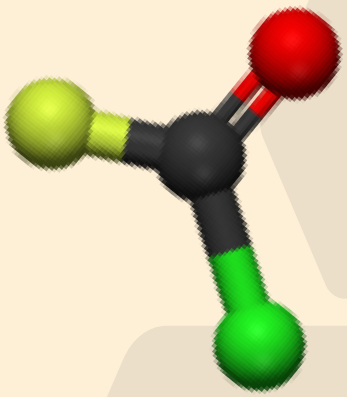
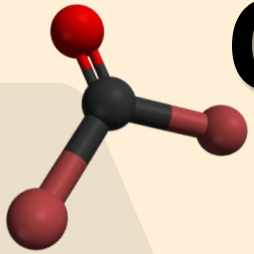
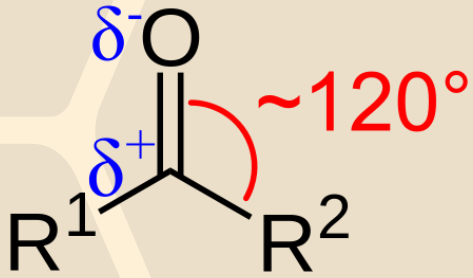






CHAPTER 9 : CARBONYL COMPOUNDS

9.1 Introduction

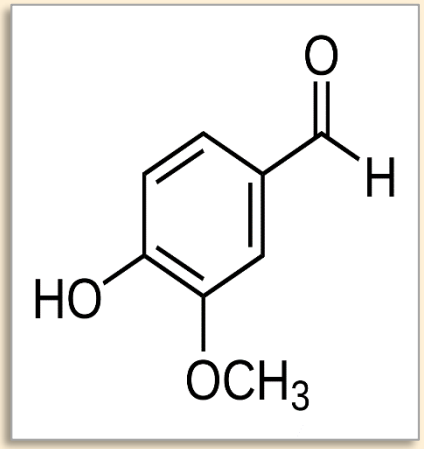
9.2 Nomenclature

9.3 Preparation

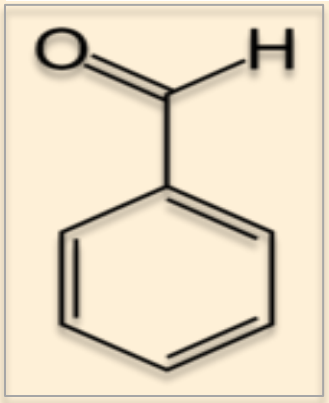
9.4 Chemical Properties

9.1 Introduction – Carbonyl compounds in daily life

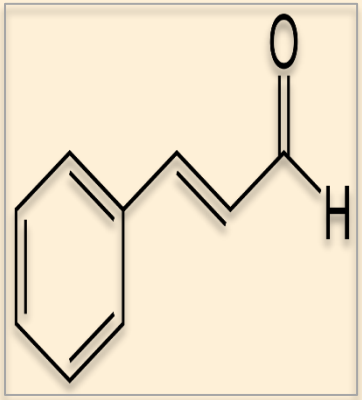
Vanilla beans:
Vanilin



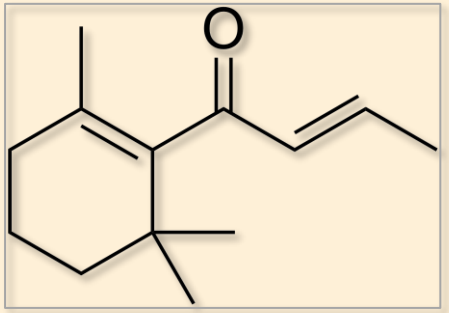
Bitter almonds
benzaldehyde



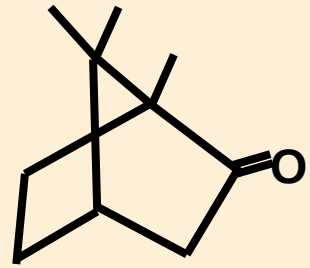
Cinnamon
cinnamaldehyde



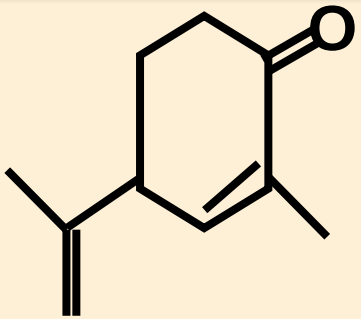
Odor of roses
α-damascone



9.1 Introduction



camphor



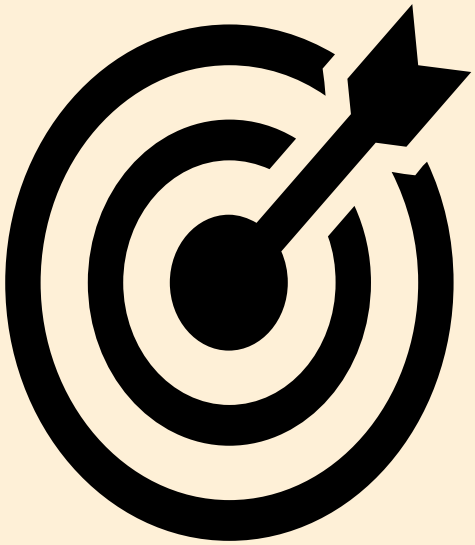
carvone

FORMALIN

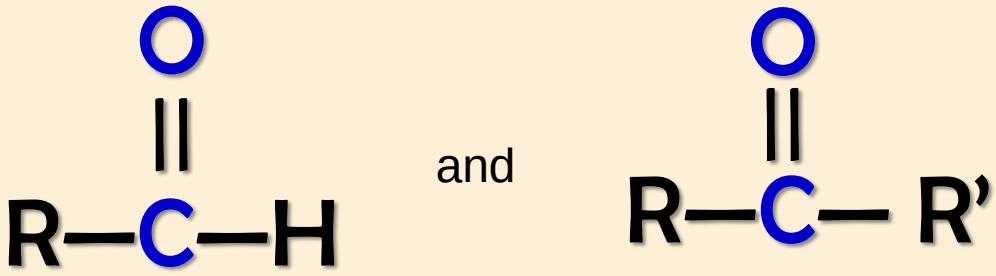
aqueous solution of 37% formaldehyde (by mass)

Learning Outcomes:

9.1 **a)**



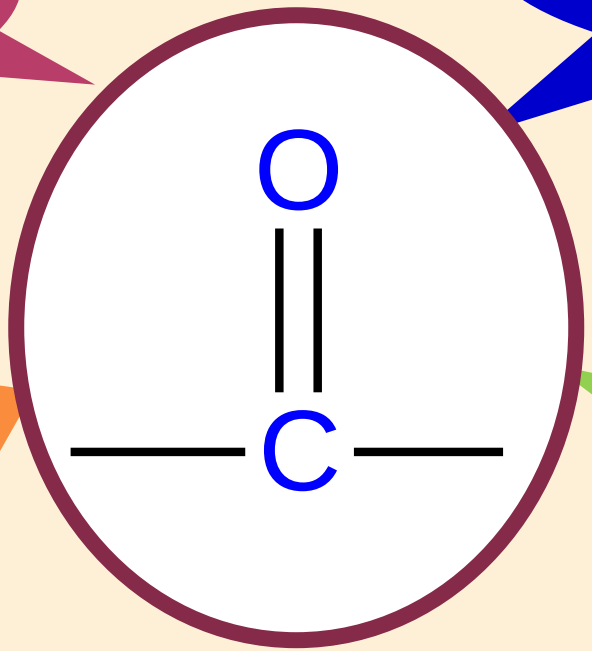
State the general formula of aldehyde and ketones:



9.1 Introduction

General formula: $C_nH_{2n}O$

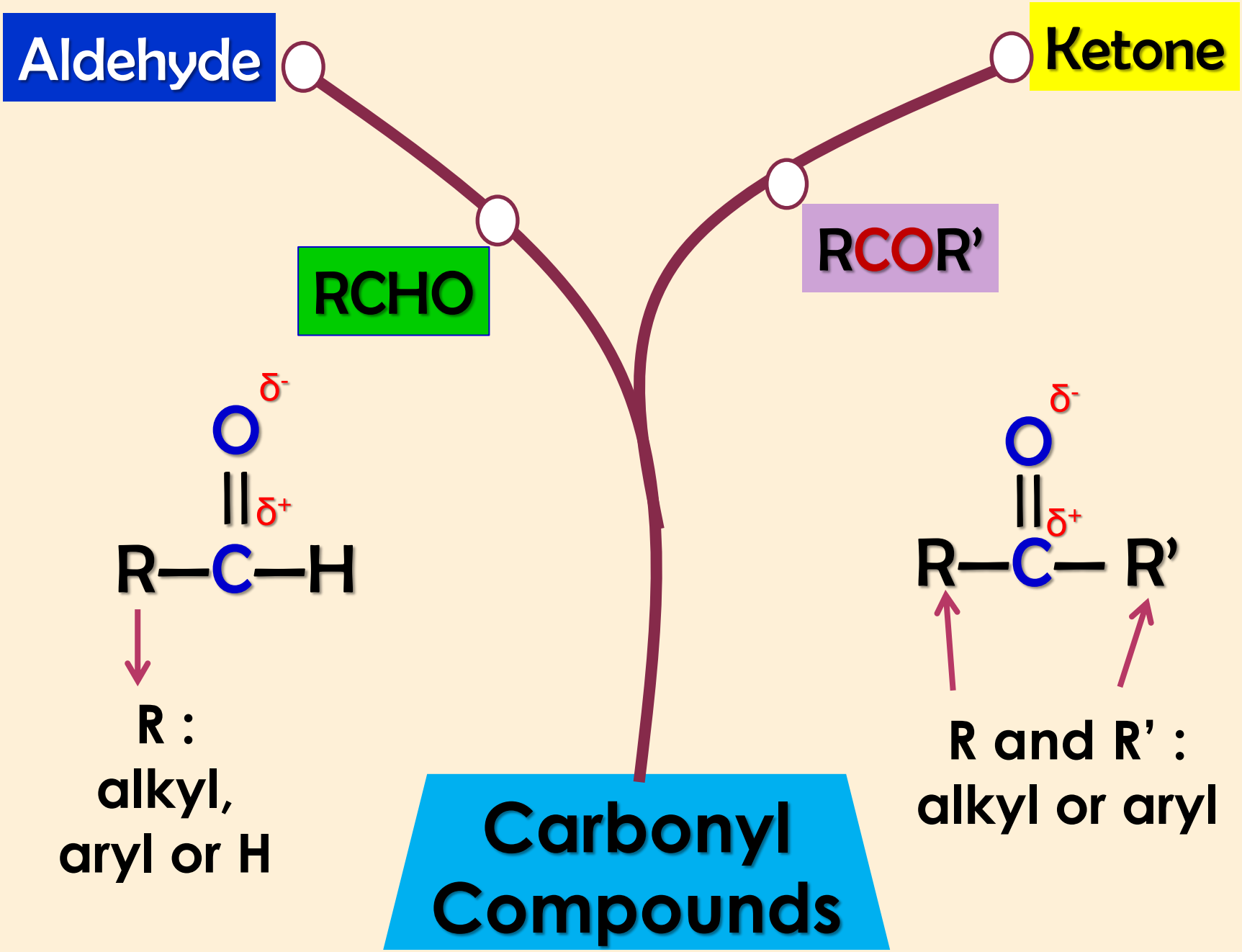
Aldehyde & Ketone are isomeric



aldehyde is more reactive than ketone towards nucleophilic addition reaction

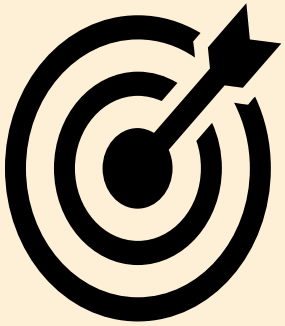
polar compound

Functional group: Carbonyl


Aldehyde
Ketone
RCHO
RCOR'
δ-
O
δ+
R—C—H
δ-
O
δ+
R—C— R'
R :
alkyl,
aryl or H
R and R' :
alkyl or aryl
Carbonyl
Compounds

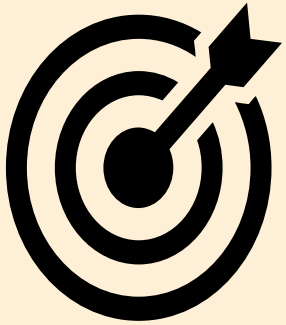
Learning Outcomes:

9.1 b)



Give name for aldehydes and ketones according to the IUPAC nomenclature.

9.1 c)



Give the structures for aldehydes and ketones in 9.1 b) (parent chain ≤ C_{10})

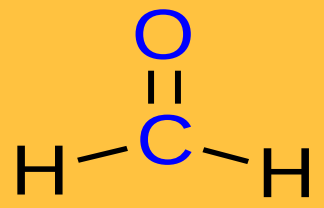
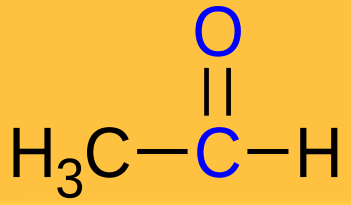
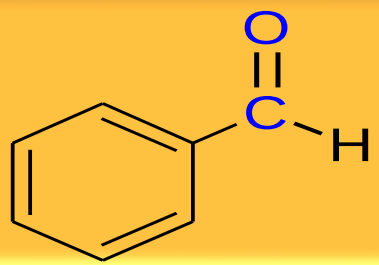
9.1 Nomenclature Aldehyde

ALDEHYDE is named by substituting the letter –e of the corresponding alkane with -al.

BASIC NAME depends on the longest chain with –CHO group.

The **CHAIN** is **NUMBERED** by starting with –CHO group as C_1.

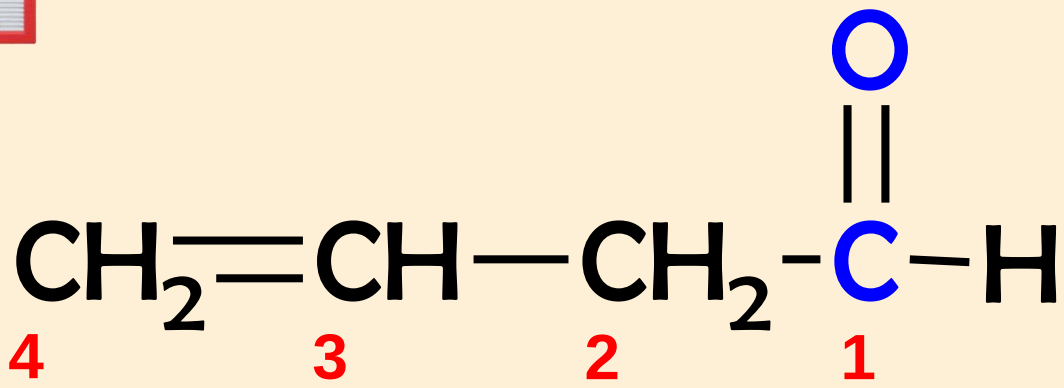
SIMPLE ALDEHYDE

Structure	IUPAC name	Common name
	Methanal	Formaldehyde
	Ethanal	Acetaldehyde
	phenylmethanal	benzenecarbaldehyde (benzaldehyde)

ALDEHYDE

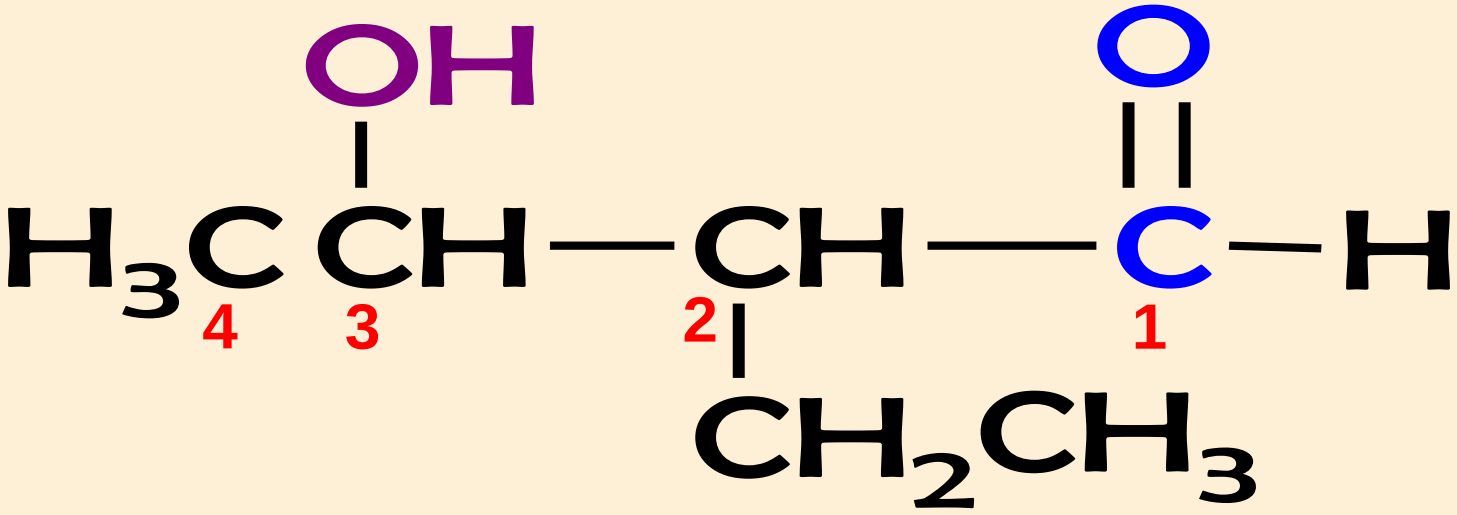
The chain is <u>numbered</u> by starting with –CHO group as C_1.

