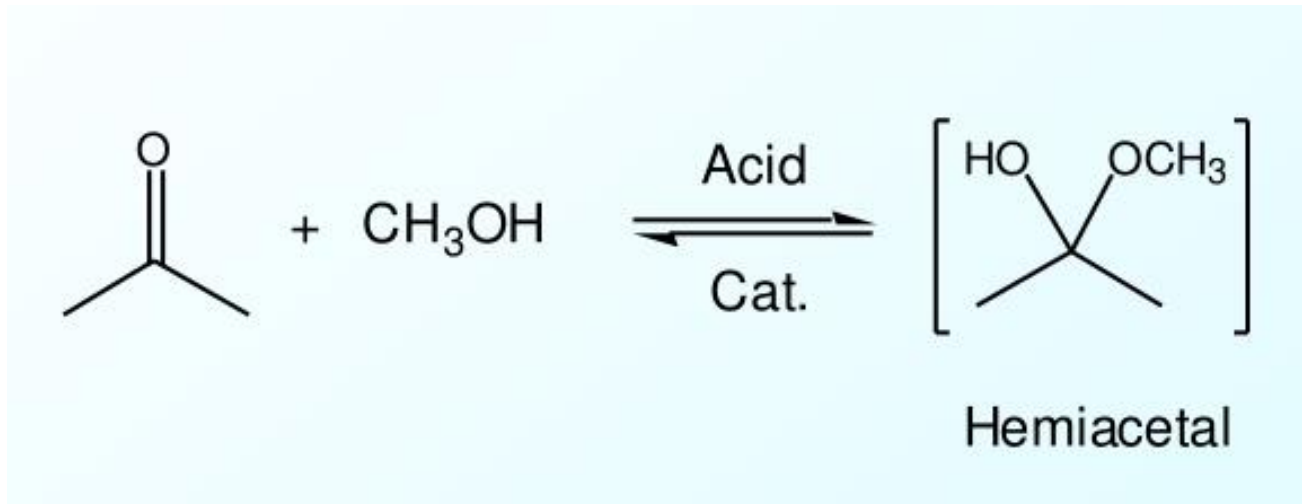
A protonated carbonyl group is strongly electrophilic because of the positive charge on carbon.

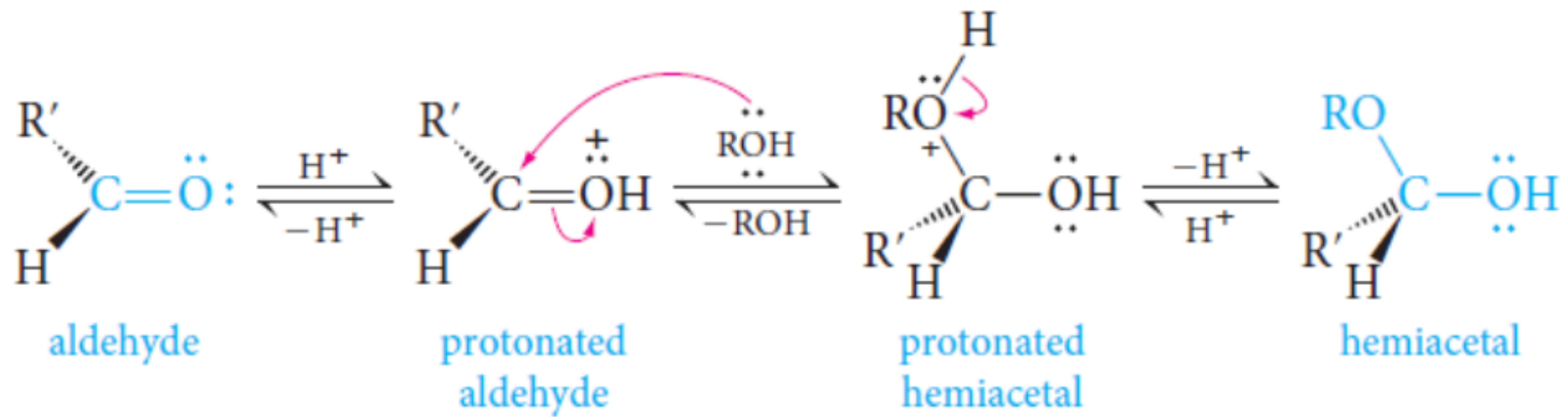


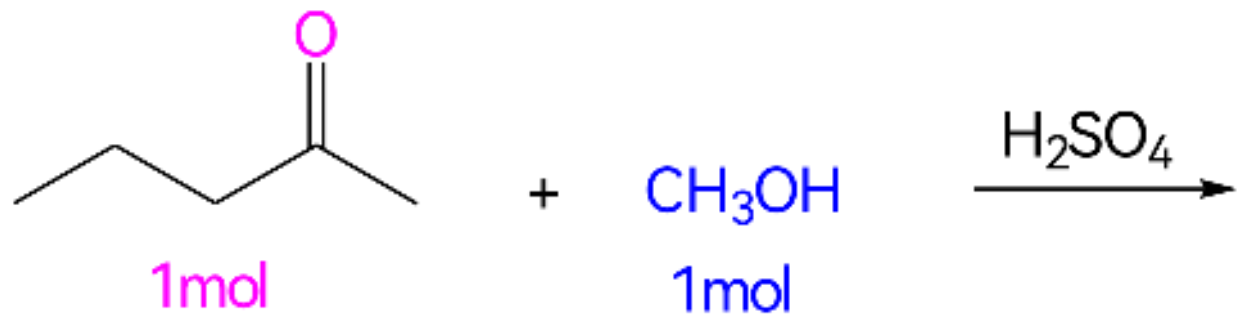
Acids can catalyze the addition of weak nucleophiles to carbonyl compounds by protonating the carbonyl oxygen atom.

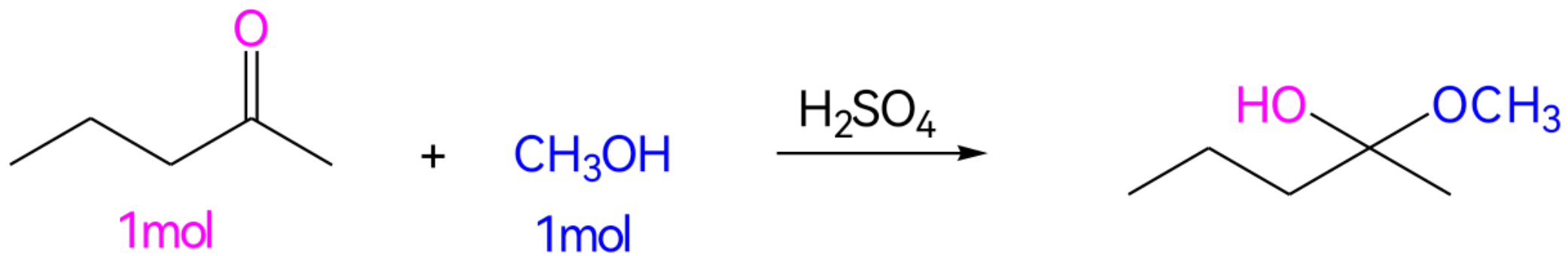


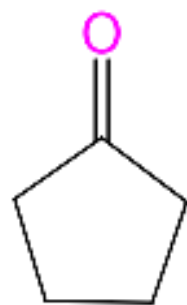
9.7 Addition of Alcohols: Formation of Hemiacetals and Acetals









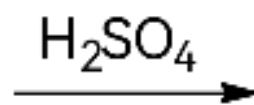


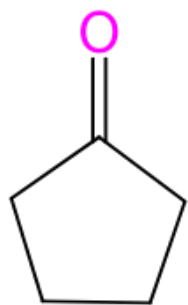
1mol

+

CH₃CH₂OH

1mol



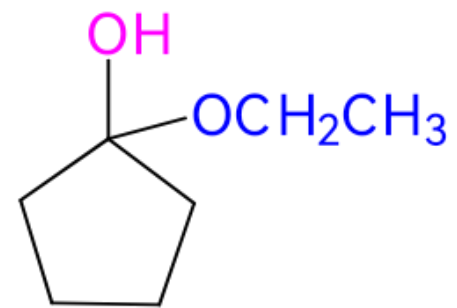
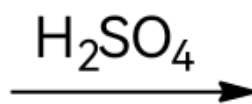


