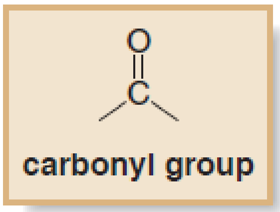
الكلية	**كلية التربية للعلوم الصرفة**
القسم	**قسم الكيمياء**
المادة باللغة الانجليزية	**Organic chemistry**
المادة باللغة العربية	**الكيمياء العضوية**
المرحلة الدراسية	**المرحلة الثانية**
اسم التدريسي	**د. عمر جمال مهدي العسافي**
عنوان المحاضرة باللغة الانجليزية	**Aldehyde**
عنوان المحاضرة باللغة العربية	**الالديهايد**
رقم المحاضرة	**السادسة**
المصادر والمراجع	***Organic Chemistry*** 6^{ed} , William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric V. Anslyn, Bruce M. Novak, 2012
	Organic Chemistry 3^{ed} , Janice Gorzynski Smith, 2011
	Organic Chemistry" by Jonathan Clayden, Nick Greeves, and Stuart Warren

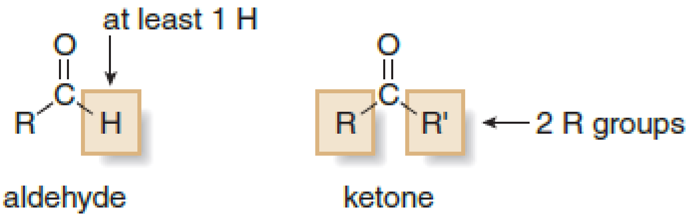
Introduction

Two broad classes of compounds contain a ***carbonyl group:***

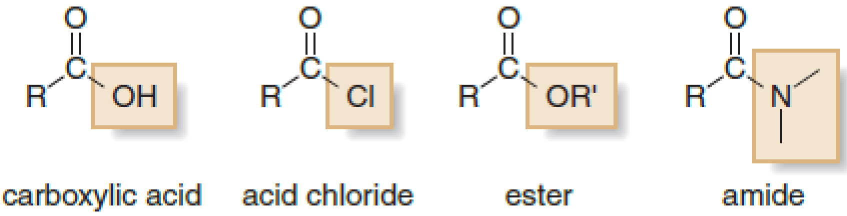


[1] Compounds that have only carbon and hydrogen atoms bonded to the carbonyl group:-

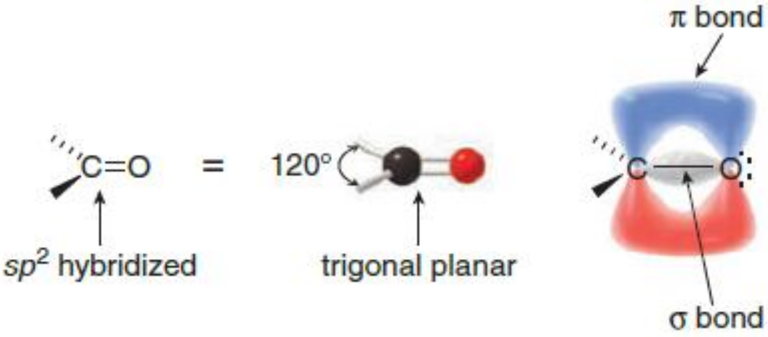
- An **aldehyde** has at least one H atom bonded to the carbonyl group.
- A **ketone** has two alkyl or aryl groups bonded to the carbonyl group.



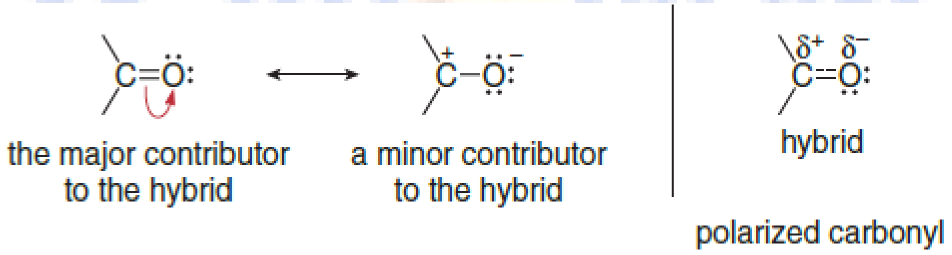
[2] Compounds that contain an electronegative atom bonded to the carbonyl group.



The carbonyl carbon atom is sp2 hybridized and trigonal planar, and all bond angles are ~120°. The double bond of a carbonyl group consists of one σ bond and one π bond. The π bond is formed by the overlap of two p orbitals, and extends above and below the plane. In these features the carbonyl group resembles the trigonal planar, sp2 hybridized carbons of a C – C double bond.



In one important way, though, a C=O and C=C are very different. The electronegative oxygen atom in the carbonyl group means that the bond is polarized, making the carbonyl carbon electron deficient. Using a resonance description, the carbonyl group is represented by two resonance structures, with a charge-separated resonance structure a minor contributor to the hybrid.

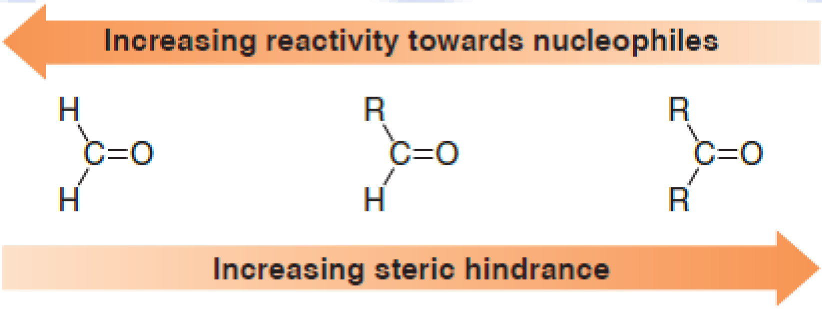


Two structural features determine the chemistry and properties of aldehydes and ketones.

The carbonyl group is sp2 hybridized and trigonal planar, making it relatively uncrowded.

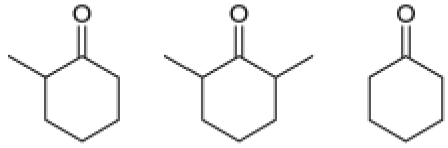
- The electronegative oxygen atom polarizes the carbonyl group, making the carbonyl carbon electrophilic.

The relative reactivity of the carbonyl group is determined by the number of R groups bonded to it. As the number of R groups around the carbonyl carbon increases, the reactivity of the carbonyl compound decreases, resulting in the following order of reactivity:



Problem Rank the compounds in each group in order of increasing reactivity towards nucleophilic attack.

a. $CH_3CH{=}O$ $CH_2{=}O$ $(CH_3)_2C{=}O$ b.



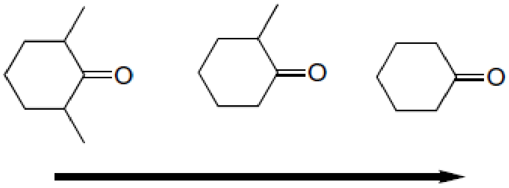
Solution:-

a. $(CH_3)_2C{=}O$ $CH_3CH{=}O$ $CH_2{=}O$

2 R groups 1 R group 0 R groups

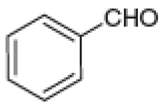
Increasing reactivity
decreasing alkyl substitution

b.