Example : 1



3-butenal

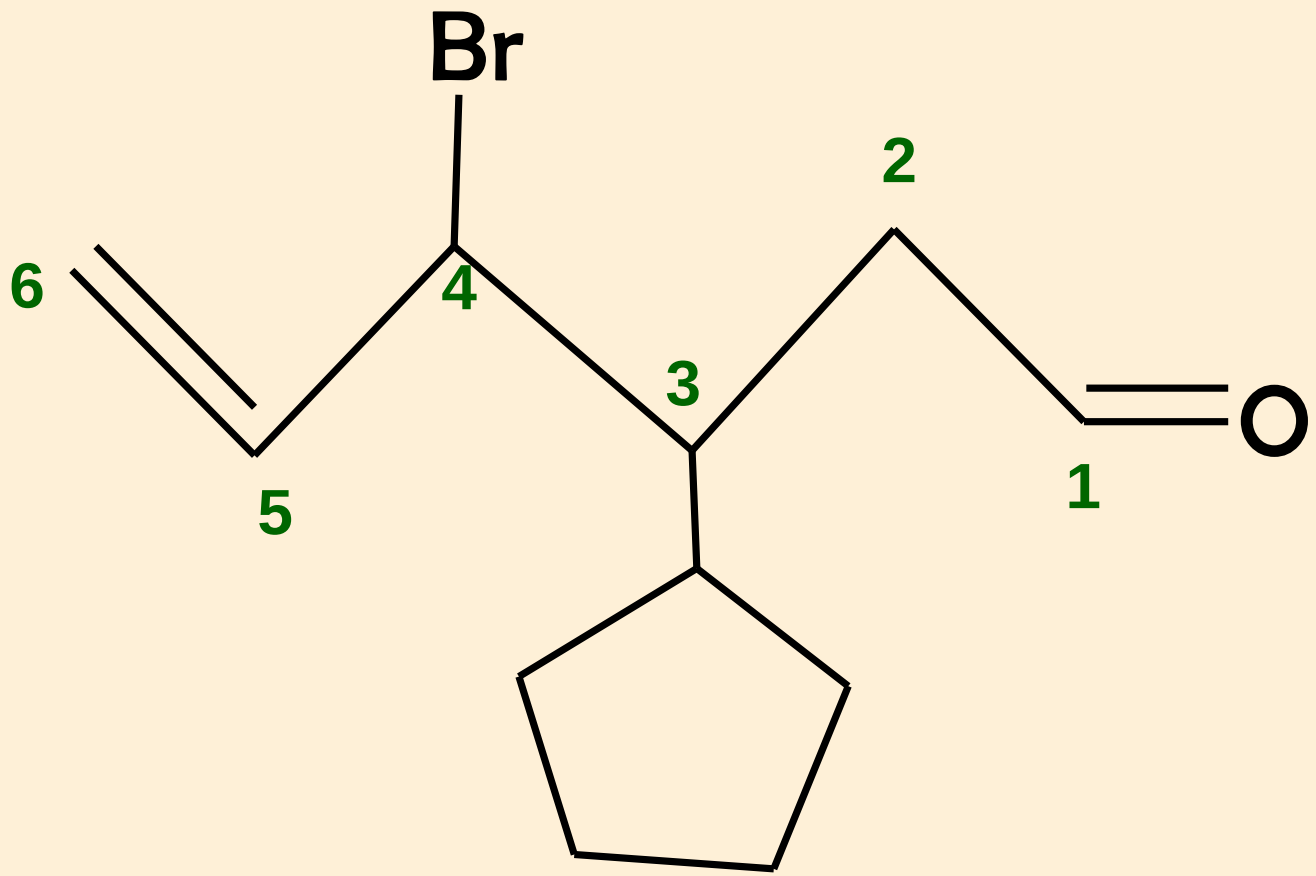
Example : 2



2-ethyl-3-hydroxybutanal

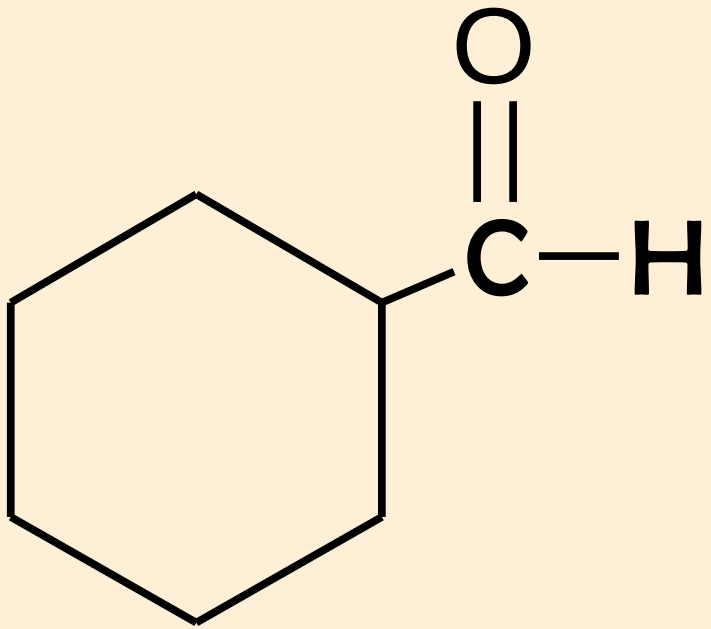
*alphabetical order; e followed by h

Example : 3



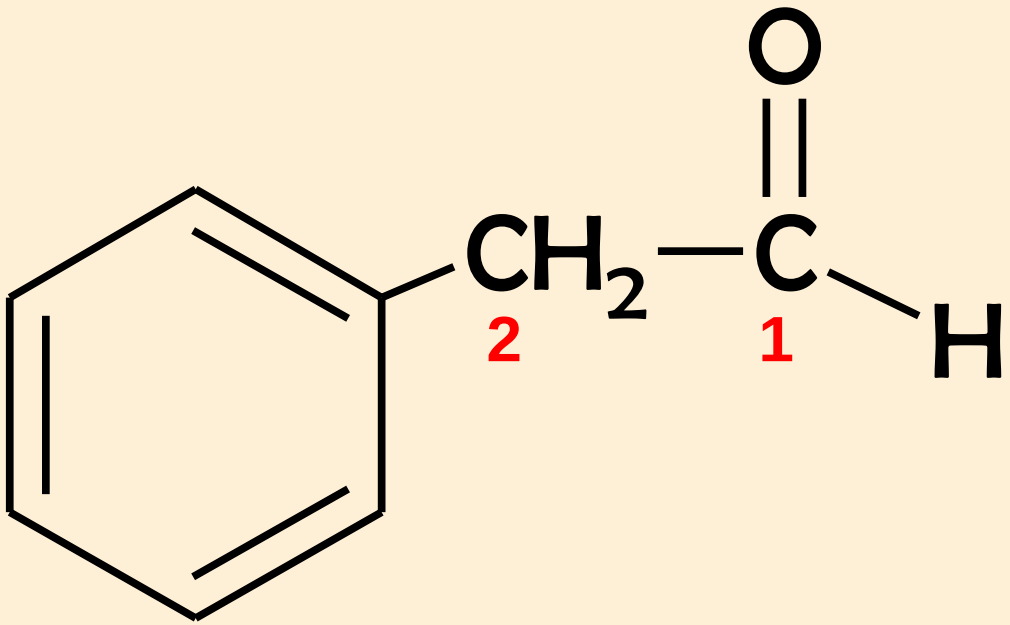
4-bromo-3-cyclopentylhex-5-enal

Example : 4



cyclohexane carbaldehyde

Example : 5



2-phenylethanal

9.1 Nomenclature Ketone

KETONE is named by substituting the letter **–e** of the corresponding alkane with **–one.**

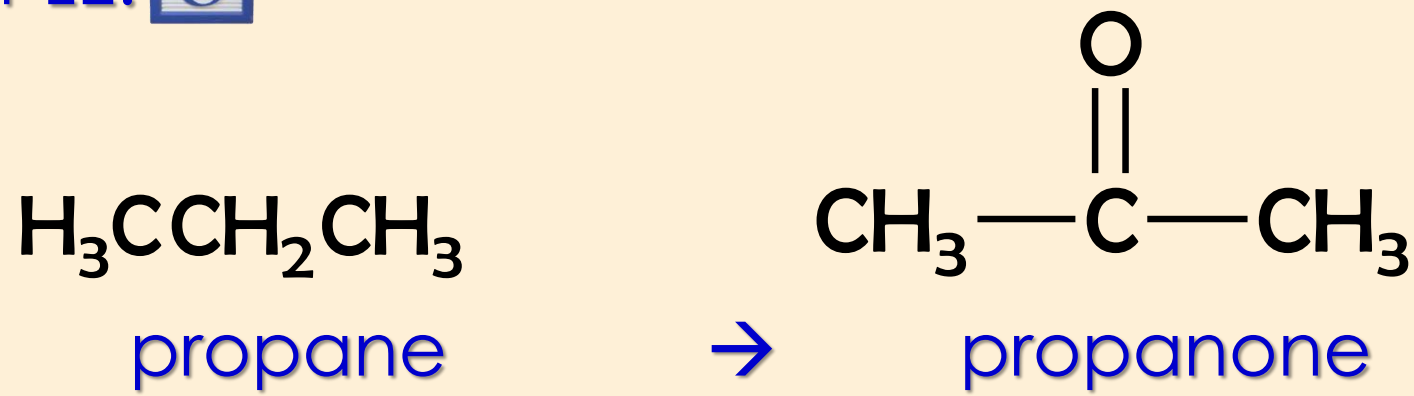
BASIC NAME depends on the **longest chain with carbonyl group.**

Chain is numbered in the way that gives the carbonyl carbon atom the **lower possible number**, this number is used to designated its position.

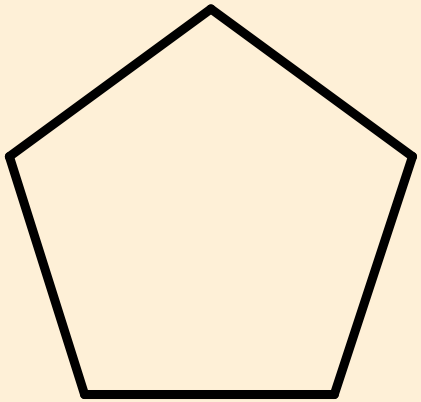
Common functional group names for ketones separately naming the two groups attached to carbonyl group and adding the word ketone as a separate word.

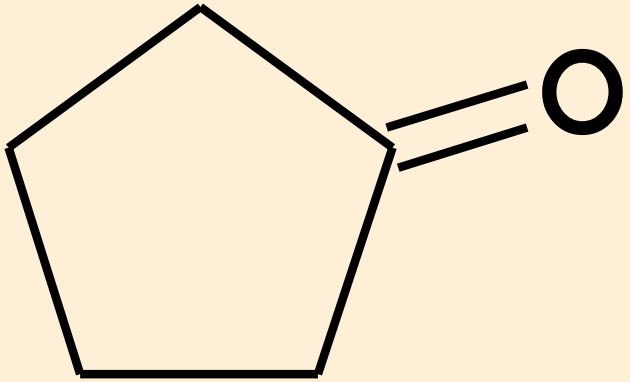
KETONE

EXAMPLE: 6



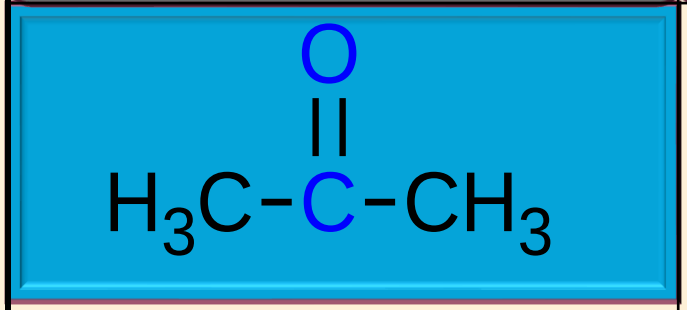
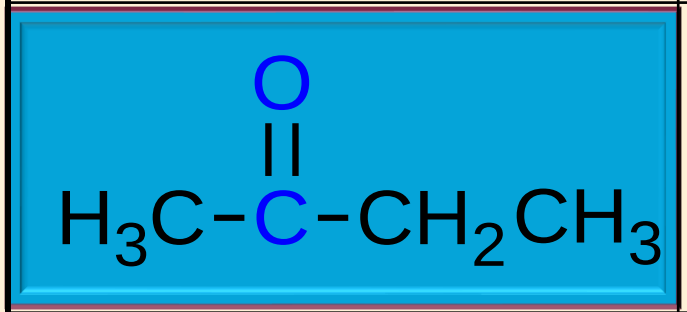
EXAMPLE: 7