1mol

+

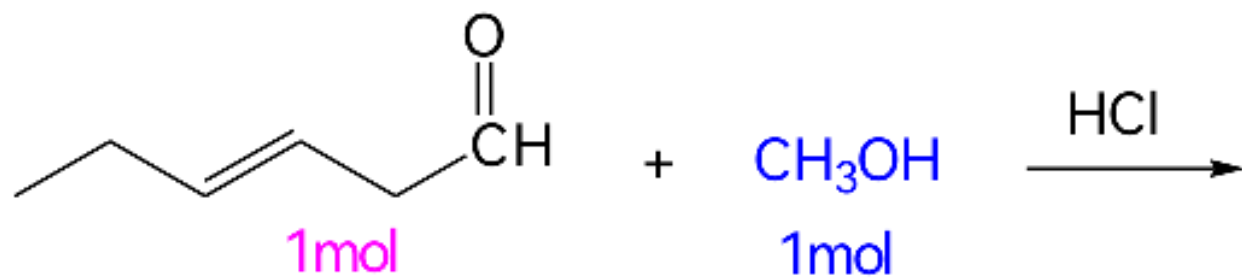


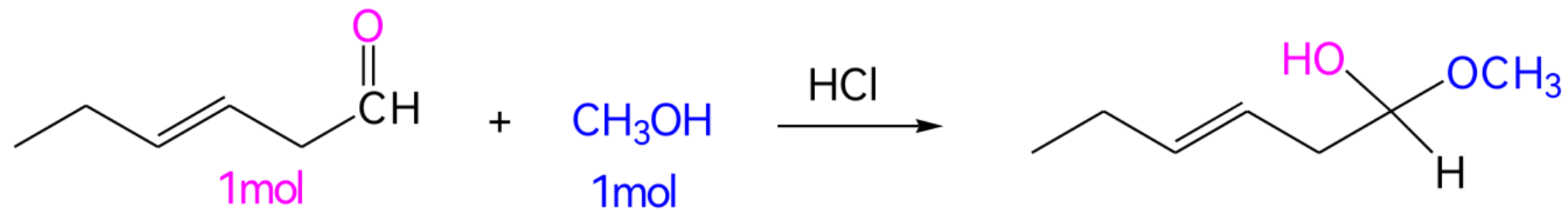
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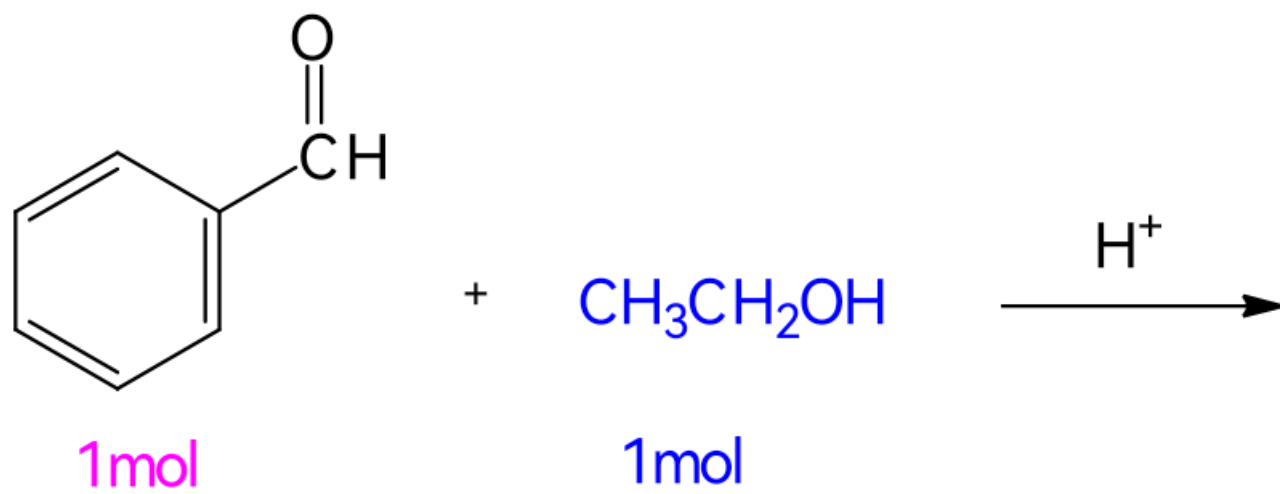


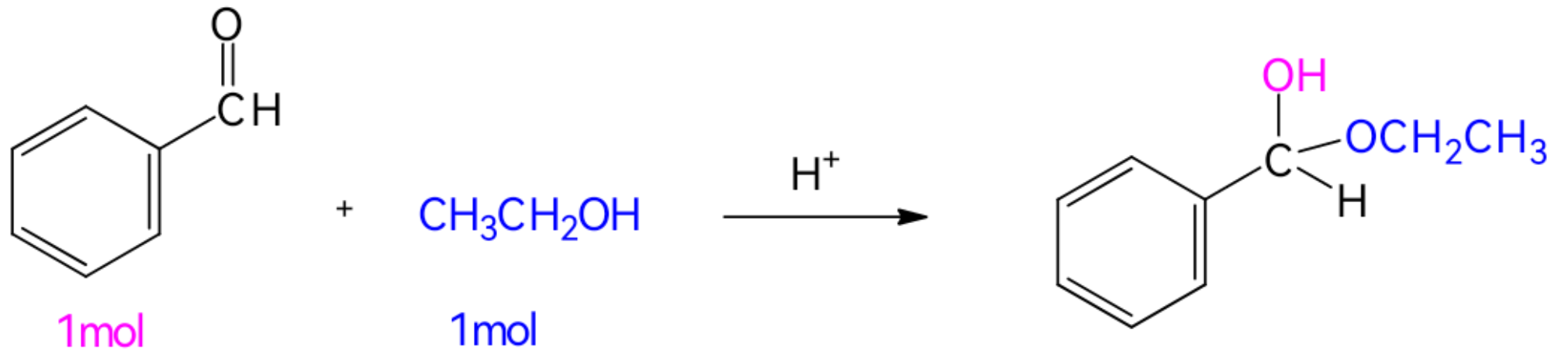
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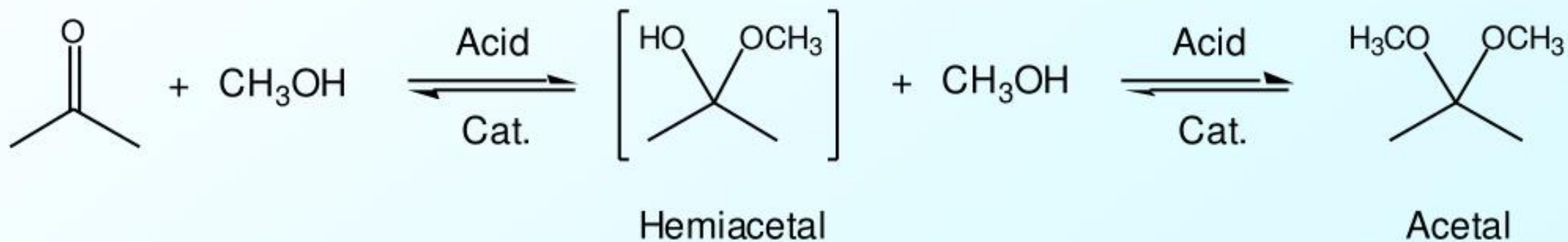


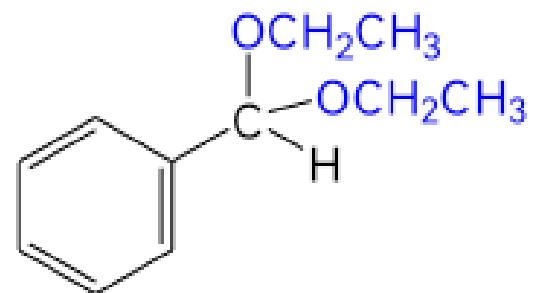
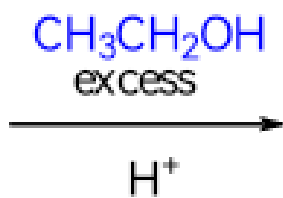
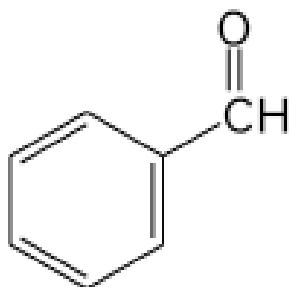
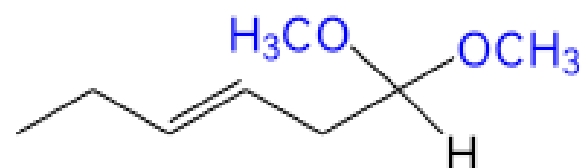
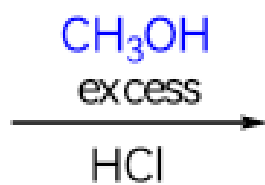
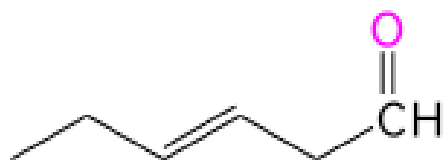
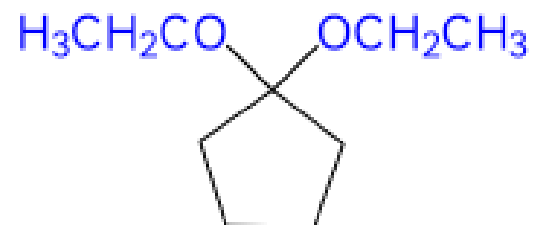
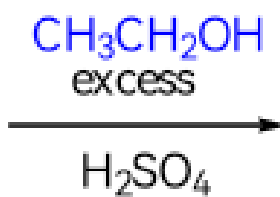
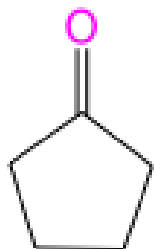
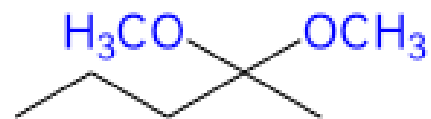
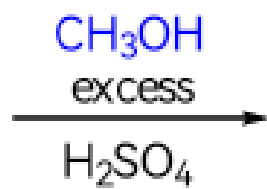
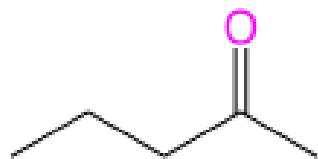