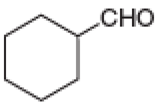


Increasing reactivity
decreasing steric hindrance

Problem Explain why benzaldehyde is less reactive than cyclohexanecarbaldehyde towards nucleophilic attack.

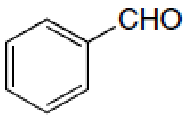


benzaldehyde

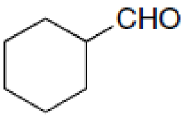


cyclohexanecarbaldehyde

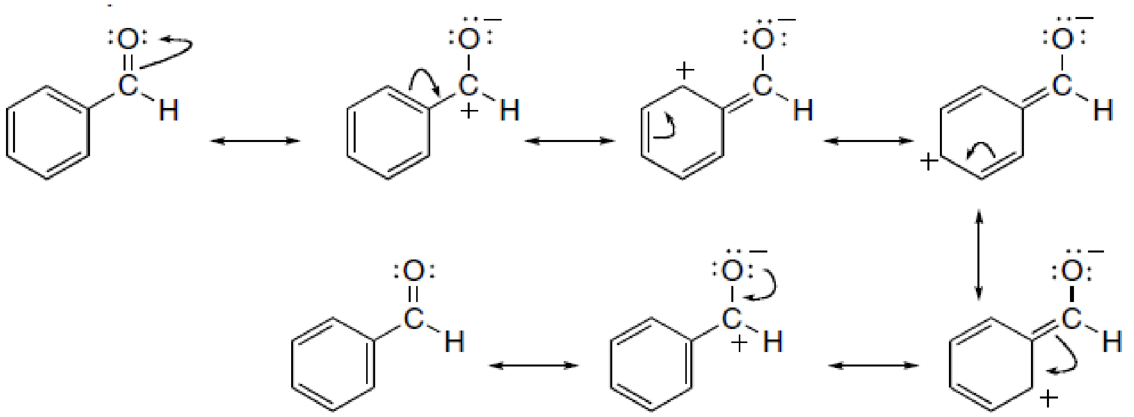
Solution:-



benzaldehyde



cyclohexanecarbaldehyde



2. Nomenclature

IUPAC and common name is used for aldehydes.

Naming Aldehydes in the IUPAC System.

In IUPAC nomenclature, aldehydes are identified by a suffix added to the parent name of the longest chain. Two different suffixes are used, depending on whether the CHO group is bonded to a chain or a ring.

To name an aldehyde using the IUPAC system:

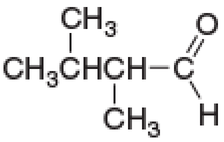
[1] If the CHO is bonded to a chain of carbons, find the longest chain containing the CHO group, and change the -e ending of the parent alkane to the suffix -*al*. If the CHO group is bonded to a ring, name the ring and add the suffix ***-carbaldehyde.***

[2] Number the chain or ring to put the CHO group at C1, but omit this number from the name.

Apply all of the other usual rules of nomenclature.

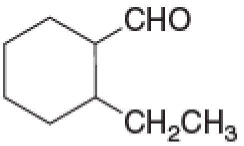
Problem Give the IUPAC name for each compound.

a.



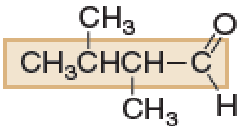
$CH_3CH(CH_3)CH(CH_3)CHO$

b.



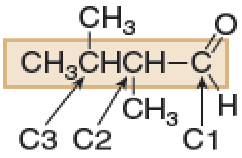
Solution:-

a. [1] Find and name the longest chain containing the CHO:



butan*e* ⟶ butan*al*
(4 C's)

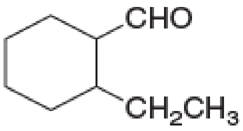
[2] Number and name substituents:



Answer: 2,3-dimethylbutanal

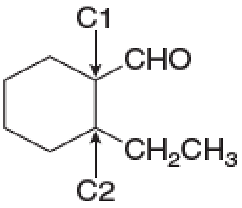
---

b. [1] Find and name the ring bonded to the CHO group:



cyclohexane + carbaldehyde
(6 C's)

[2] Number and name substituents:

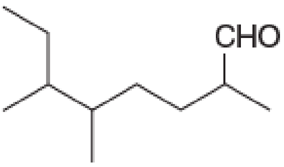


Answer:
2-ethylcyclohexanecarbaldehyde

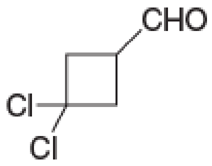
Problem Give the IUPAC name for each aldehyde.

a. $(CH_3)_3CC(CH_3)_2CH_2CHO$

b.

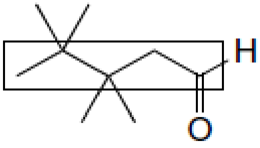


c.

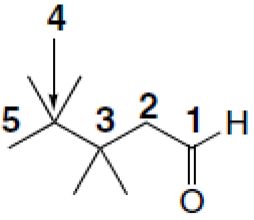


Solution:-

a. $(CH_3)_3CC(CH_3)_2CH_2CHO$

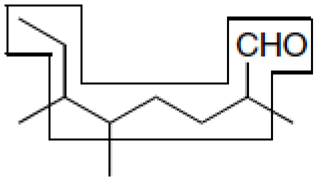


5 C chain = pentanal

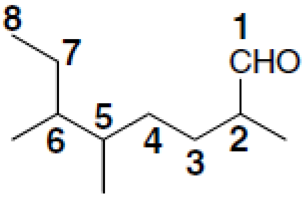


3,3,4,4-tetramethylpentanal

b.

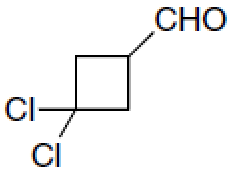


8 C chain = octanal

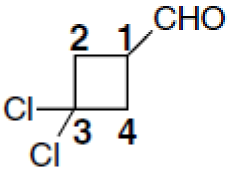


2,5,6-trimethyloctanal

c.



4 C ring =
cyclobutanecarbaldehyde



**3,3-dichlorocyclobutane-
carbaldehyde**

Problem Give the structure corresponding to each IUPAC name.

a. 2-isobutyl-3-isopropylhexanal

b. *trans*-3-methylcyclopentanecarbaldehyde

c. 1-methylcyclopropanecarbaldehyde

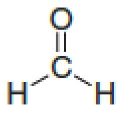
d. 3,6-diethylnonanal

Common Names for Aldehydes

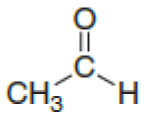
many simple aldehydes have common names that are widely used.

- A common name for an aldehyde is formed by taking the common parent name and adding the suffix -aldehyde.

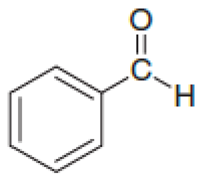
The common names formaldehyde, acetaldehyde, and benzaldehyde are virtually always used instead of their IUPAC names.



formaldehyde
(methanal)

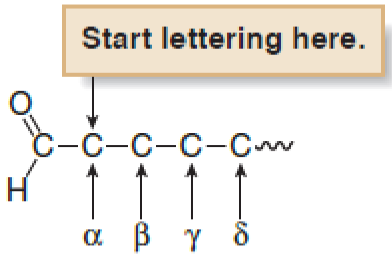


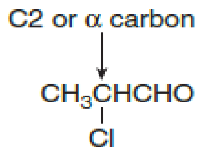
acetaldehyde
(ethanal)



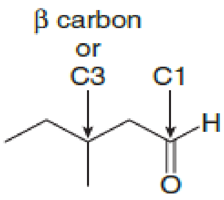
benzaldehyde
(benzenecarbaldehyde)

Greek letters are used to designate the location of substituents in common names. **The carbon adjacent to the CHO group is the α carbon,** and so forth down the chain.