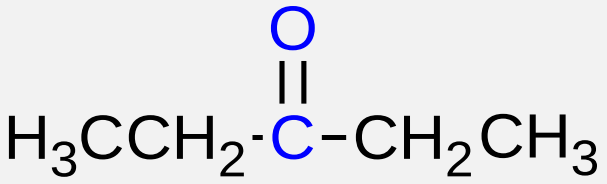
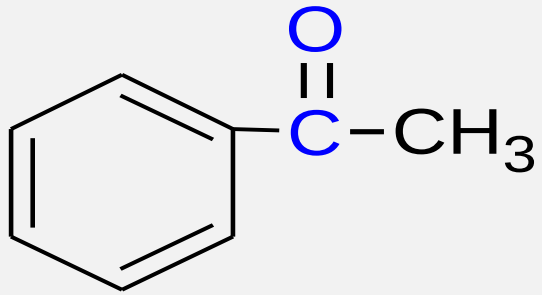
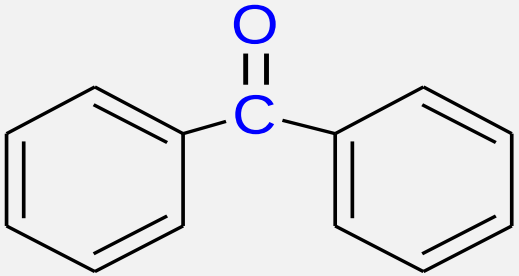


cyclopentane → cyclopentanone

SIMPLE KETONE

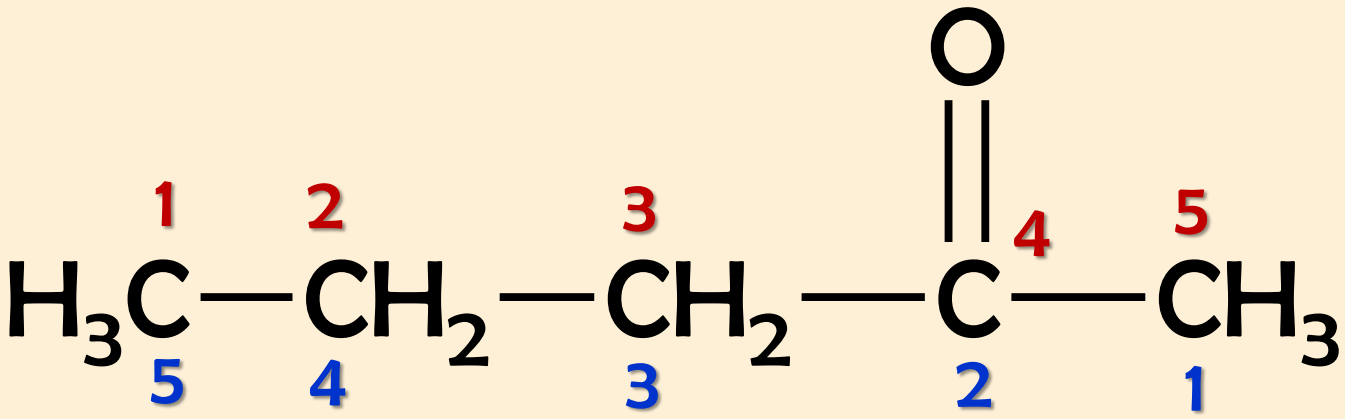
Structure	IUPAC name	Common name
	propanone	Acetone
	butanone	ethyl methyl ketone
	pentan-2-one @ 2-pentanone	Methyl propyl ketone

SIMPLE KETONE

Structure	IUPAC name	Common name
	pentan-3-one @ 3-pentanone	Diethyl ketone
	phenylethanone	Acetophenone (methyl phenyl ketone)
	diphenylmethanone Benzophenone (diphenyl ketone)	

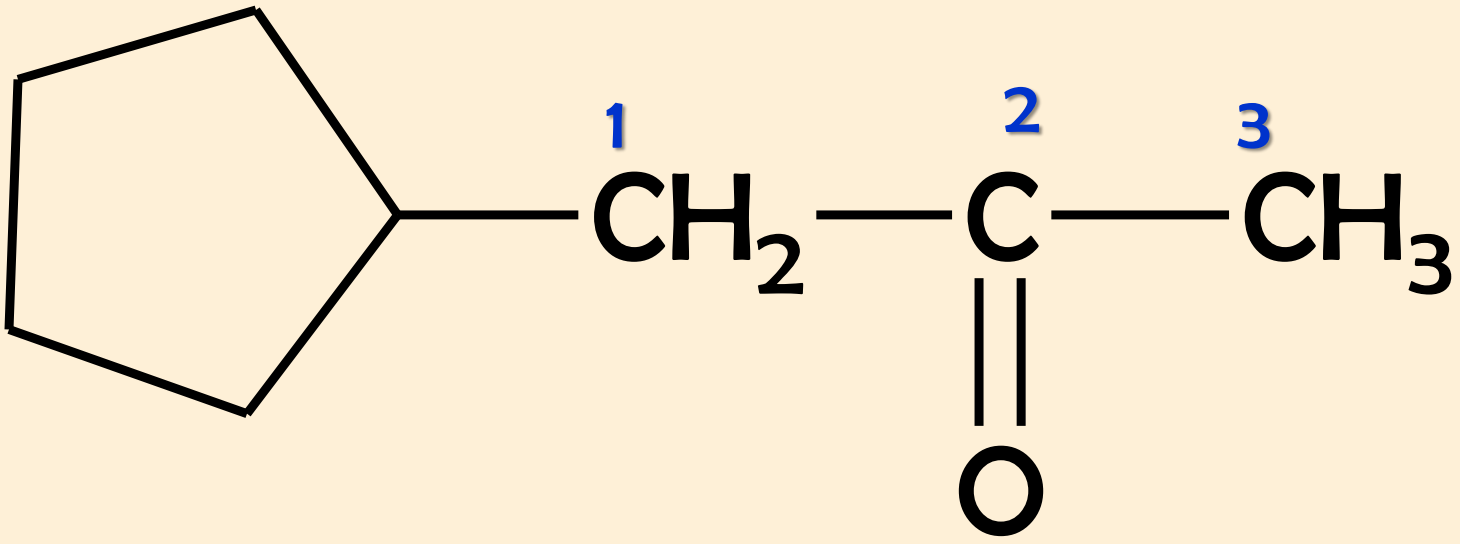
The longest chain with carbonyl group is numbered so that C in carbonyl group gets the smallest number.

EXAMPLE: 8



pentan-2-one or **2-pentanone**

EXAMPLE: 9

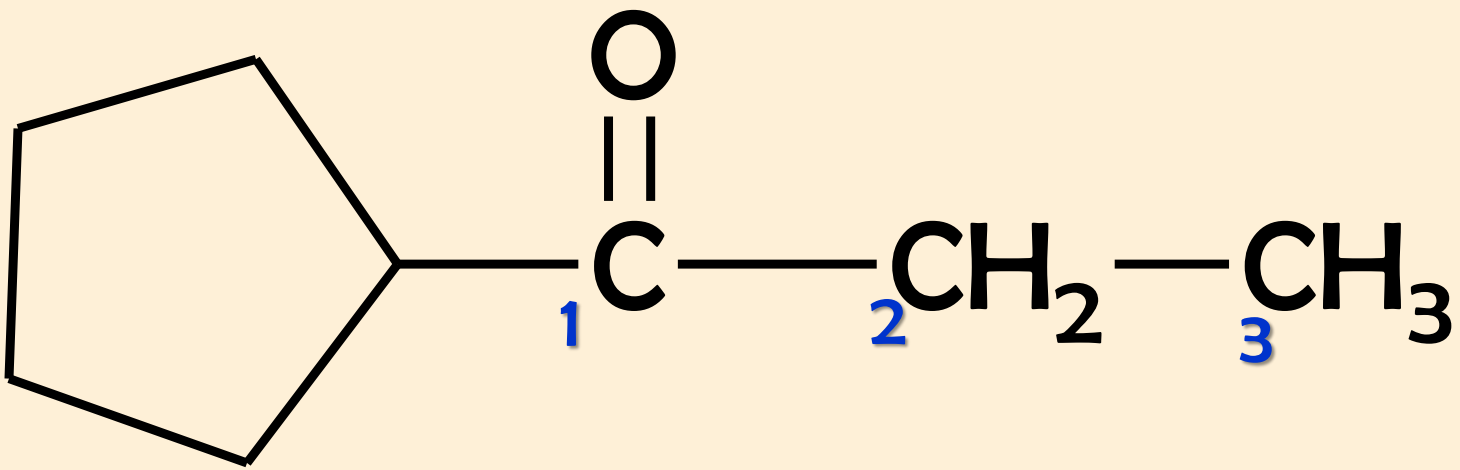


1-cyclopentylpropan-2-one

@ 1-cyclopentyl-2-propanone

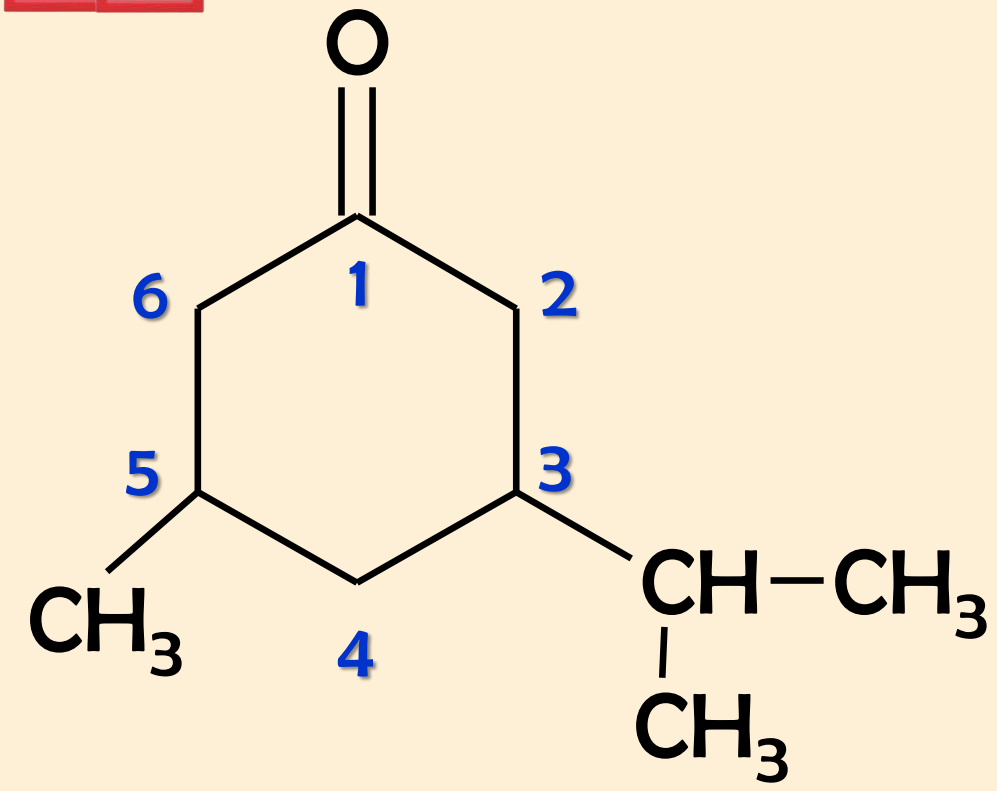
Refer : pg 808, Wade., Organic Chemistry, 17th Ed, Prentice Hall