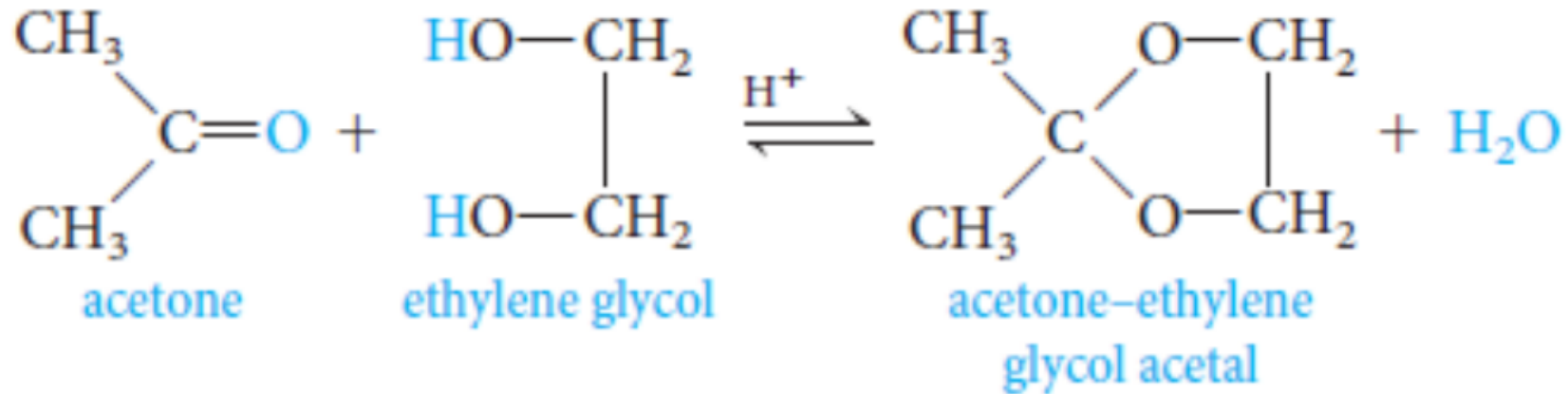
Nucleophilic Addition of Alcohols: Acetal Formation

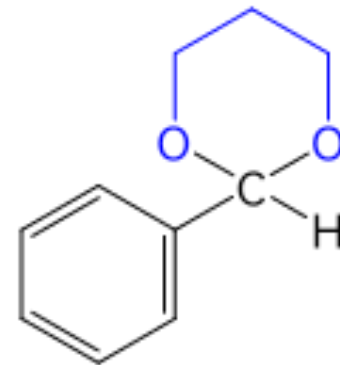
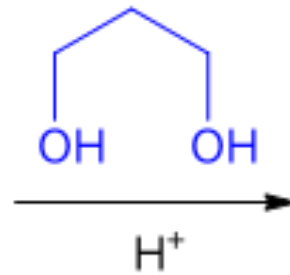
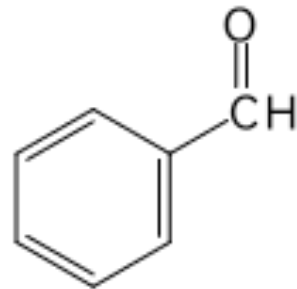
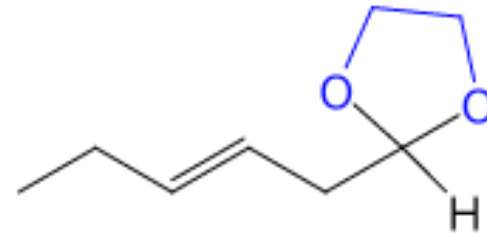
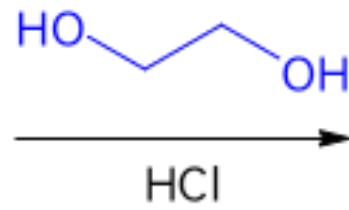
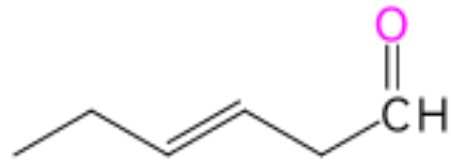
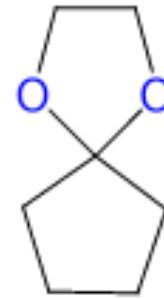
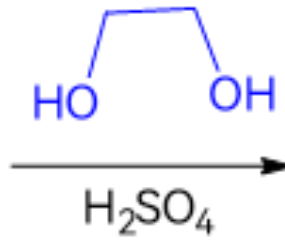
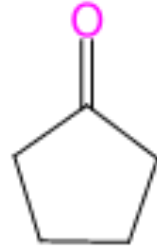
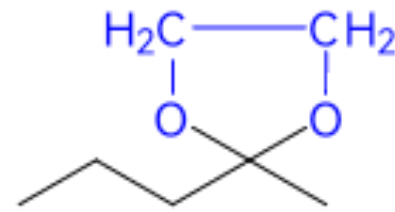
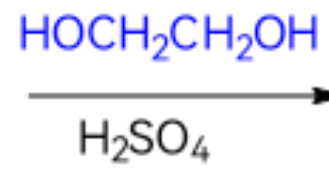
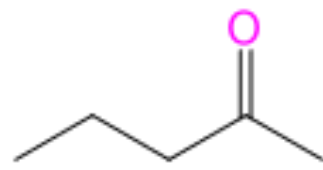




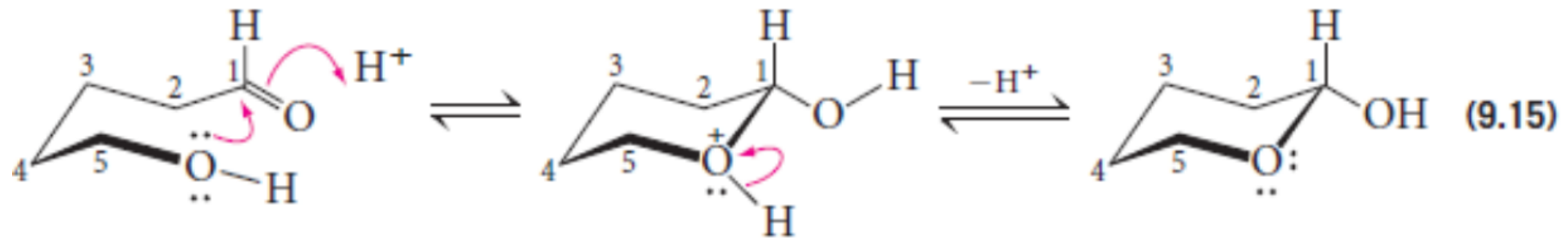
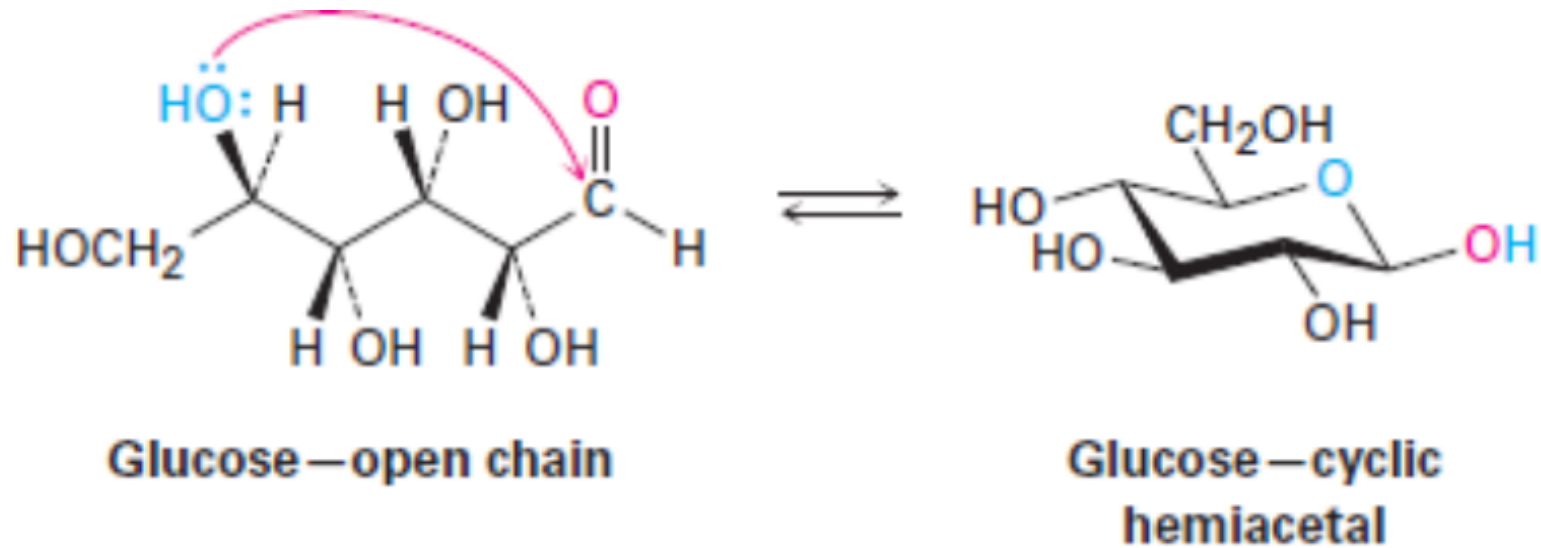
Cyclic acetal

A glycol is used as the alcohol to react with ketones to produce cyclic acetal .