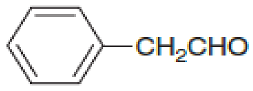




2-chloropropanal
(α-chloropropionaldehyde)



3-methylpentanal
(β-methylvaleraldehyde)



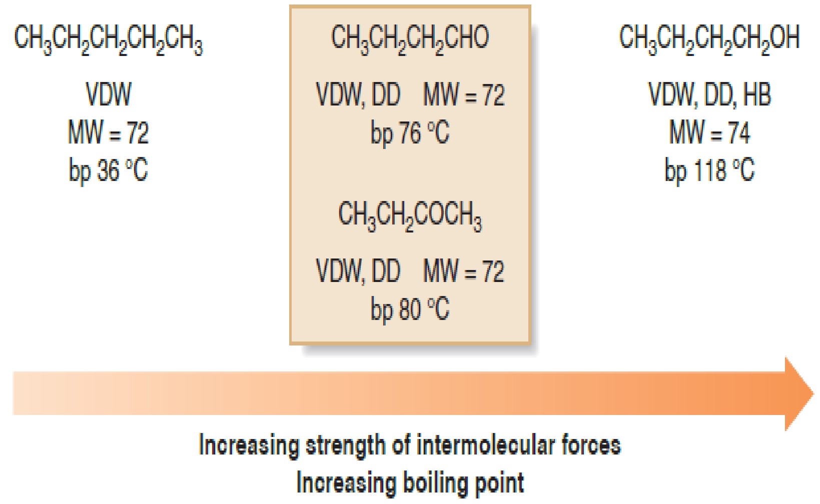
phenylethanal
(phenylacetaldehyde)

(Common names are in parentheses)

3. Physical Properties

Aldehydes and ketones exhibit dipole–dipole interactions because of their polar carbonyl group. Because they have no O – H bond, two molecules of RCHO or RCOR are incapable of intermolecular hydrogen bonding, making them less polar than alcohols and carboxylic acids. How these intermolecular forces affect the physical properties of aldehydes and ketones is summarizedin Table.

Table Physical Properties of Aldehydes and Ketones

Property	Observation
Boiling point and melting point	• For compounds of comparable molecular weight, bp's and mp's follow the usual trend: The stronger the intermolecular forces, the higher the bp or mp.  $CH_3CH_2CH_2CH_2CH_3$ VDW MW = 72 bp 36 °C $CH_3CH_2CH_2CHO$ VDW, DD MW = 72 bp 76 °C $CH_3CH_2COCH_3$ VDW, DD MW = 72 bp 80 °C $CH_3CH_2CH_2CH_2OH$ VDW, DD, HB MW = 74 bp 118 °C **Increasing strength of intermolecular forces** **Increasing boiling point**
Solubility	• RCHO and RCOR are soluble in organic solvents regardless of size. • RCHO and RCOR having ≤ 5 C's are H_2O soluble because they can hydrogen bond with H_2O (Section 3.4C). • RCHO and RCOR having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent.

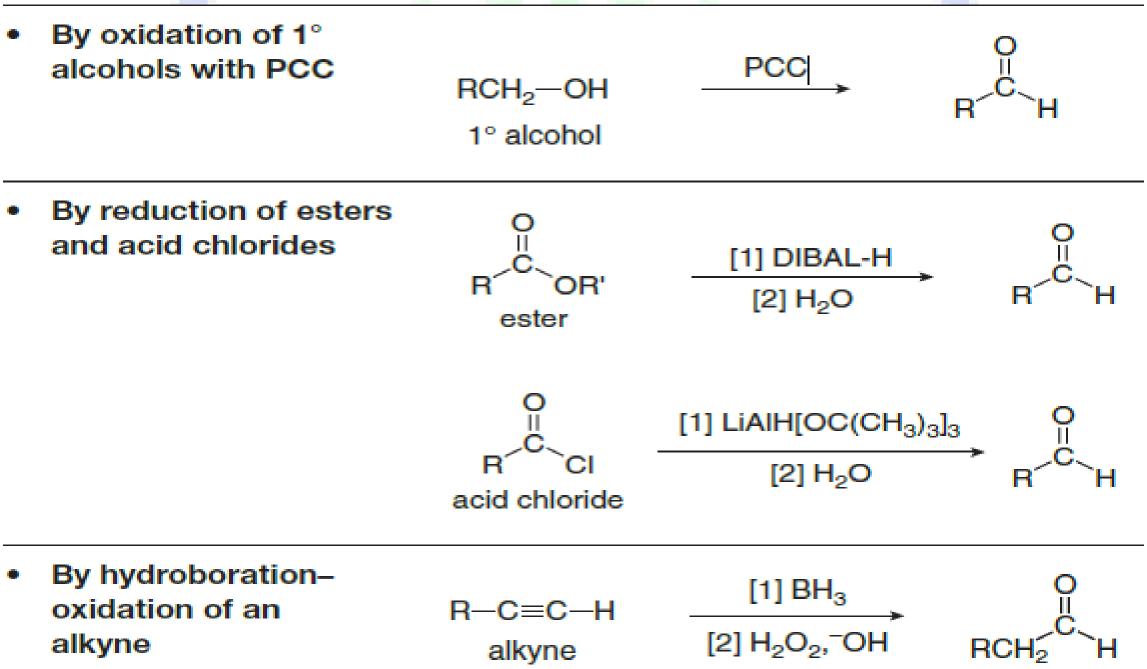
Key: VDW = van der Waals, DD = dipole–dipole, HB = hydrogen bonding, MW = molecular weight

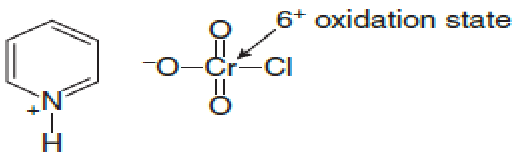
4. Preparation of Aldehydes

Aldehydes can be prepared by a variety of methods. Because these reactions are needed for many multistep syntheses, summarizes earlier reactions that synthesize an aldehyde.

Common Methods to Synthesize Aldehydes

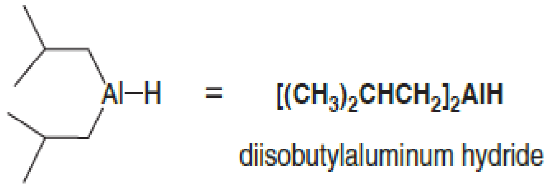
Aldehydes are prepared from 1° alcohols, esters, acid chlorides, and alkynes.