EXAMPLE: 10



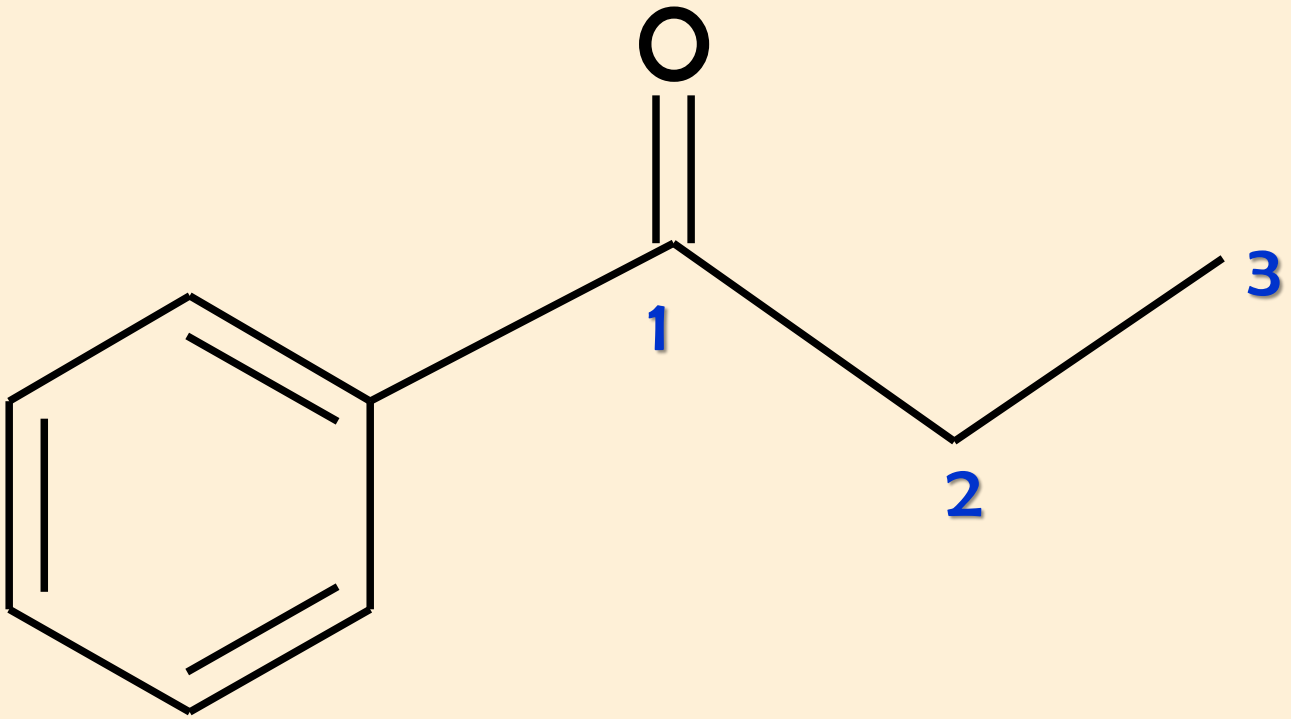
1-cyclopentylpropan-1-one

EXAMPLE: 11



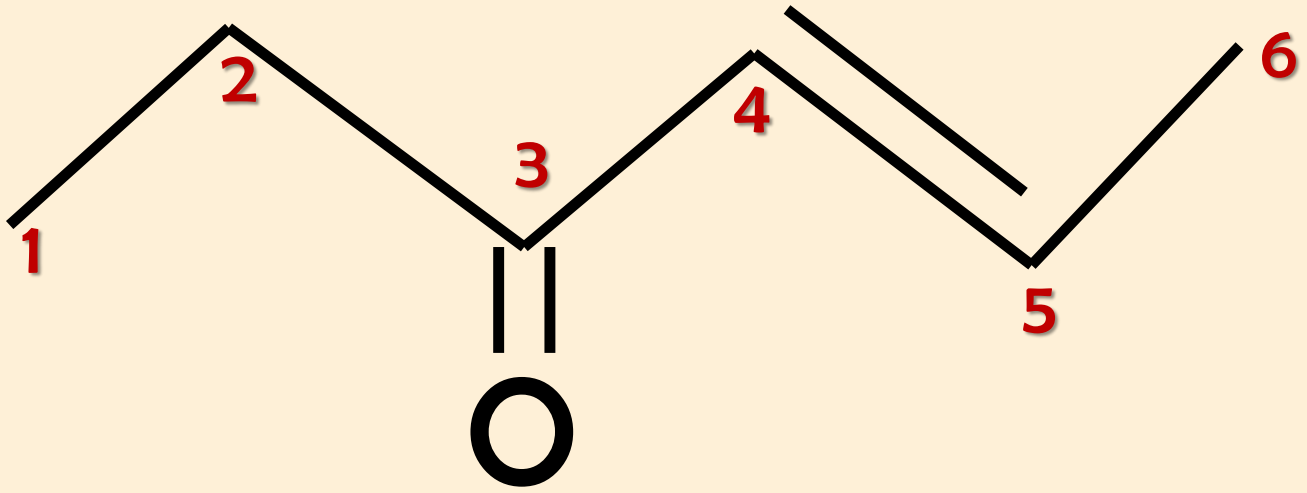
3-isopropyl -5-methylcyclohexanone

EXAMPLE: 1 2



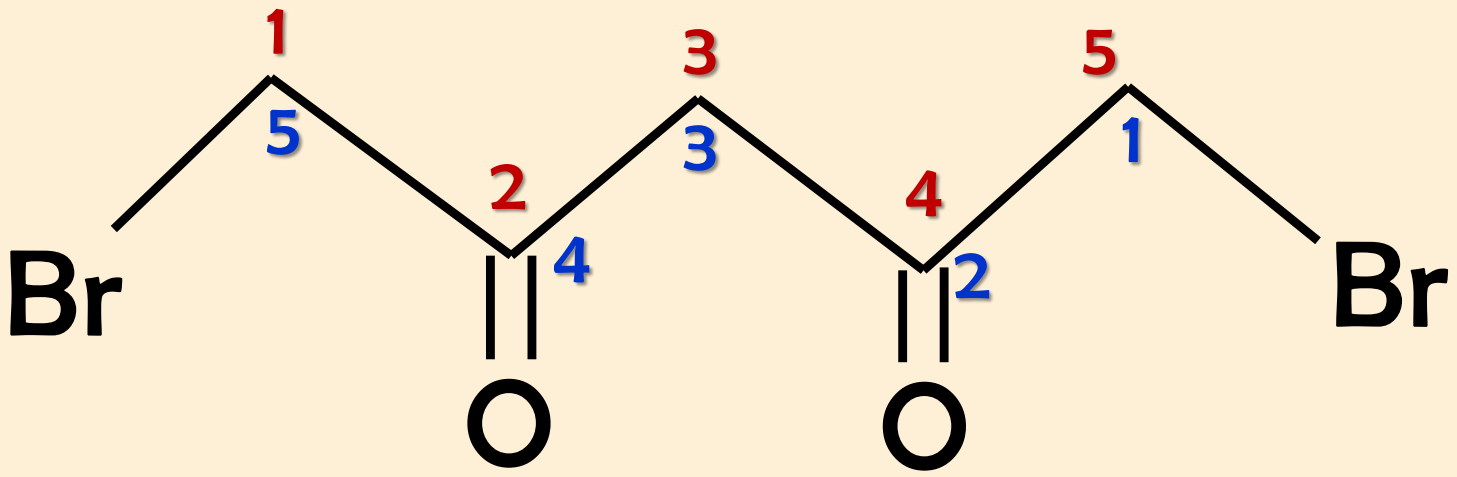
1-phenylpropan-1-one

EXAMPLE: 13



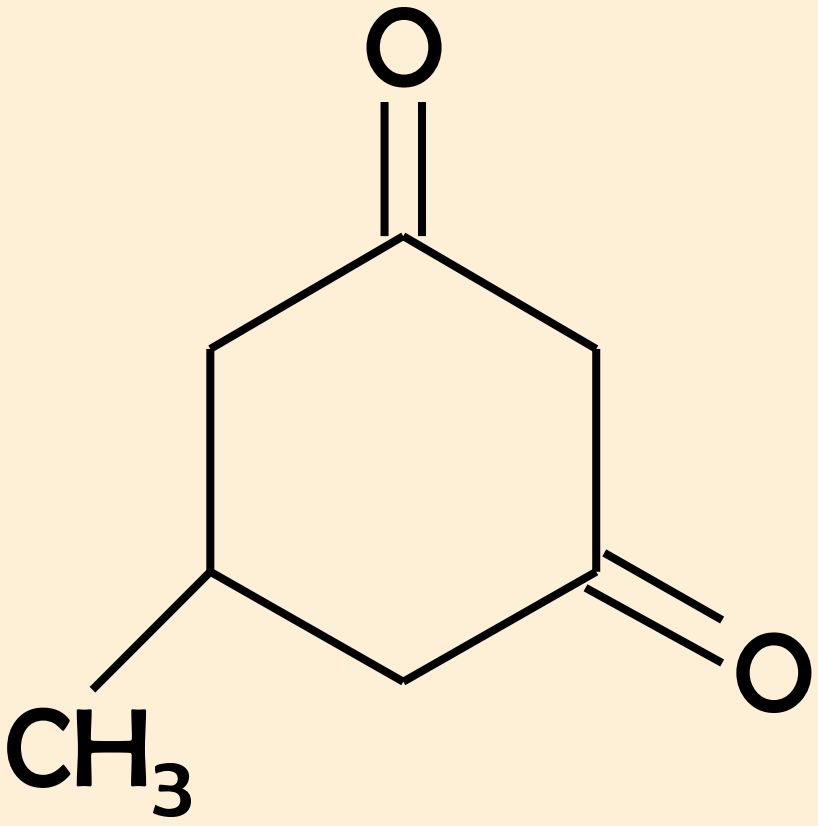
hex-4-en-3-one @ 4-hexene-3-one

EXAMPLE: 14



1,5-dibromopentan-2,4-dione

EXAMPLE: 15



5-methyl cyclohexan-1,3-dione

Exercise:

Draw all structural formulae for carbonyl compounds with molecular formula $C_5H_{10}O$ and give the IUPAC name.