Acetal and hemiacetal groups in carbohydrate chemistry



Thanks to chemistry channel at youtube.com for their valued movies

www.youtube.com/channel/UCW-i85fJOjYKmOFbHa8uUNg/videos



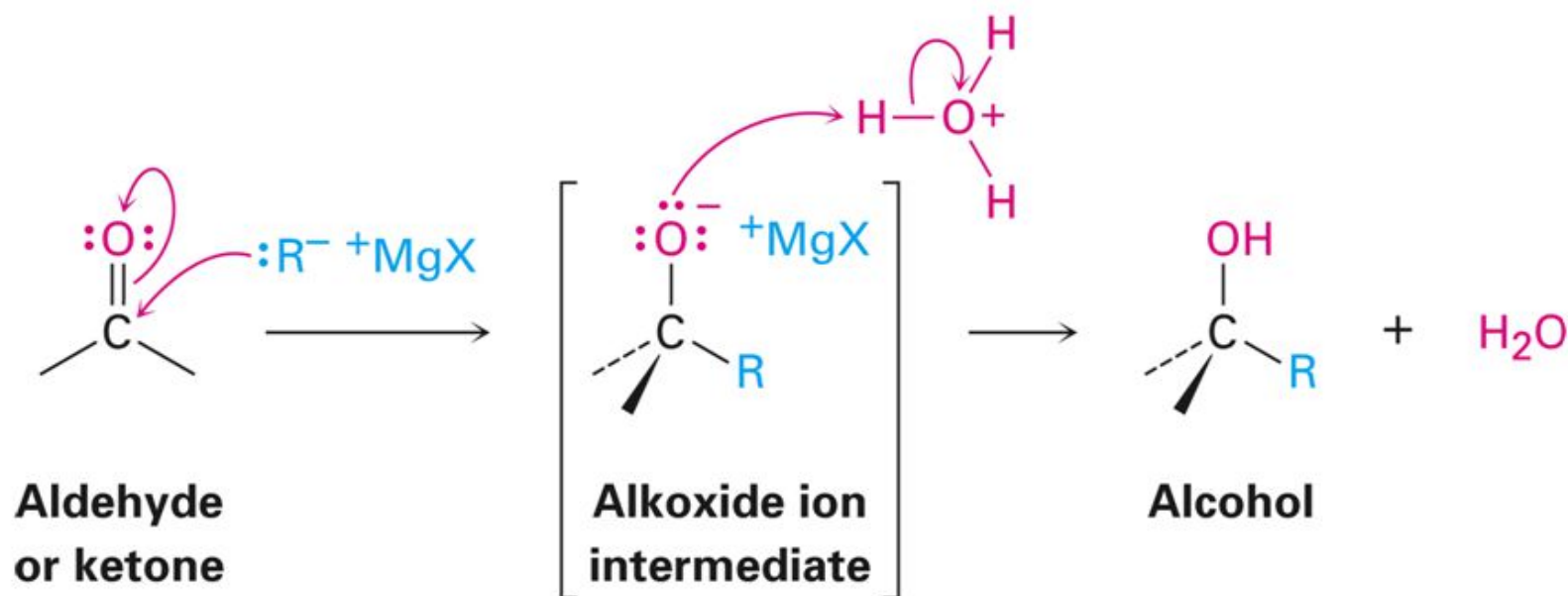
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**9.9 Addition of Grignard
Reagents and Acetylides**



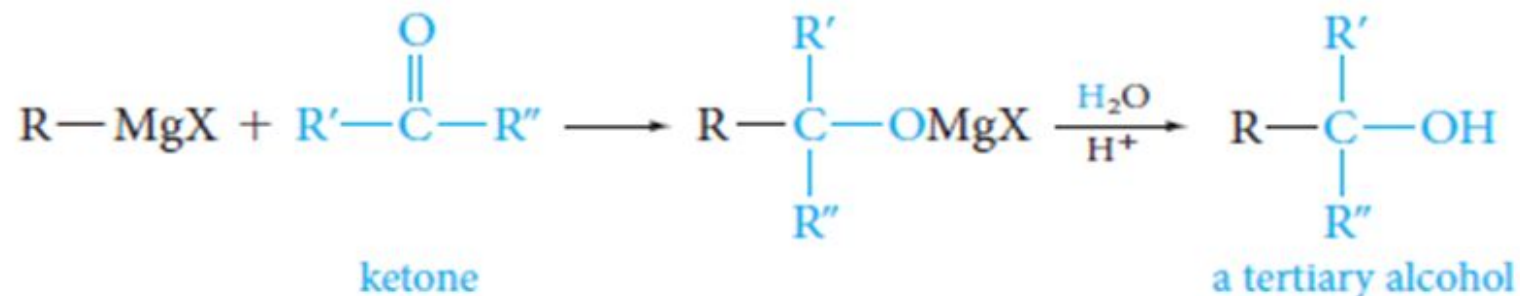
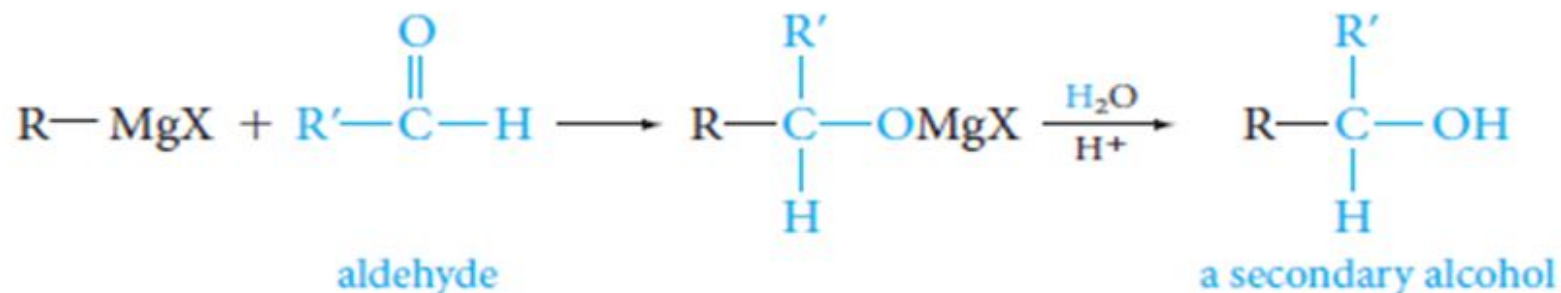
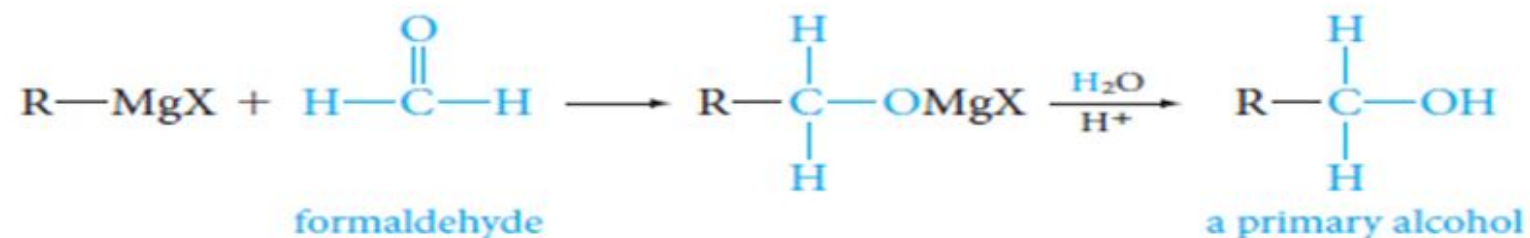
Mechanism of the Addition of a Grignard Reagent

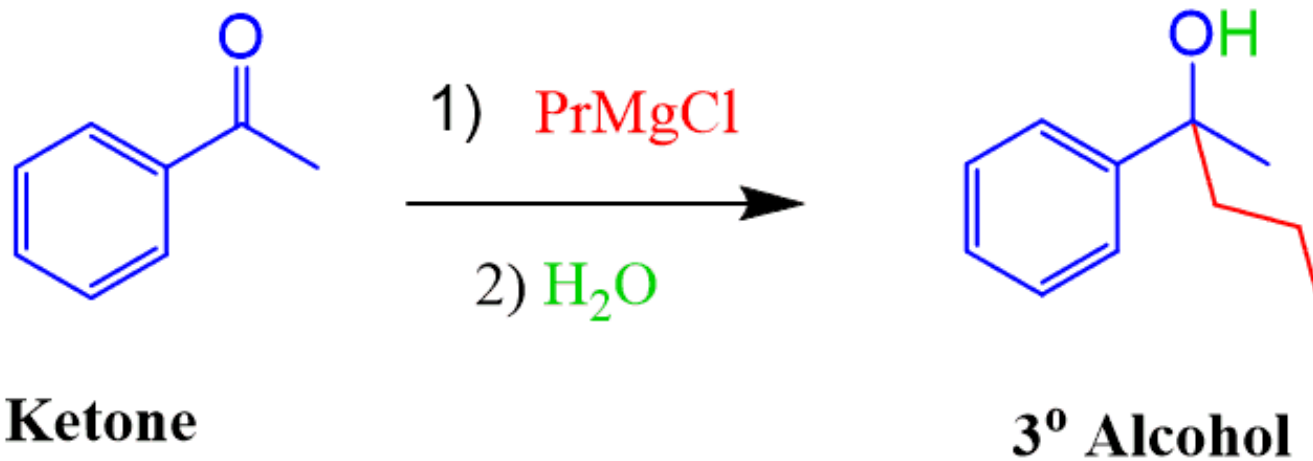
- The nucleophile is a **carbanion** ($R:^-$) from the Grignard reagents
- Undergo nucleophilic addition mechanism under basic conditions
- The reaction is irreversible



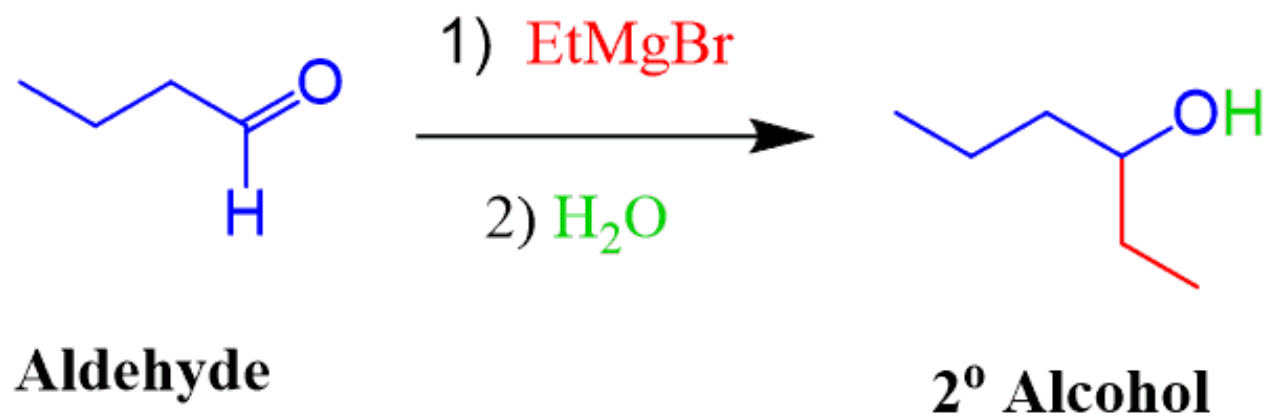
Addition of Grignard Reagents to Aldehydes and ketones

The R group of the Grignard reagent adds irreversibly to the carbonyl carbon, forming a new carbon-carbon bond.