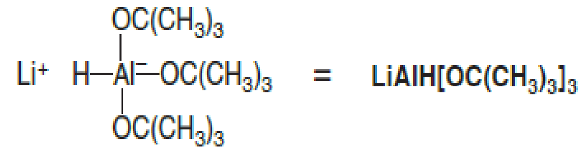
pyridinium chlorochromate

PCC



diisobutylaluminum hydride

DIBAL-H

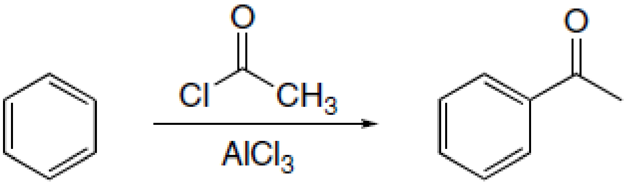


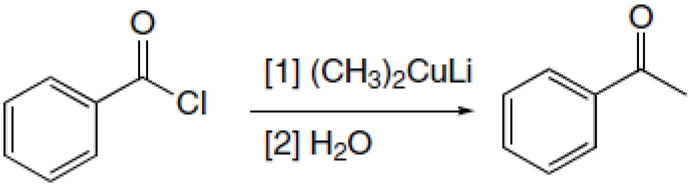
lithium tri-*tert*-butoxyaluminum hydride

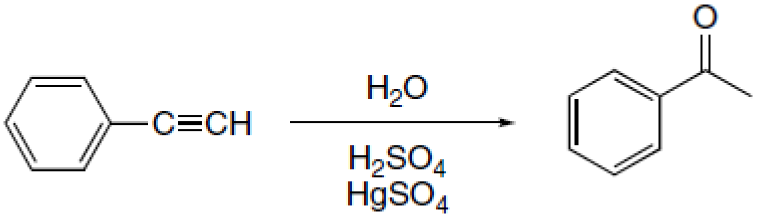
Problem What reagents are needed to convert each compound into acetophenone (C6H5COCH3):

(a) benzene; (b) C_6H_5COCl; (c) $C_6H_5C{\equiv}CH$?

Solution:-

a.


b.


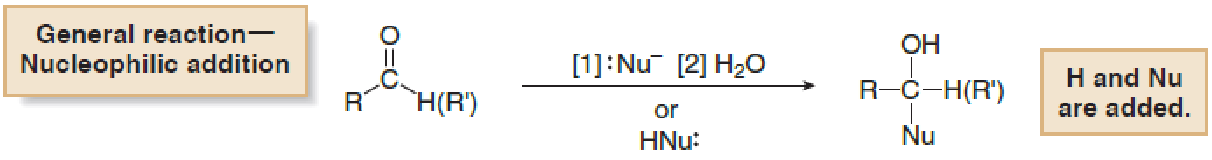
c.


5. Reactions of Aldehydes

the two general kinds of reactions that aldehydes and ketones undergo.

Reaction at the carbonyl carbon

the uncrowded, electrophilic carbonyl carbon makes aldehydes and ketones susceptible to nucleophilic addition reactions.

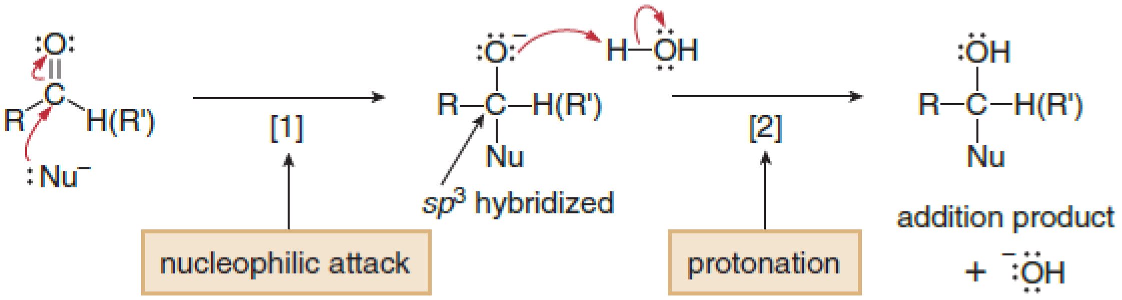


The General Mechanism of Nucleophilic Addition

In Step [1], **the nucleophile attacks the carbonyl group,** cleaving the π bond and moving an electron pair onto oxygen. This forms an *sp*3 hybridized intermediate with a new C – Nu bond.

In Step [2], **protonation of the negatively charged O atom by H2O** forms the addition product.

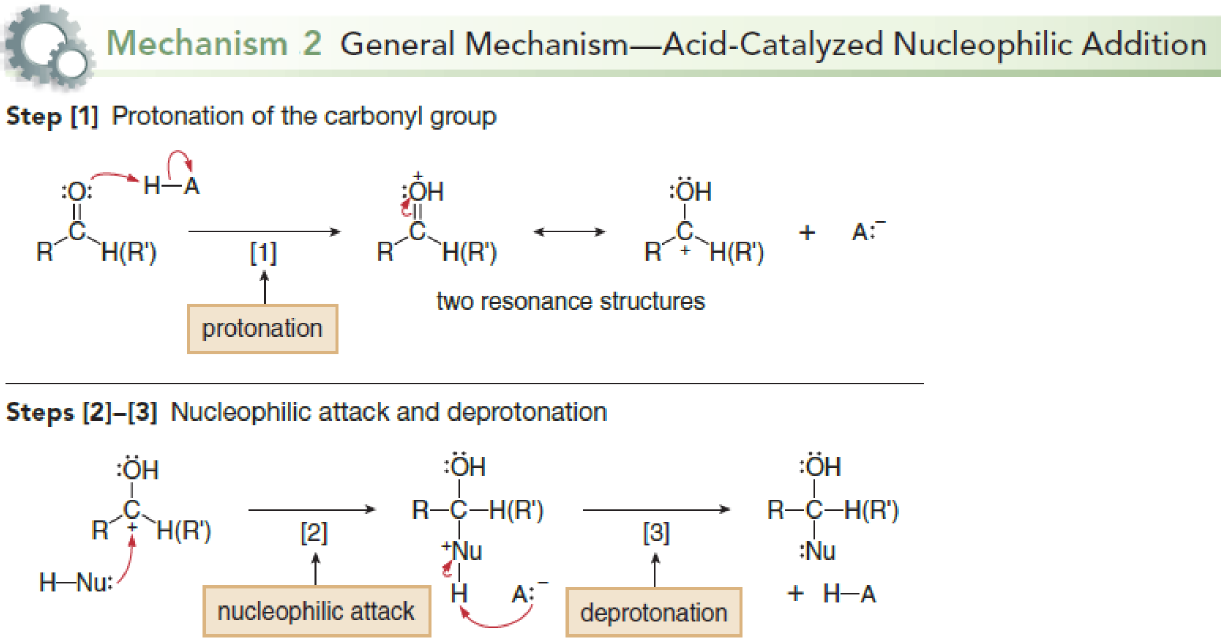
Mechanism General Mechanism—Nucleophilic Addition



Protonation of the carbonyl oxygen forms a resonance-stabilized cation that bears a full positive charge.

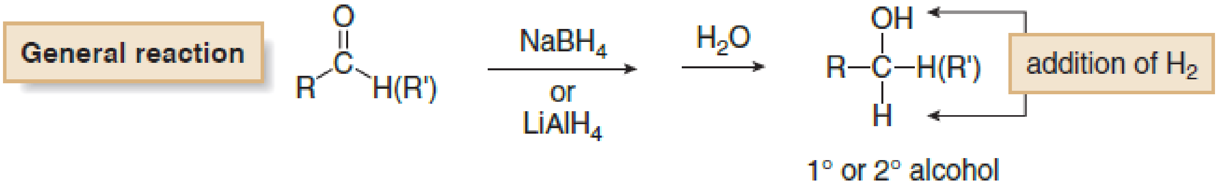
In Step [2], the nucleophile attacks, and then deprotonation forms the neutral addition product in Step [3].