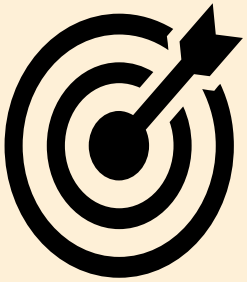
(Hint : 7 possible carbonyl structures)

Answer : Possible structural formulae:

1) **Pentanal**
2) **3-methylbutanal**
3) **2-methylbutanal**
4) **2,2-dimethylpropanal**
5) **2-pentanone**
6) **3-pentanone**
7) **3-methyl-2-butanone**

Learning Outcomes:

9.2 a) Preparation



Explain the preparation of carbonyl compounds through:

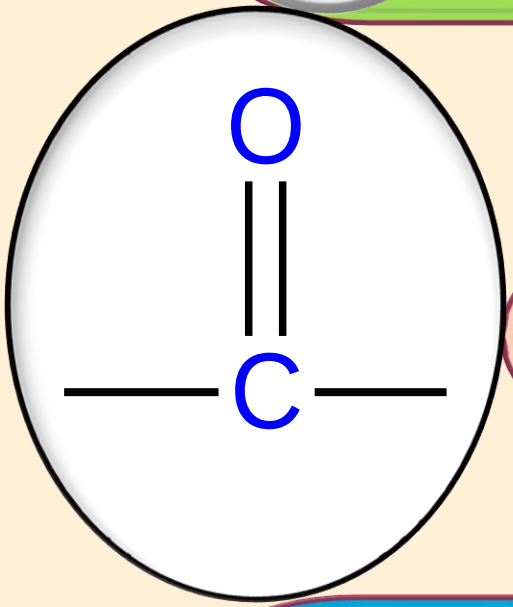
i. Ozonolysis of alkene.

ii. Friedel-Crafts acylation to produce aromatic ketone.

iii. Oxidation of alcohol.

9.2 Preparation of Carbonyl Compound

I. Ozonolysis of alkene.



II. Friedel-Crafts Acylation

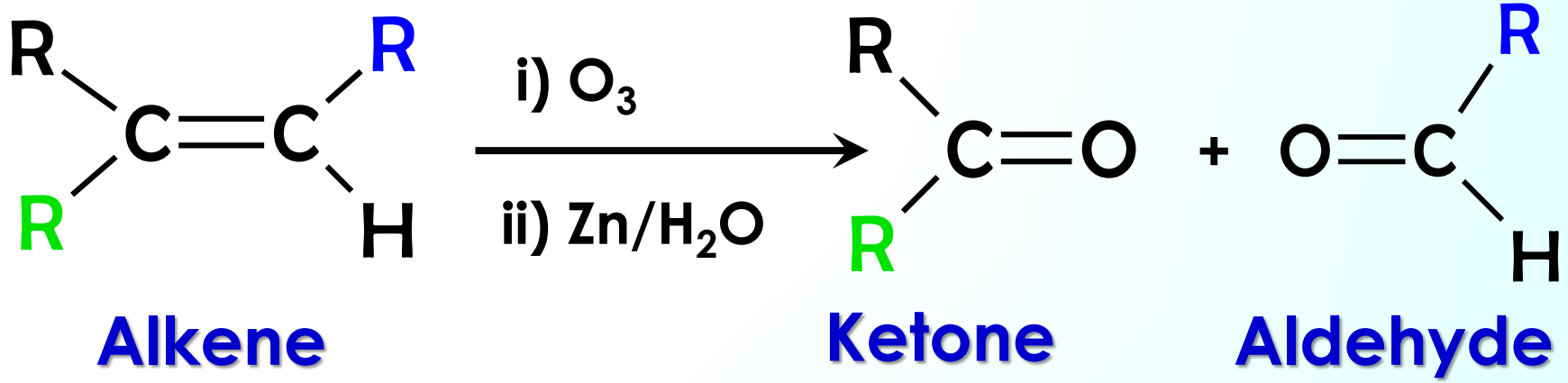
III. Oxidation of Alcohols

I. Ozonolysis of alkene.

Produces:

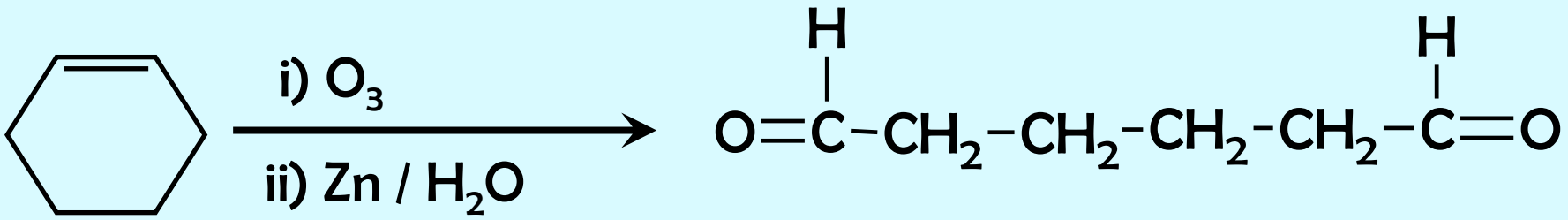
aldehyde or ketone or both.

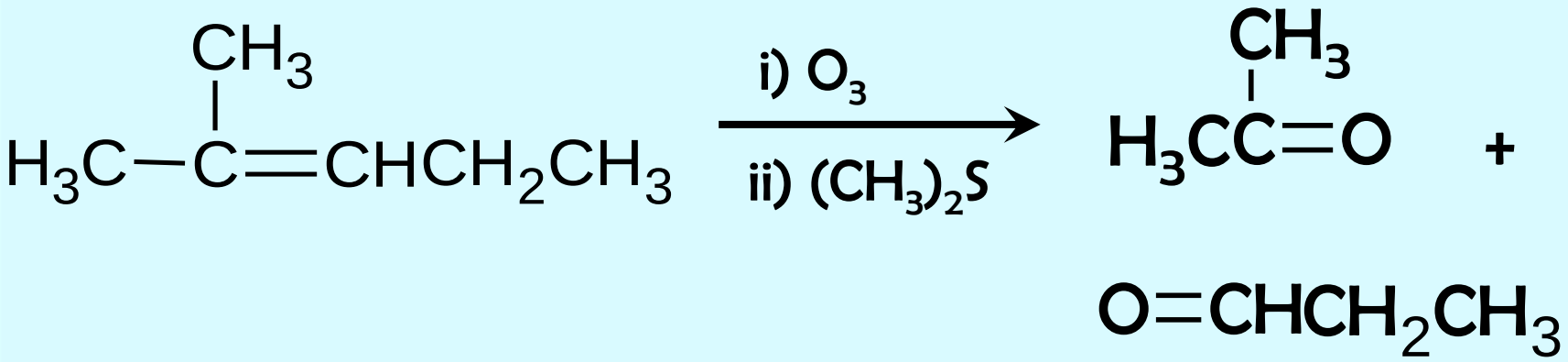
General reaction :



Refer 5.2 k(i)

Example :