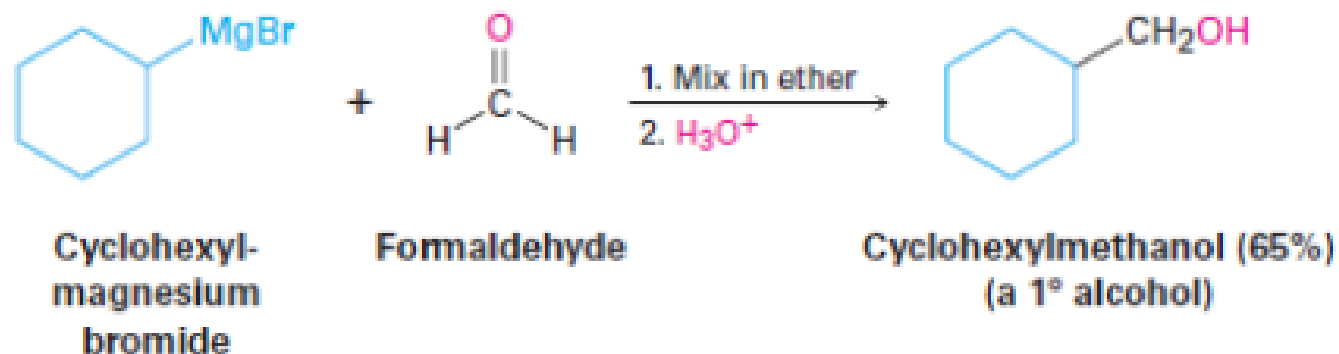




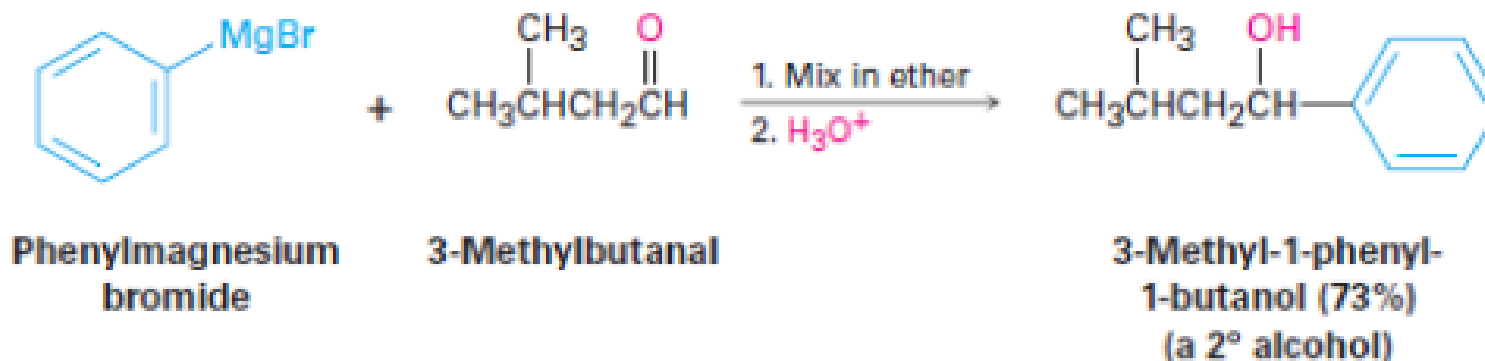
Always number the steps!



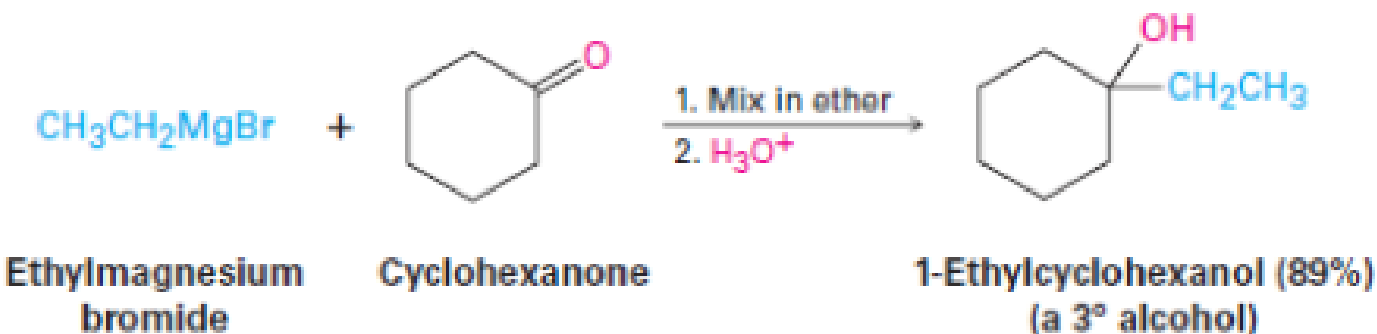
Formaldehyde reaction



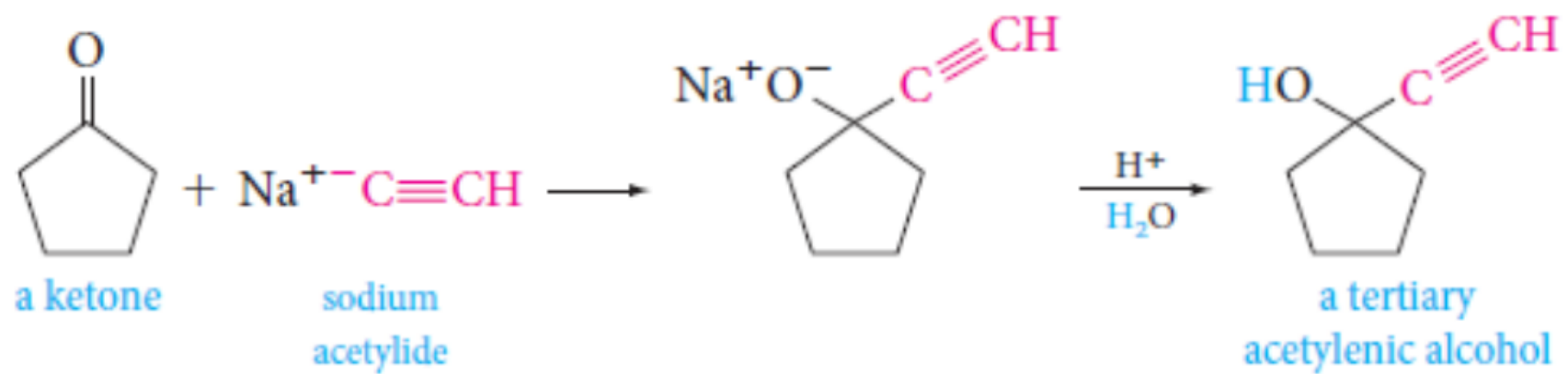
Aldehyde reaction



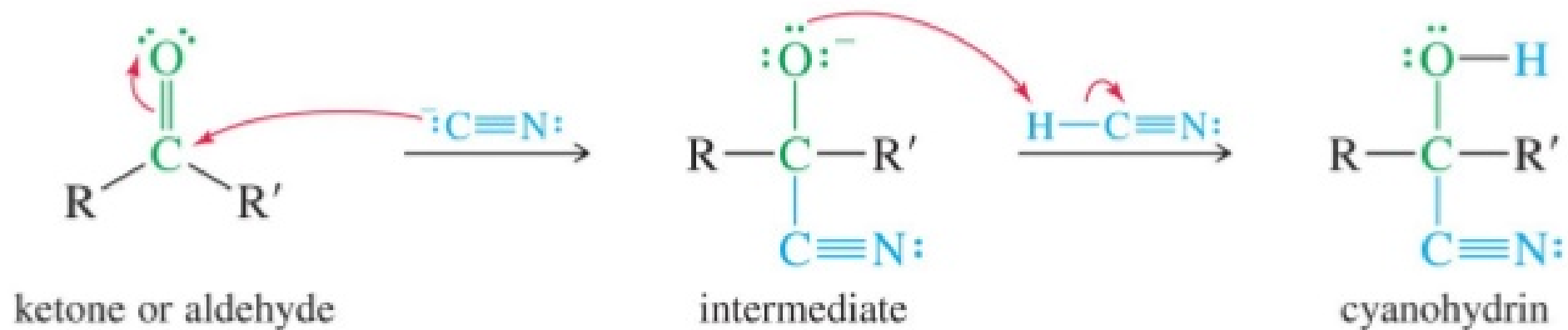
Ketone reaction

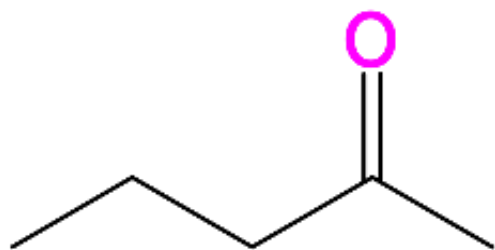


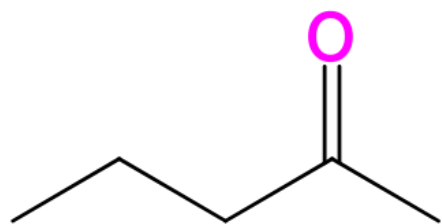
Addition of Acetylides to Aldehydes and ketones