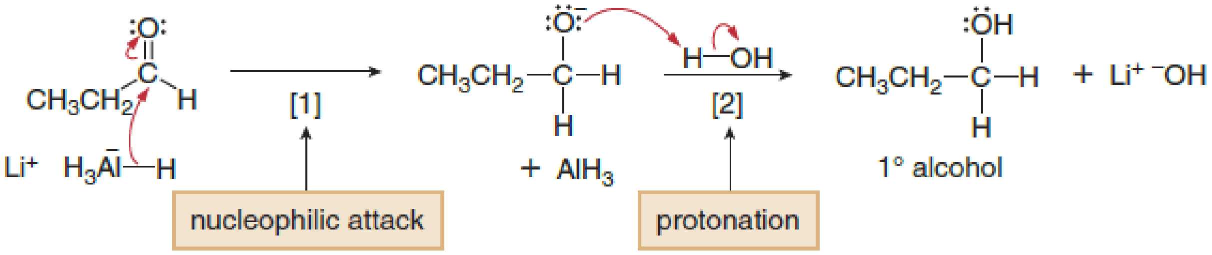
- The overall result is the addition of H and Nu to the carbonyl group.



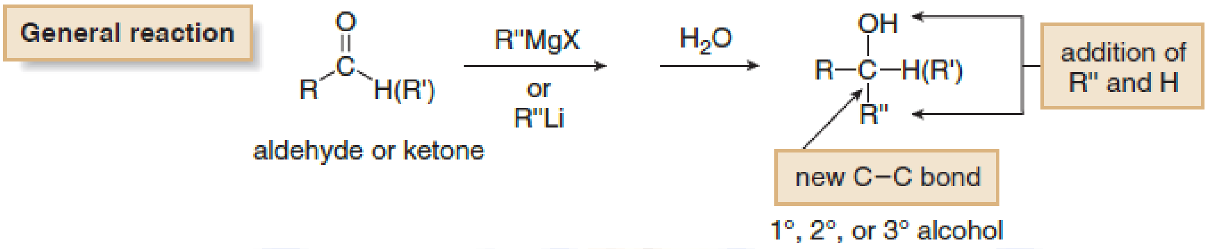
Nucleophilic Addition of H– and R–

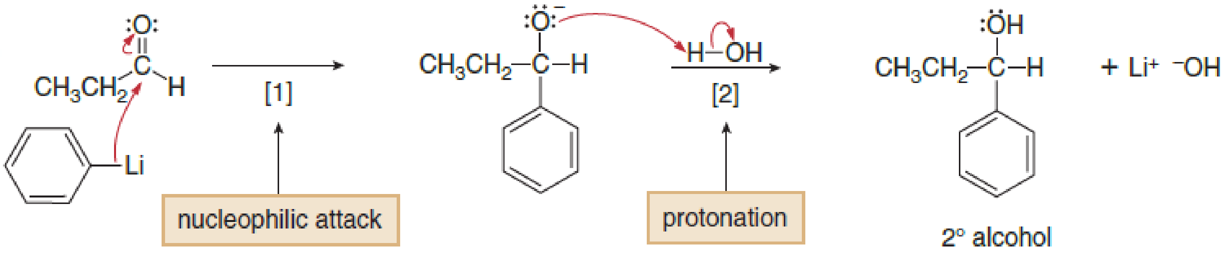
Treatment of an aldehyde or ketone with either NaBH4 or LiAlH4 followed by protonation forms a 1° or 2° alcohol. NaBH4 and LiAlH4 serve as a source of hydride, H:–the nucleophile—and the reaction results in addition of the elements of H2 across the C – O π bond. Addition of H2 reduces the carbonyl group to an alcohol.



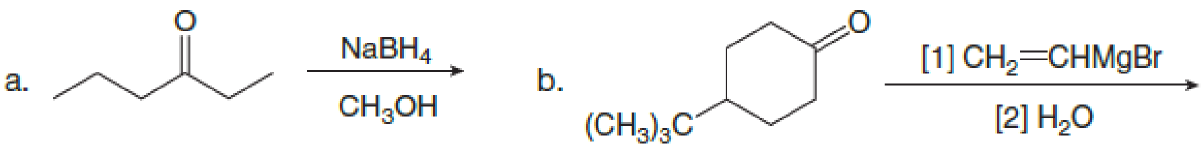


Treatment of an aldehyde or ketone with either an organolithium (R"Li) or Grignard reagent (R"MgX) followed by water forms a 1°, 2°, or 3° alcohol containing a new carbon– carbon bond. R"Li and R"MgX serve as a source of a carbanion (R")——the nucleophile—and the reaction results in addition of the elements of R" and H across the C – O π bond.

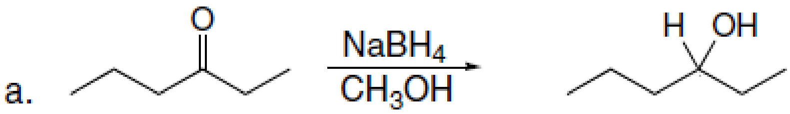


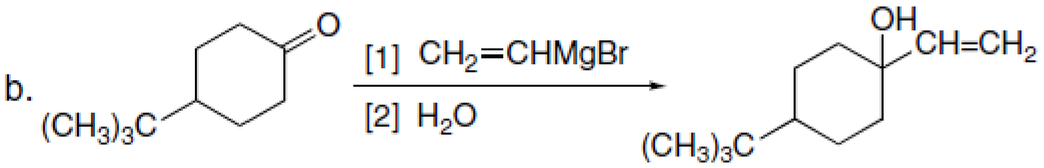


Problem Draw the products of each reaction.



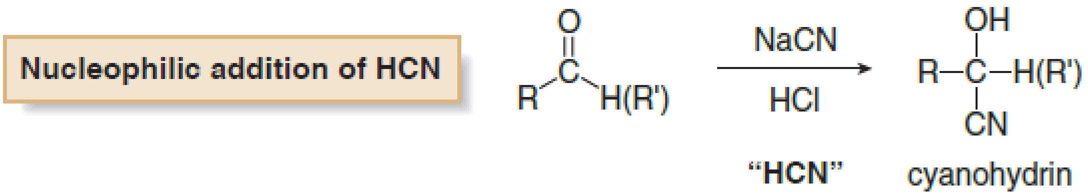
Solution:-

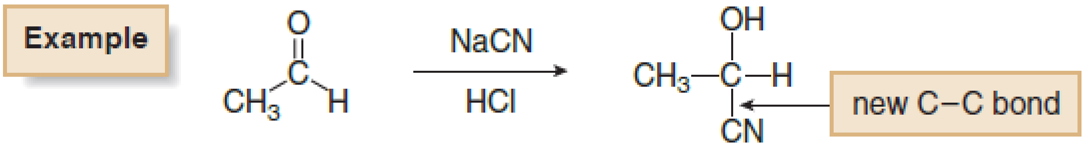




Nucleophilic Addition of CN-

Treatment of an aldehyde or ketone with NaCN and a strong acid such as HCl adds the elements of HCN across the carbon–oxygen π bond, forming a cyanohydrin.