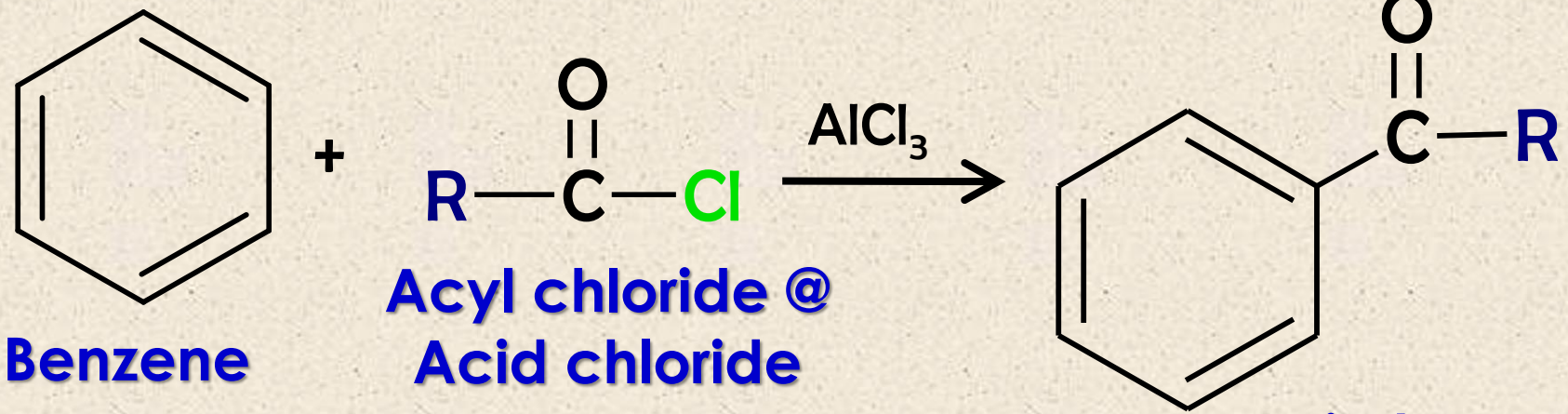




$(CH_3)_2S$ - Dimethylsulfide

II. Friedel-Crafts Acylation

General reaction



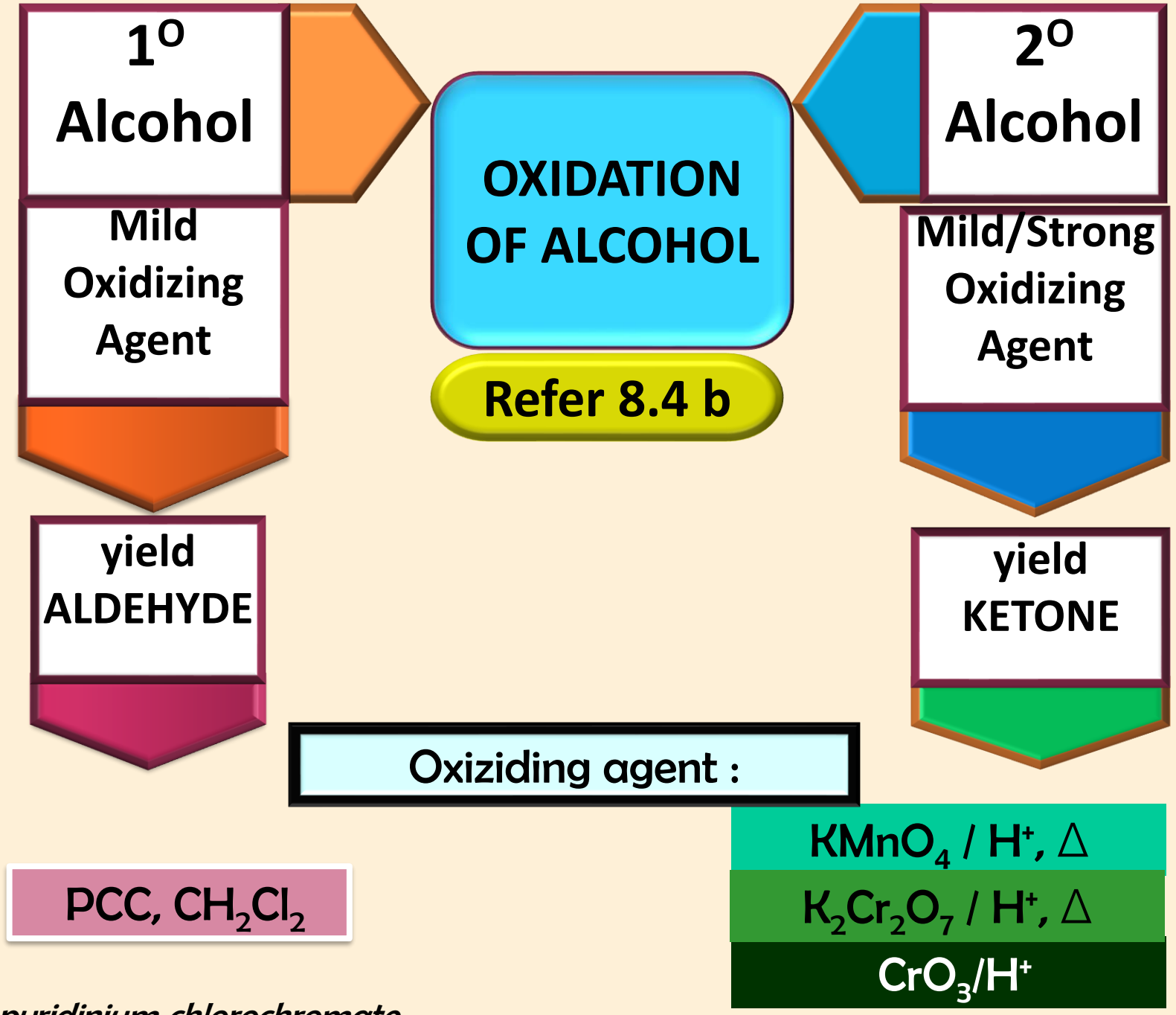
Benzene

Acyl chloride @
Acid chloride

Aromatic ketone

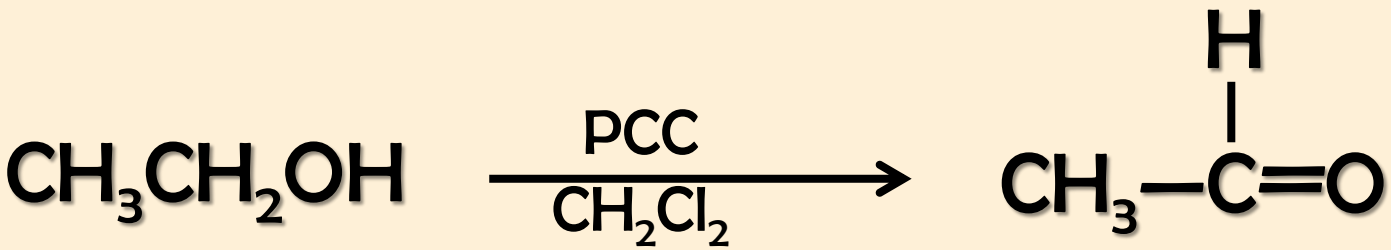
to prepare aromatic ketones

Refer 6.3 a



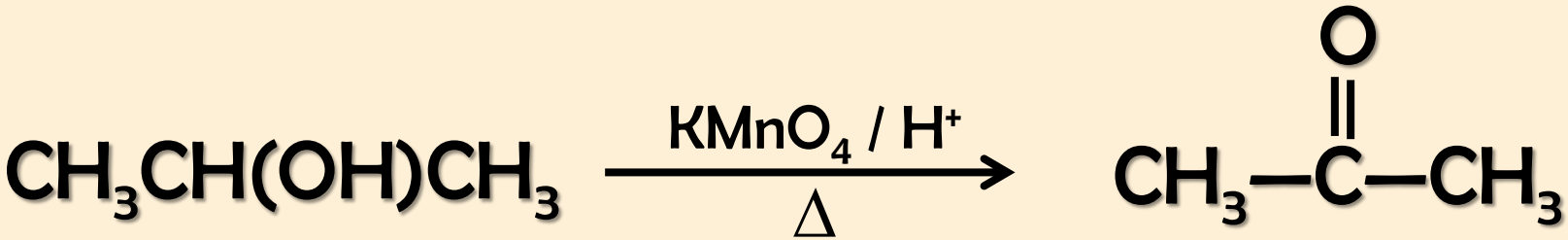
PCC- pyridinium chlorochromate

Example :



Ethanol

Ethanal

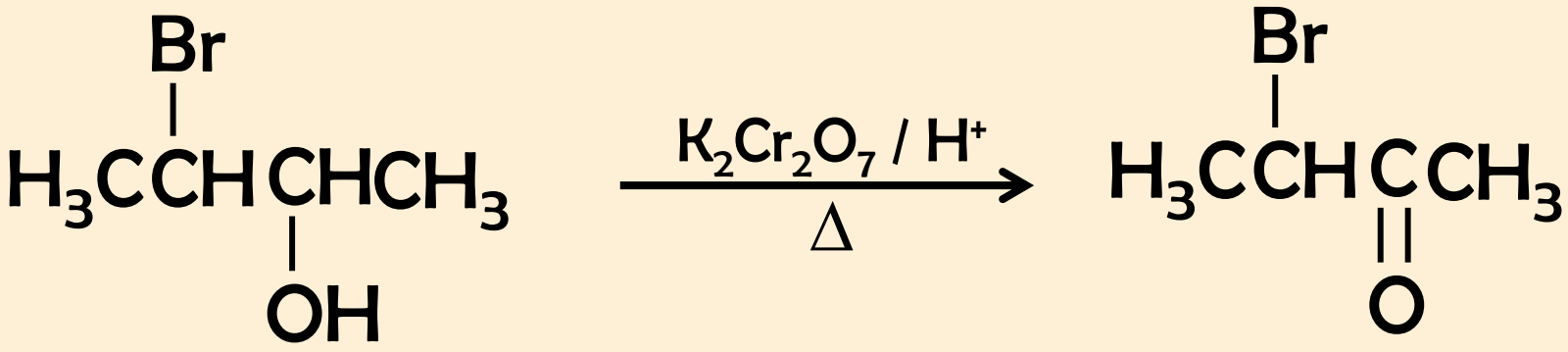


2-propanol

propanone

EXERCISE

a)

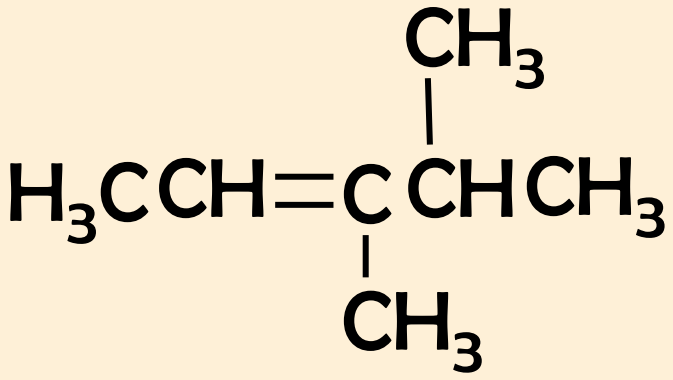


3-bromo-2-butanol

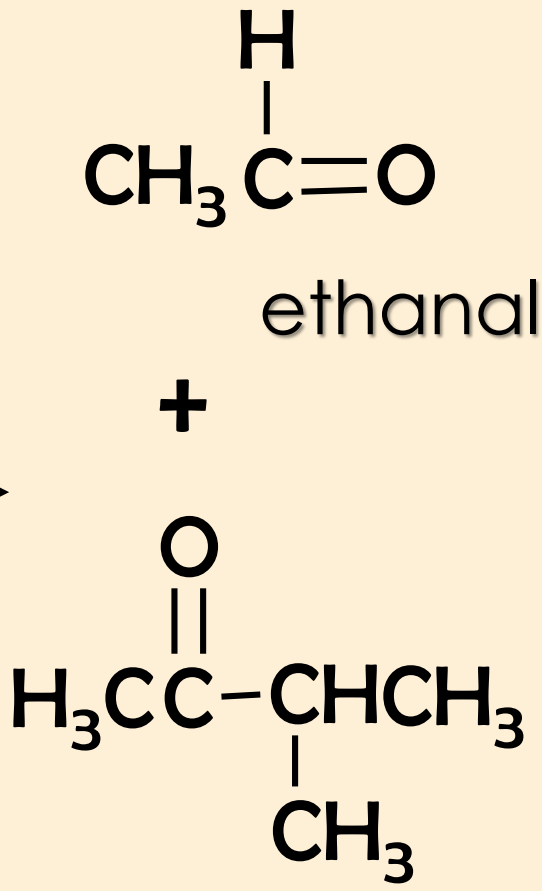
3-bromo-2-butanone

EXERCISE

b)