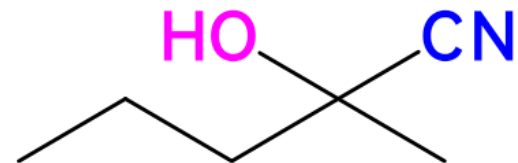
9.10 Addition of Hydrogen Cyanide; Cyanohydrins

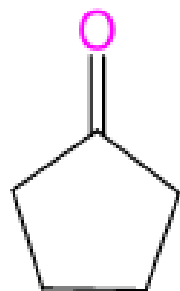




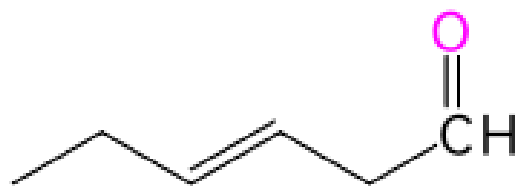
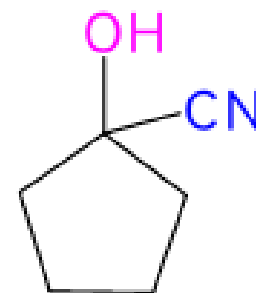


HCN

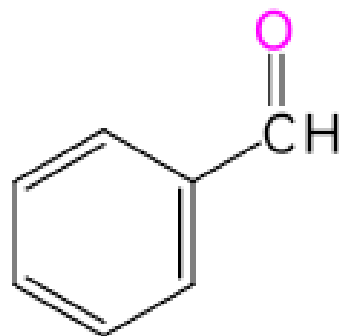
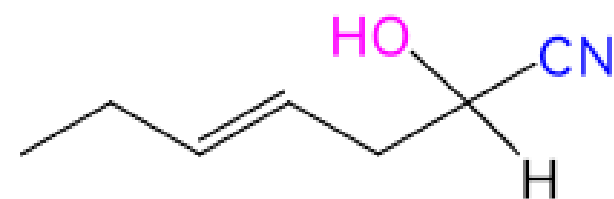