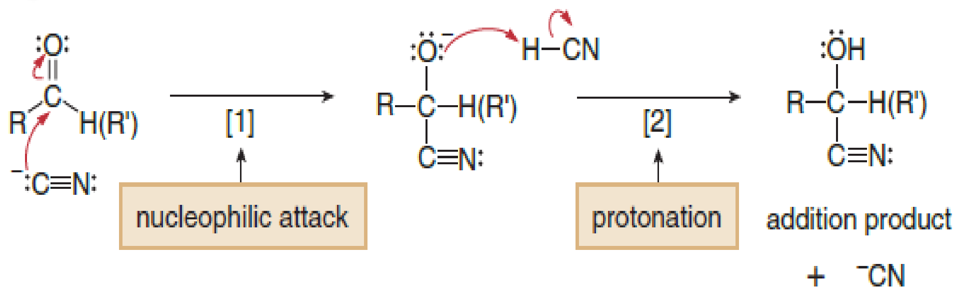




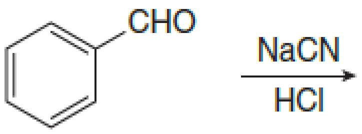
In Step [1], nucleophilic attack of –CN forms a new carbon–carbon bond with cleavage of the C – O π bond.

•In Step [2], protonation of the negatively charged O atom by HCN forms the addition product. The hydrogen cyanide (HCN) used in this step is formed by the acid–base reaction of cyanide (–CN) with the strong acid, HCl.

Mechanism Nucleophilic Addition of ⁻CN—Cyanohydrin Formation



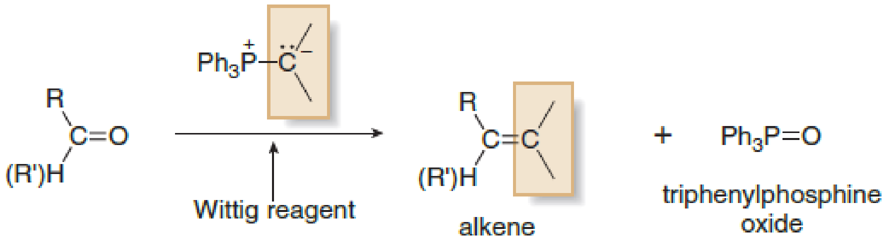
Problem Draw the products of reaction.

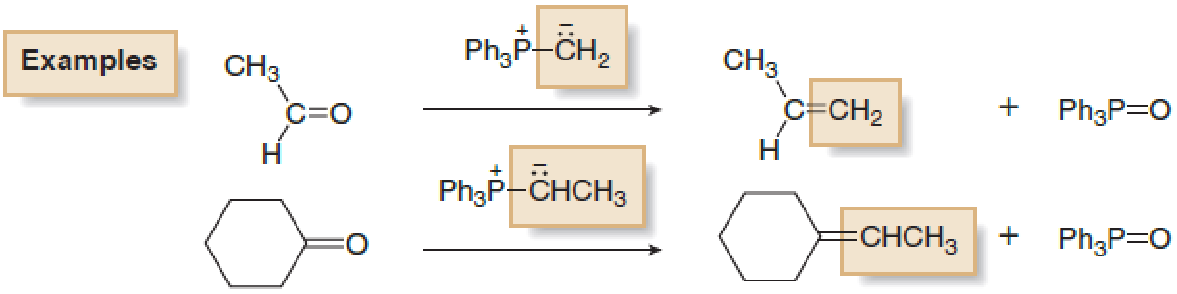


The Wittig Reaction

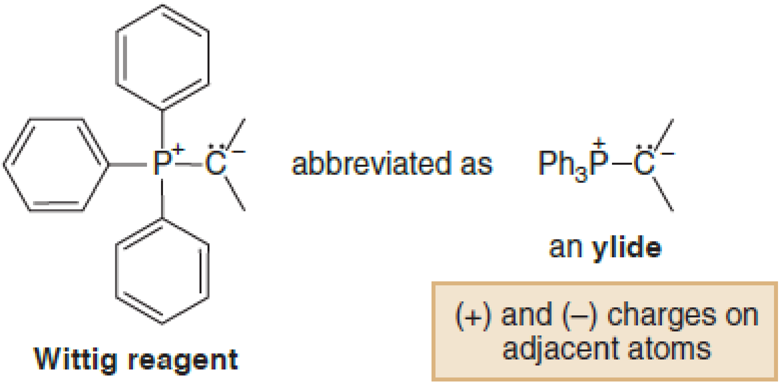
The additions of H–, R–, and –CN all involve the same two steps nucleophilic attack followed by protonation. Although they still involve attack of a nucleophile, the initial addition adduct is converted to another product by one or more reactions.

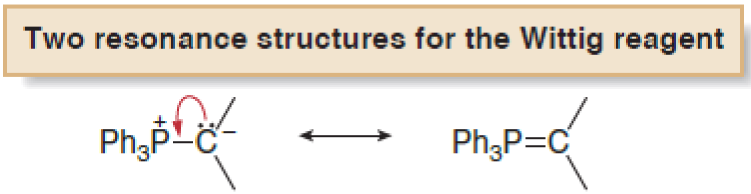
The Wittig reaction





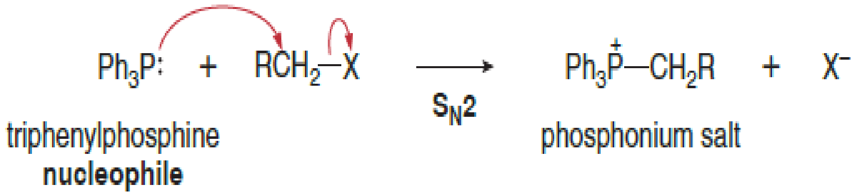
Wittig reagents



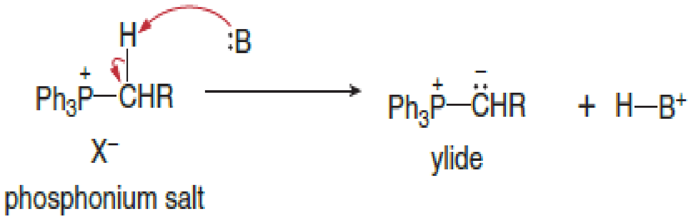


Wittig reagents are synthesized by a two-step procedure.

Step [1] S_N2 reaction of triphenylphosphine with an alkyl halide forms a phosphonium salt.



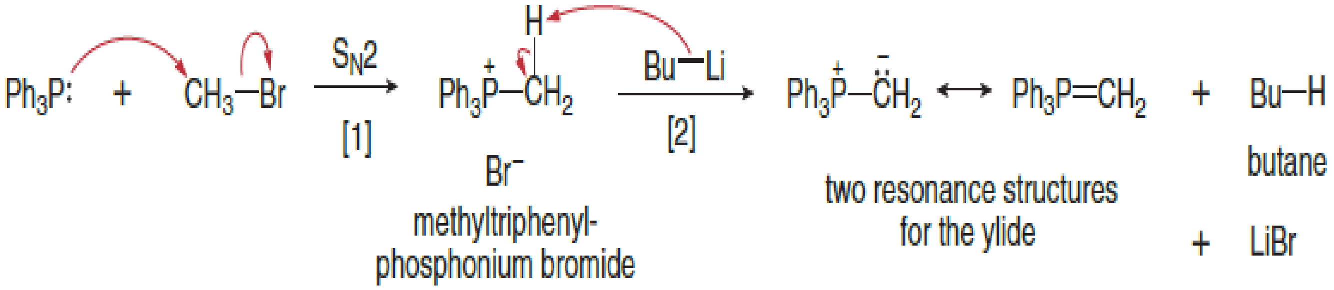
Step [2] Deprotonation of the phosphonium salt with a strong base (:B) forms the ylide.



Typical strong base:

$CH_3CH_2CH_2CH_2-Li$

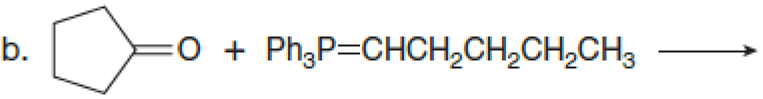
Bu—Li



- Step [1] Form the phosphonium salt by S_N2 reaction of Ph_3P: and CH_3Br.
- Step [2] Form the ylide by removal of a proton using BuLi as a strong base.

Problem Draw the products of the following Wittig reactions.

a. $(CH_3)_2C=O + Ph_3P=CH_2 \longrightarrow$

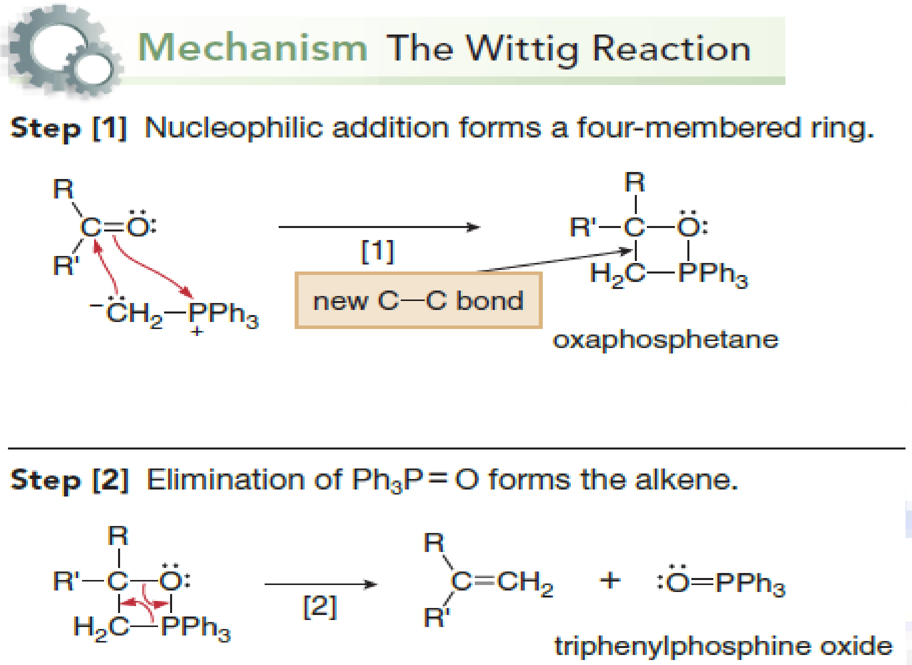
b. 

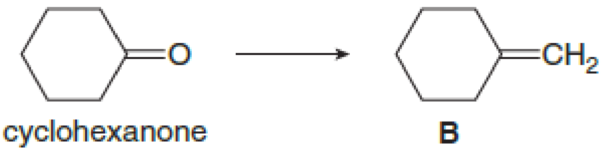
Mechanism of the Wittig Reaction

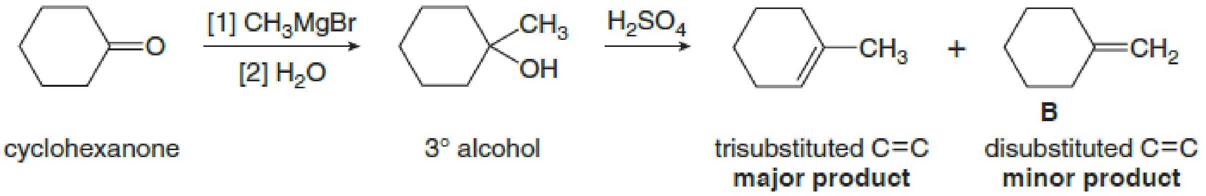
Step [1] forms two bonds and generates a four-membered ring. The negatively charged carbon atom of the ylide attacks the carbonyl carbon to form a new carbon–carbon σ bond, while the carbonyl O atom attacks the positively charged P atom.

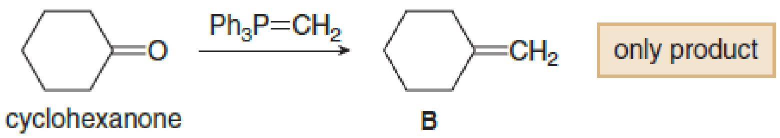
- This process generates an oxaphosphetane, a four-membered ring containing a strong P – O bond.

In Step [2], Ph3P=O (triphenylphosphine oxide) is eliminated, forming two new π bonds. The formation of the very strong P – O double bond provides the driving force for the Wittig reaction.

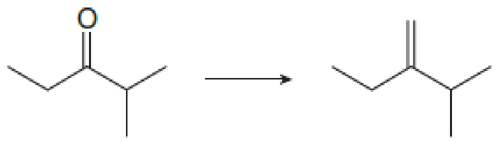


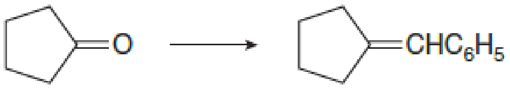






Problem Show two methods to synthesize each alkene: a one-step method using a Wittig reagent, and a two-step method that forms a carbon–carbon bond with an organometallic reagent in one of the steps.

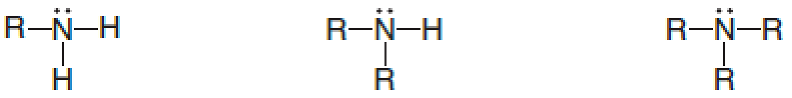
a. 

b. 

Addition of 1° Amines

We now move on to the reaction of aldehydes and ketones with nitrogen and oxygen hetero atoms.

Amines, for example, are organic nitrogen compounds that contain a nonbonded electron pair on the N atom. Amines are classified as 1°, 2°, or 3° by the number of alkyl groups bonded to the nitrogen atom.



1° amine
(1 R group on N)

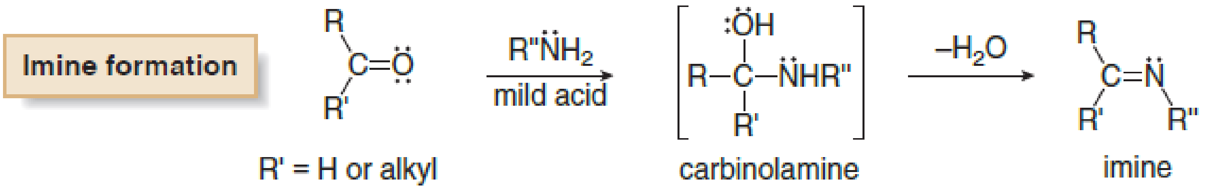
2° amine
(2 R groups on N)

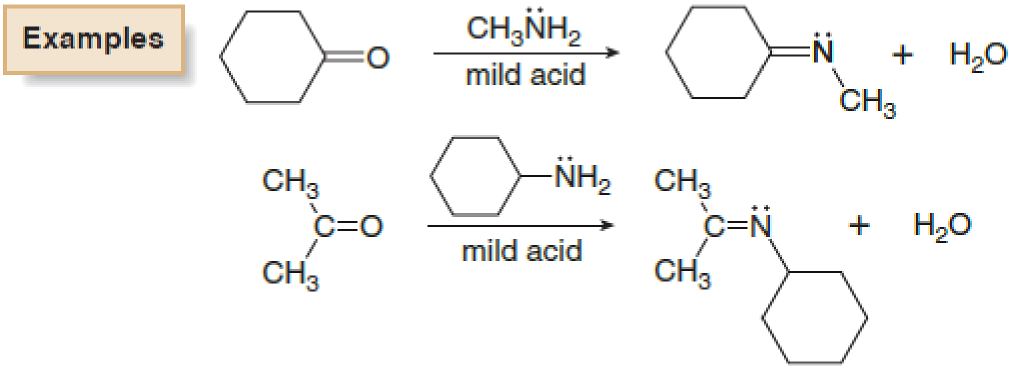
3° amine
(3 R groups on N)

Formation of Imines

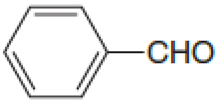
Treatment of an aldehyde or ketone with a 1° amine affords an imine (also called a Schiff base).