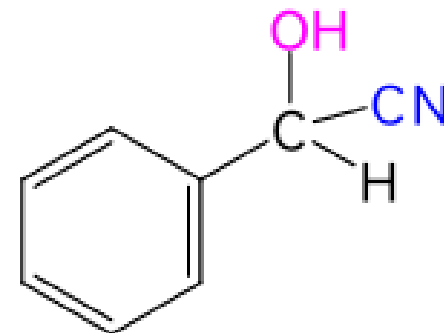
HCN



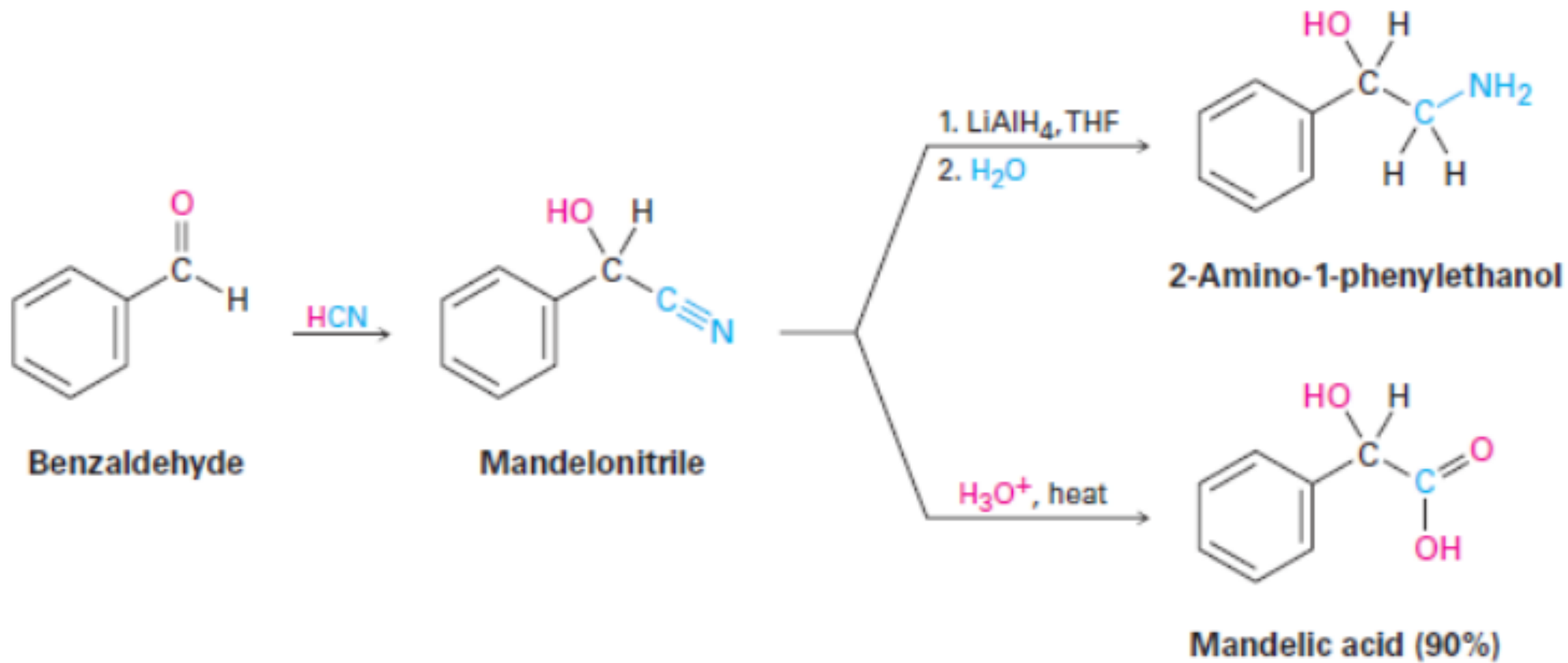
HCN



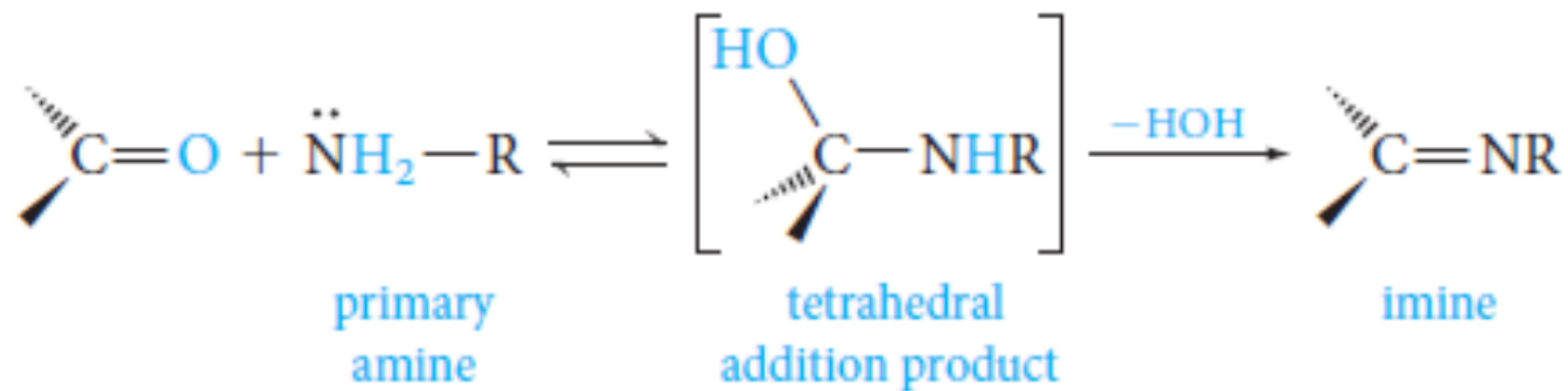
HCN

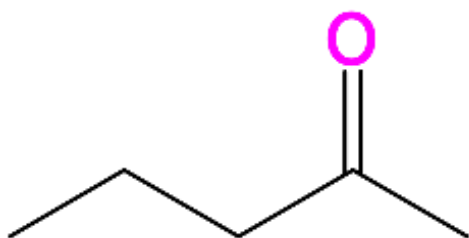


Reduction and Hydrolysis of Cyanohydrins

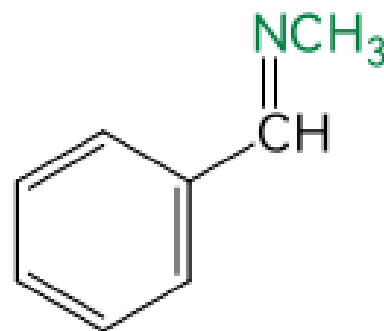
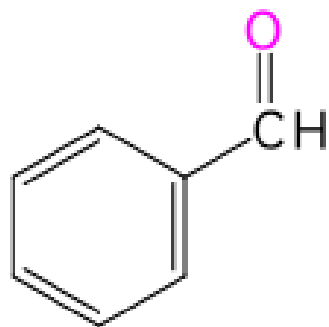
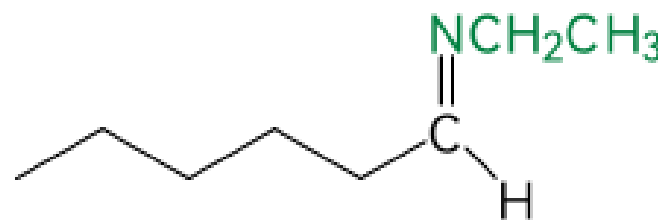
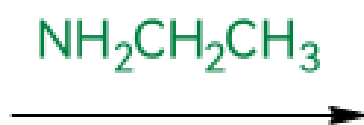
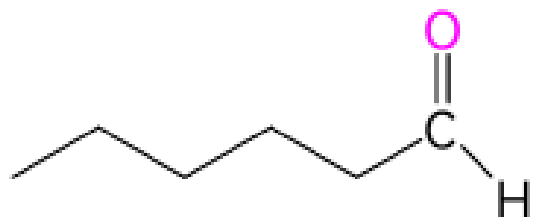
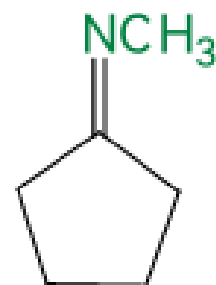
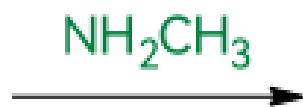
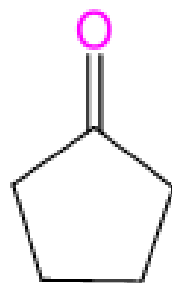


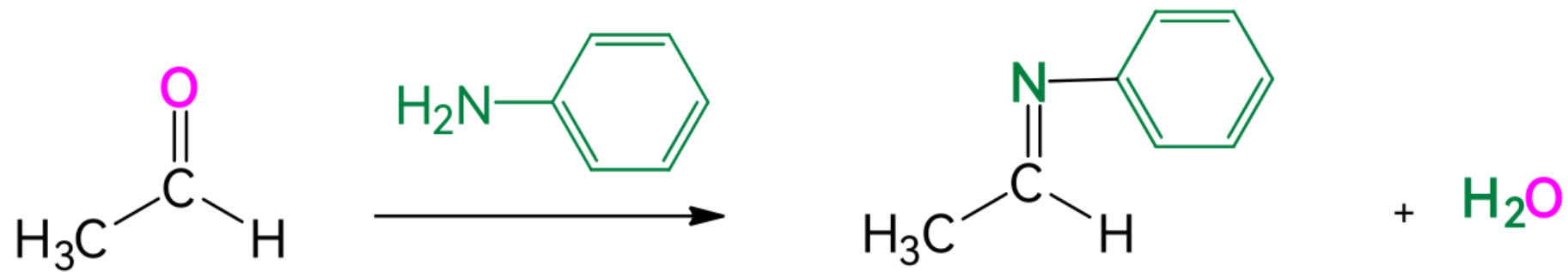
9.11 Addition of Nitrogen Nucleophiles



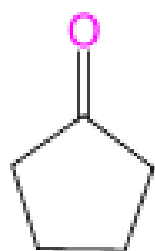




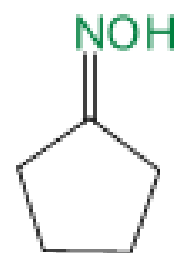




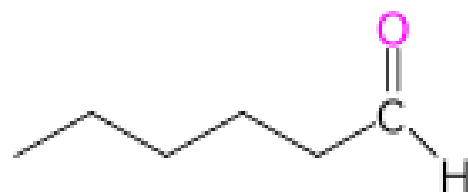
Aldehyde and ketone derivatives



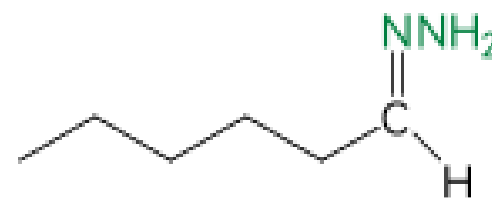
Hydroxy amine



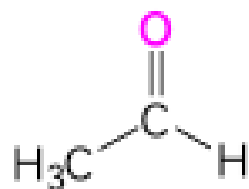
Oxime



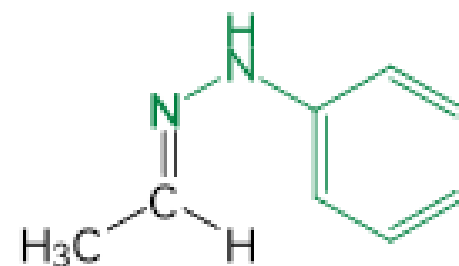
Hydrazine



Hydrazone



Phenylhydrazine



Phenylhydrazone



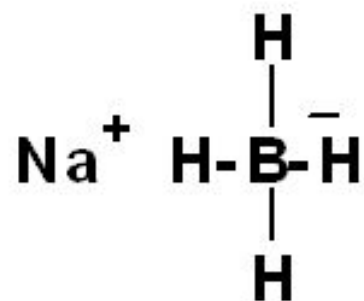
9.12 Reduction of Carbonyl Compounds



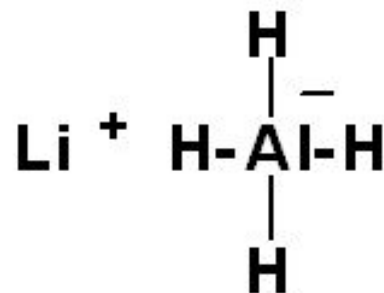
Sodium Borohydride and Lithium Aluminum hydride

The most common laboratory reagents for the reduction of aldehydes and ketones are NaBH_4 and LiAlH_4

- both reagents are sources of hydride ion, H^- , a very strong nucleophile



Sodium
borohydride



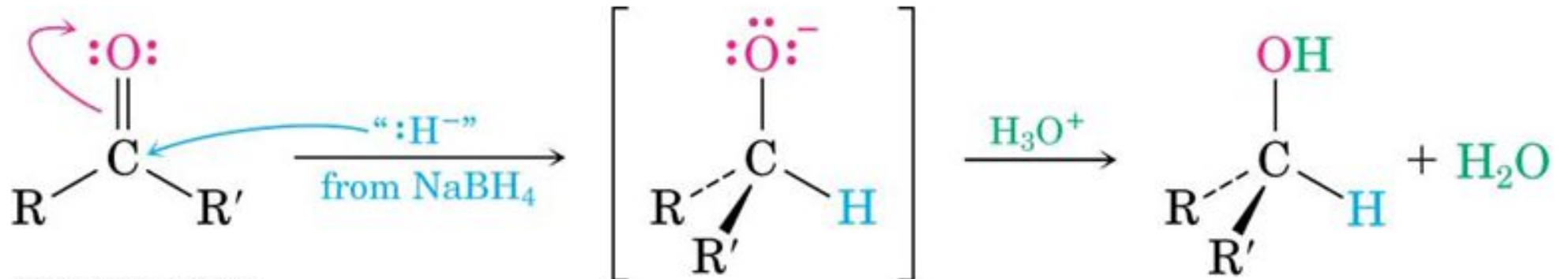
Lithium aluminum
hydride (LAH)



Hydride ion



Reduction of ketones and Aldehydes by Sodium borohydride

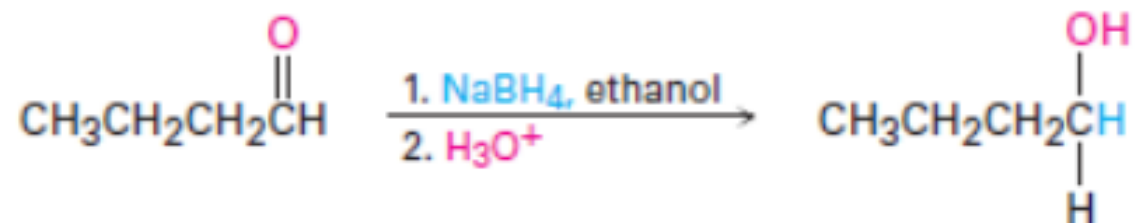


Reduction of ketones and Aldehydes by using Sodium borohydride



Reduction of ketones and Aldehydes by using Sodium borohydride

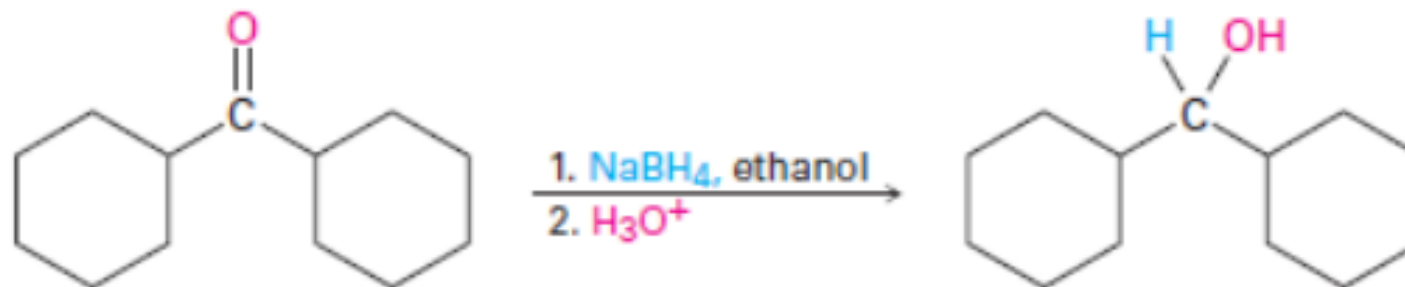
Aldehyde reduction



Butanal

1-Butanol (85%)
(a 1° alcohol)