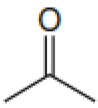
Nucleophilic attack of the 1° amine on the carbonyl group forms an unstable carbinolamine, which loses water to form an imine. The overall reaction results in replacement of C=O by C=NR.

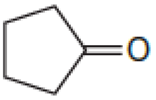




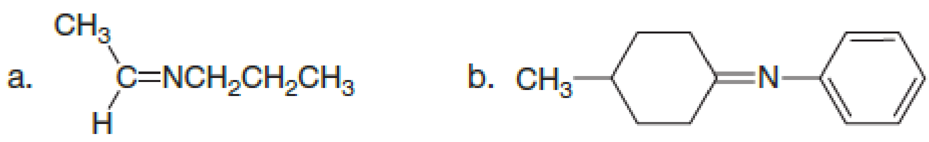
Problem Draw the product formed when CH3CH2CH2CH2NH2 reacts with each carbonyl compound in the presence of mild acid.

a. 

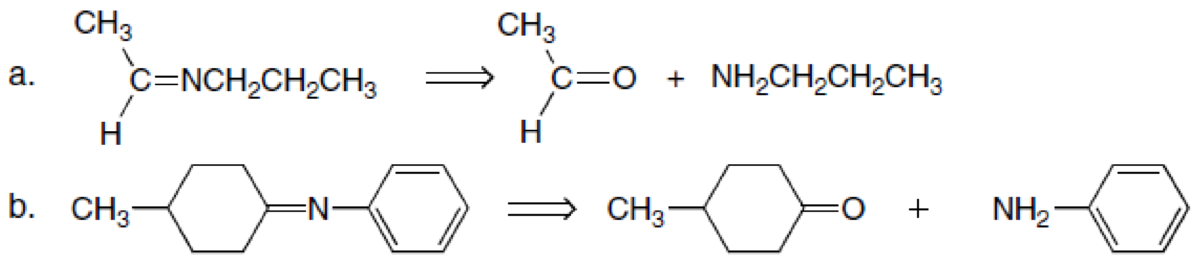
b. 

c. 

Problem What 1° amine and carbonyl compound are needed to prepare each imine?



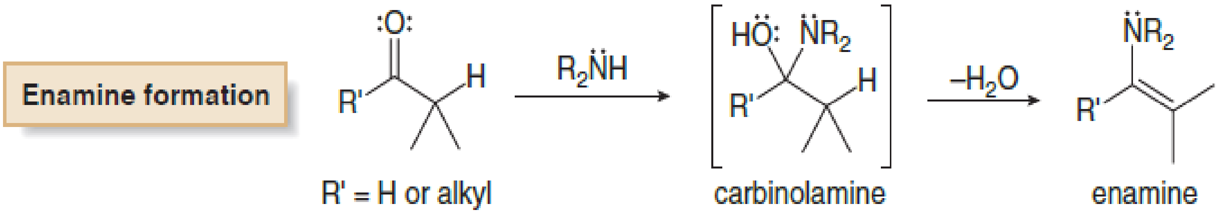
Solution:-

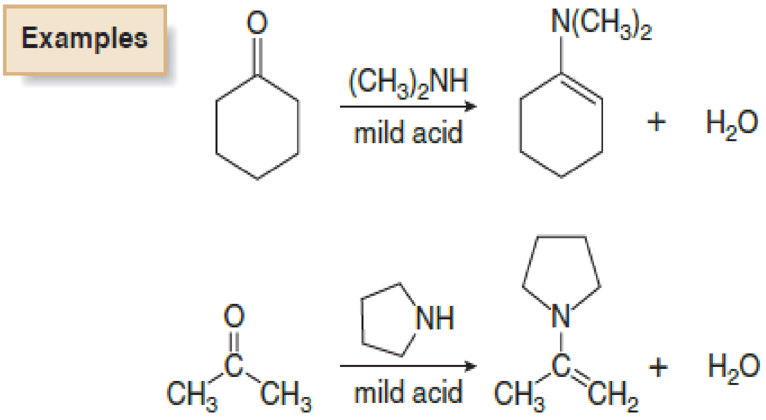


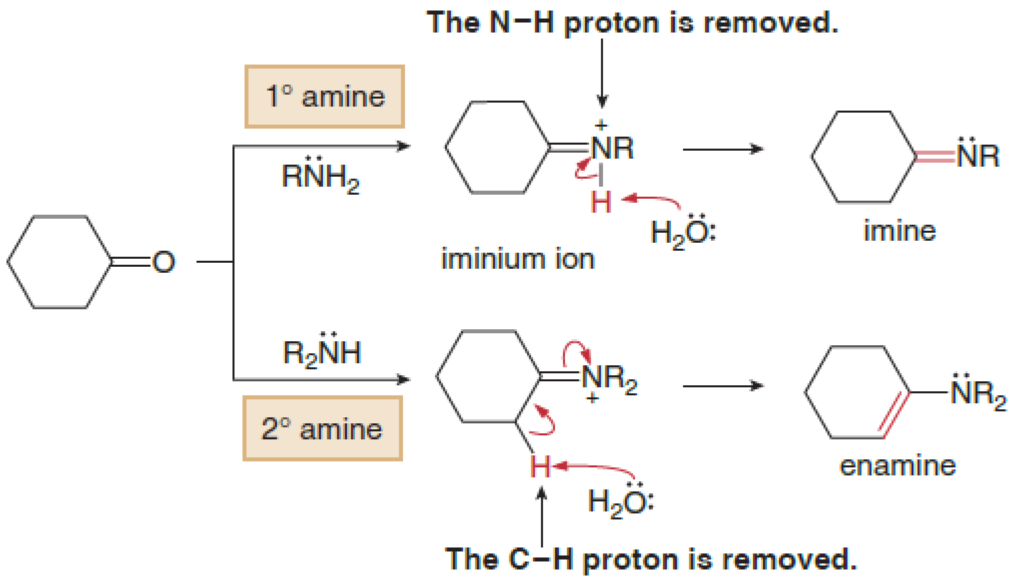
Addition of 2° Amines

Formation of Enamines

A 2° amine reacts with an aldehyde or ketone to give an enamine. Enamines have a nitrogen atom bonded to a double bond (alkene + amine = enamine).







•With a 1° amine, the intermediate iminium ion still has a proton on the N atom that may be removed to form a C=N.

•With a 2° amine, the intermediate iminium ion has no proton on the N atom. A proton must be removed from an adjacent C – H bond, and this forms a C=C.

Problem What two enamines are formed when 2-methylcyclohexanone is treated with (CH3)2NH?

Solution:-