Ketone reduction



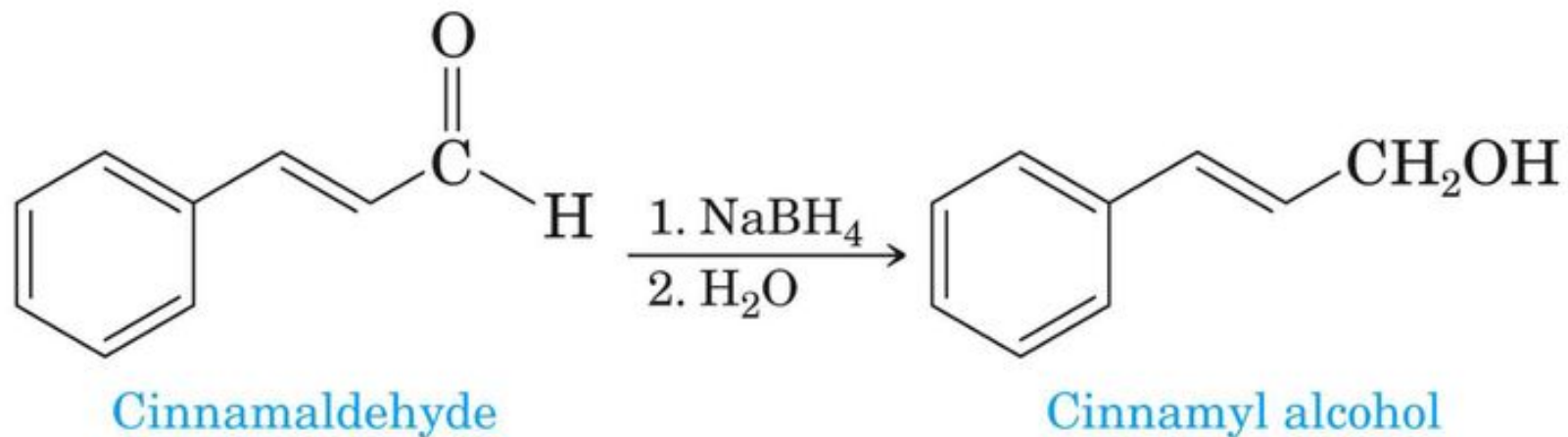
Dicyclohexyl ketone

Dicyclohexylmethanol (88%)
(a 2° alcohol)



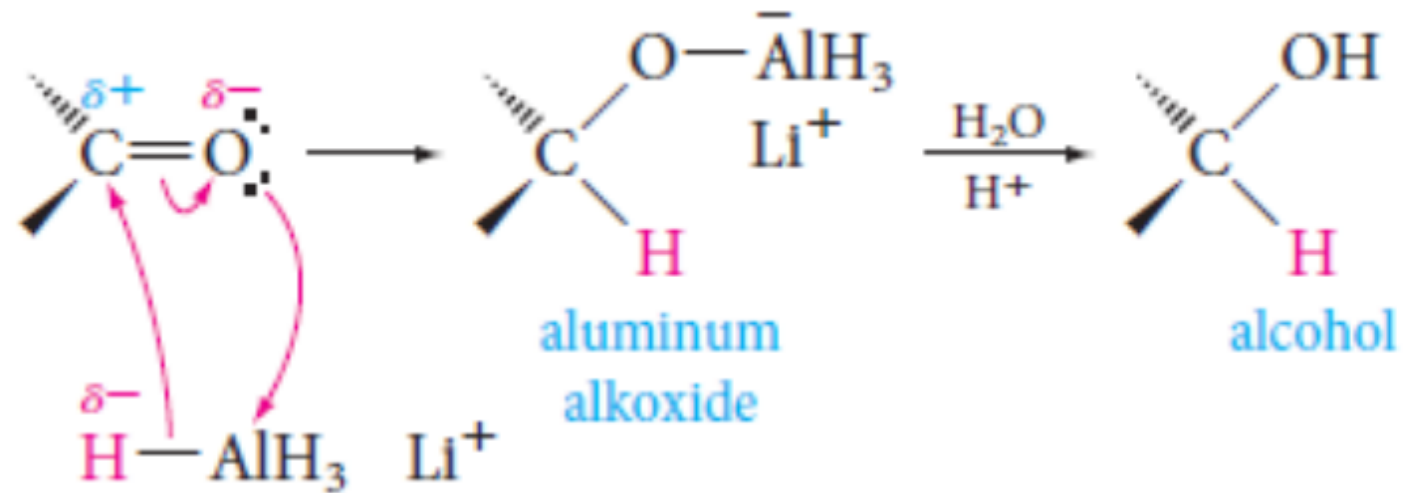
Chemoselectivity of Sodium borohydride

Reduction by NaBH_4 does not affect a carbon-carbon double bond or an aromatic ring.





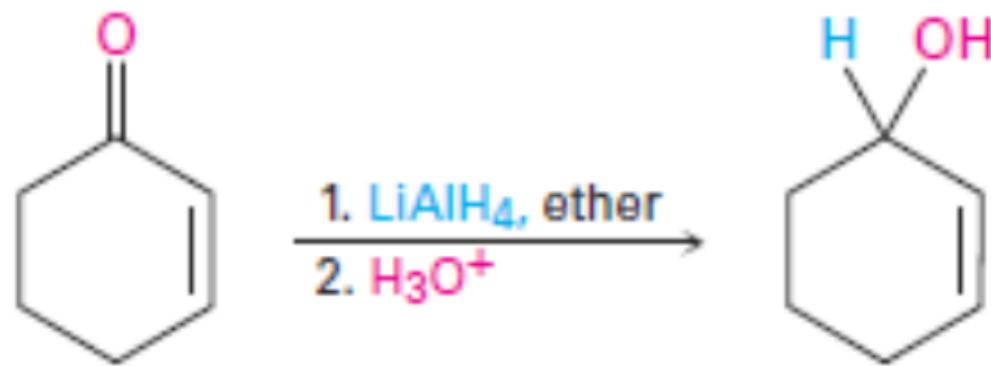
Reduction of ketones and Aldehydes by using Lithium Aluminum hydride



Reduction of ketones and Aldehydes by using Lithium Aluminum hydride



Reduction of ketones and Aldehydes by using Lithium Aluminum hydride



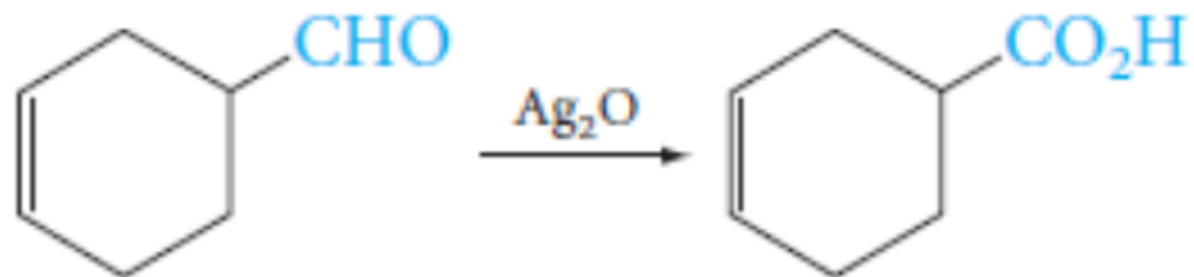
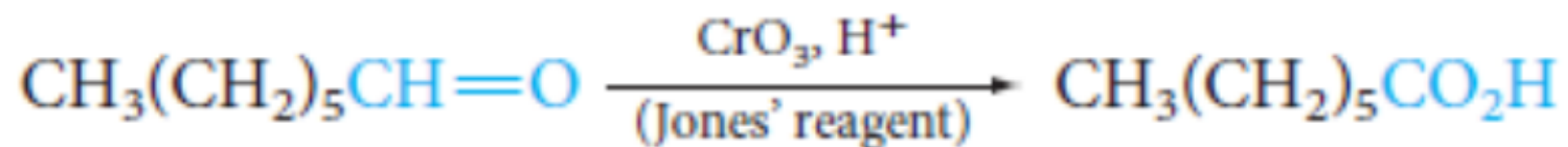
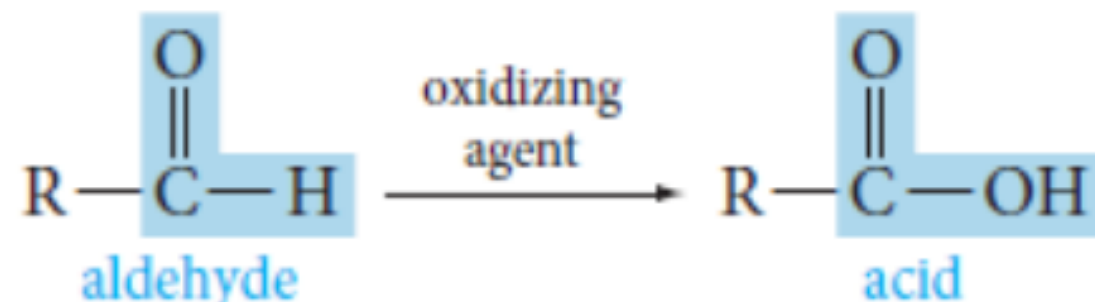
2-Cyclohexenone

2-Cyclohexenol (94%)





9.13 Oxidation of Carbonyl Compounds



Detection of Aldehydes by Tollens' reagent