3,4-dimethyl-2-pentene



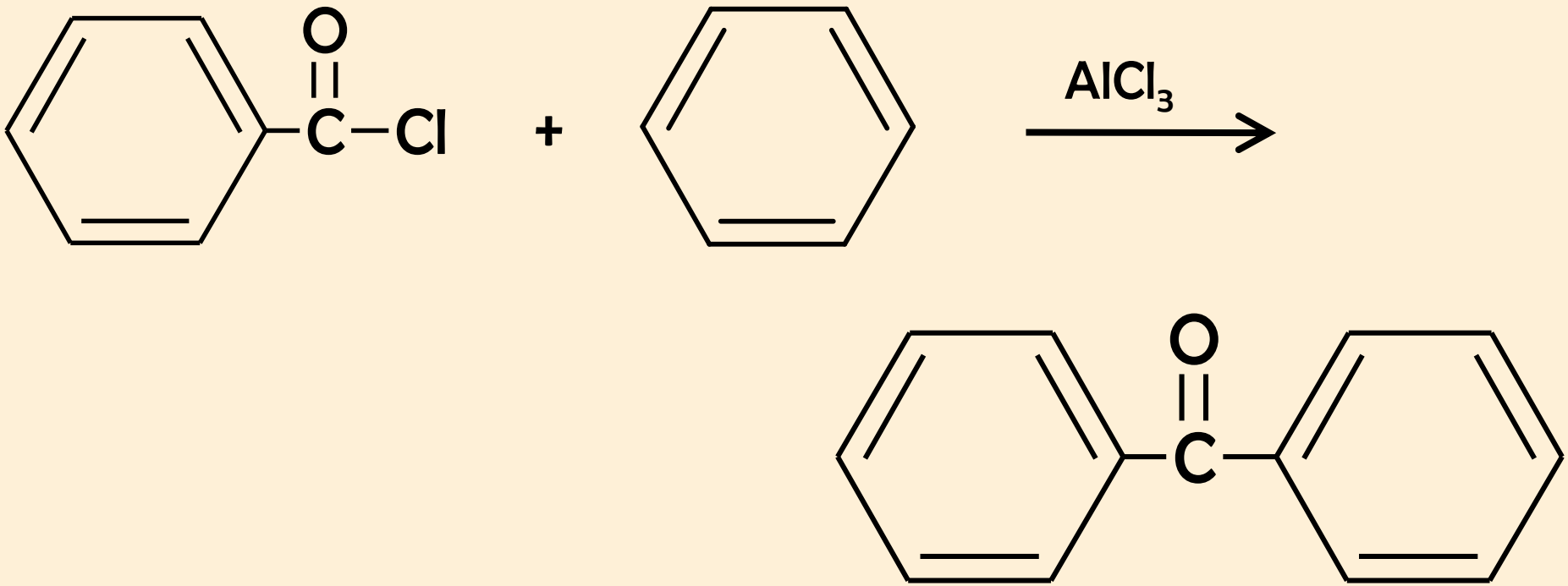
ethanal

+

3-methyl-2-butanone

EXERCISE

c)



benzophenone

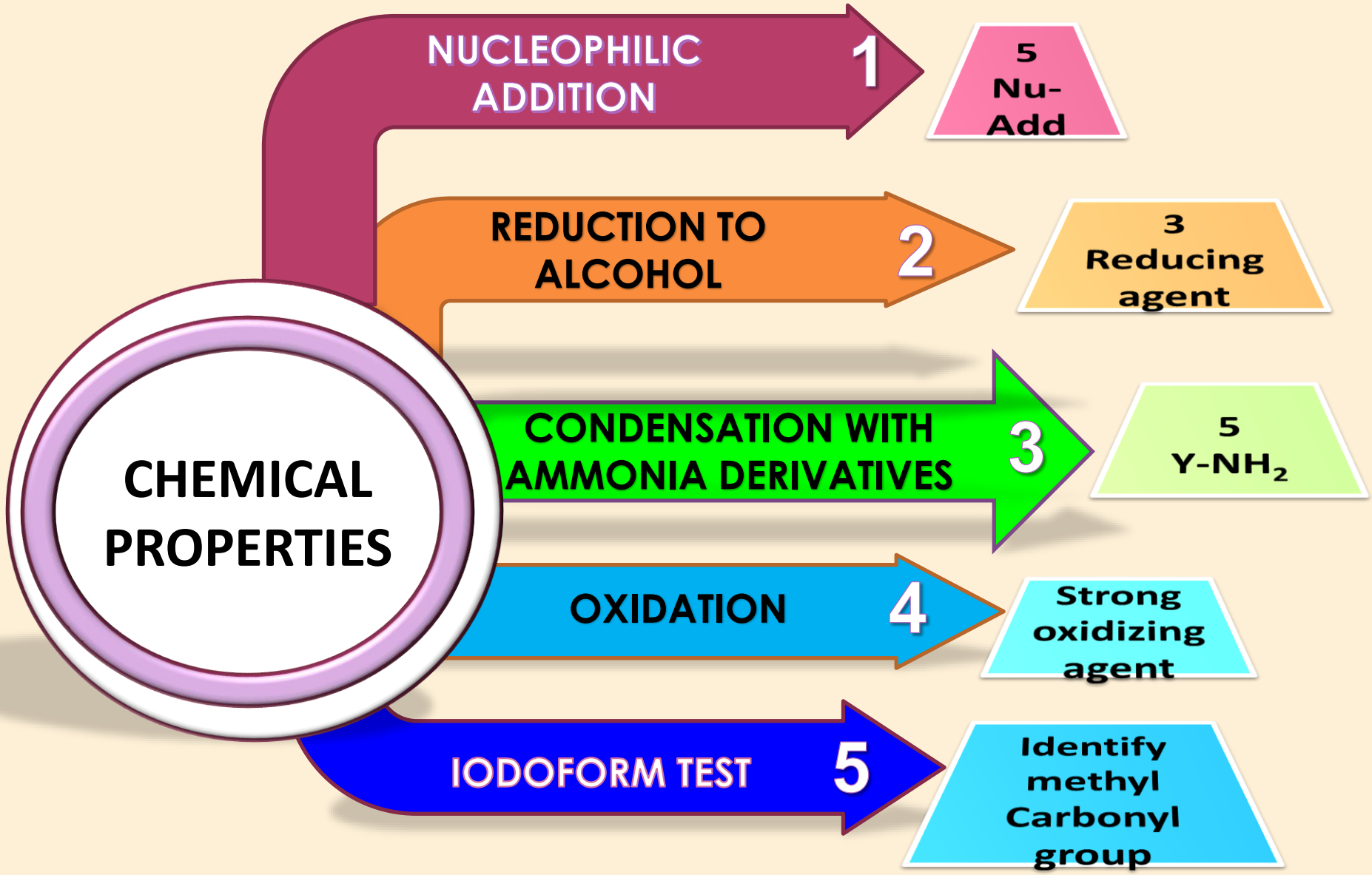
Learning Outcomes:

9.3 Chemical Properties of Carbonyl Compounds

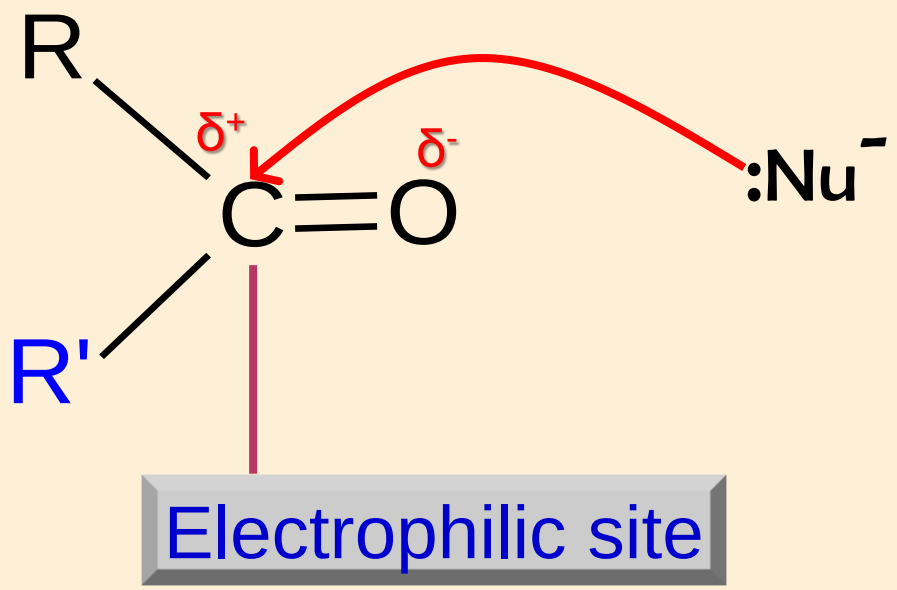
a) Explain the chemical properties of carbonyl compounds with reference to:

i. Nucleophilic addition.
ii. Reduction to alcohol.
iii. Condensation with ammonia derivatives.
iv. Oxidation
v. Iodoform Test.

9.3 (a)

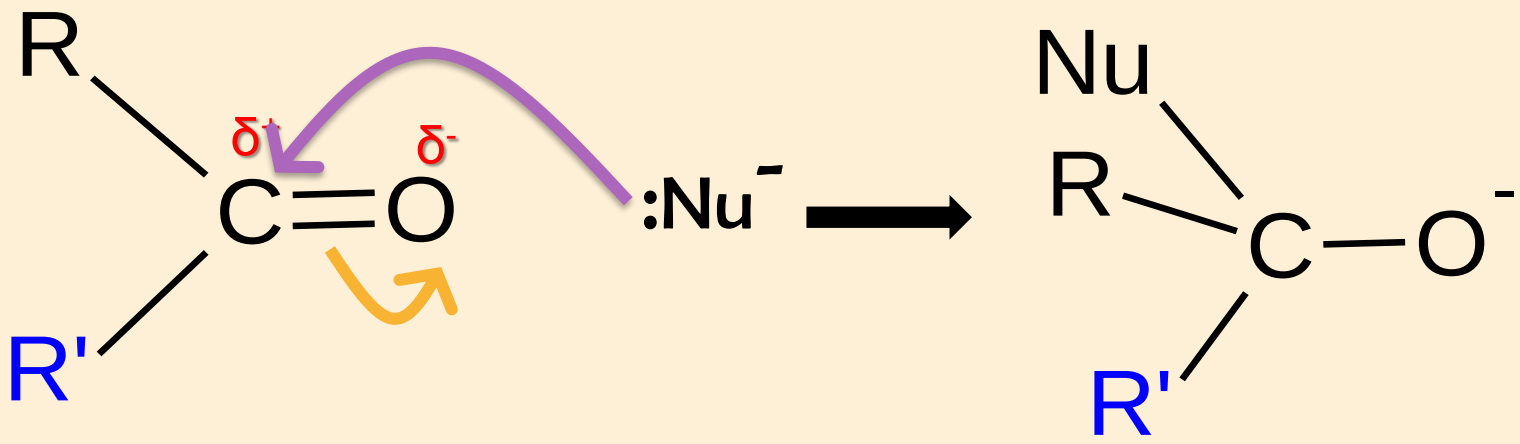

CHEMICAL PROPERTIES
NUCLEOPHILIC ADDITION
1
5 Nu-Add
REDUCTION TO ALCOHOL
2
3 Reducing agent
CONDENSATION WITH AMMONIA DERIVATIVES
3
5 Y-NH2
OXIDATION
4
Strong oxidizing agent
IODOFORM TEST
5
Identify methyl Carbonyl group

C=O is susceptible to nucleophilic addition.



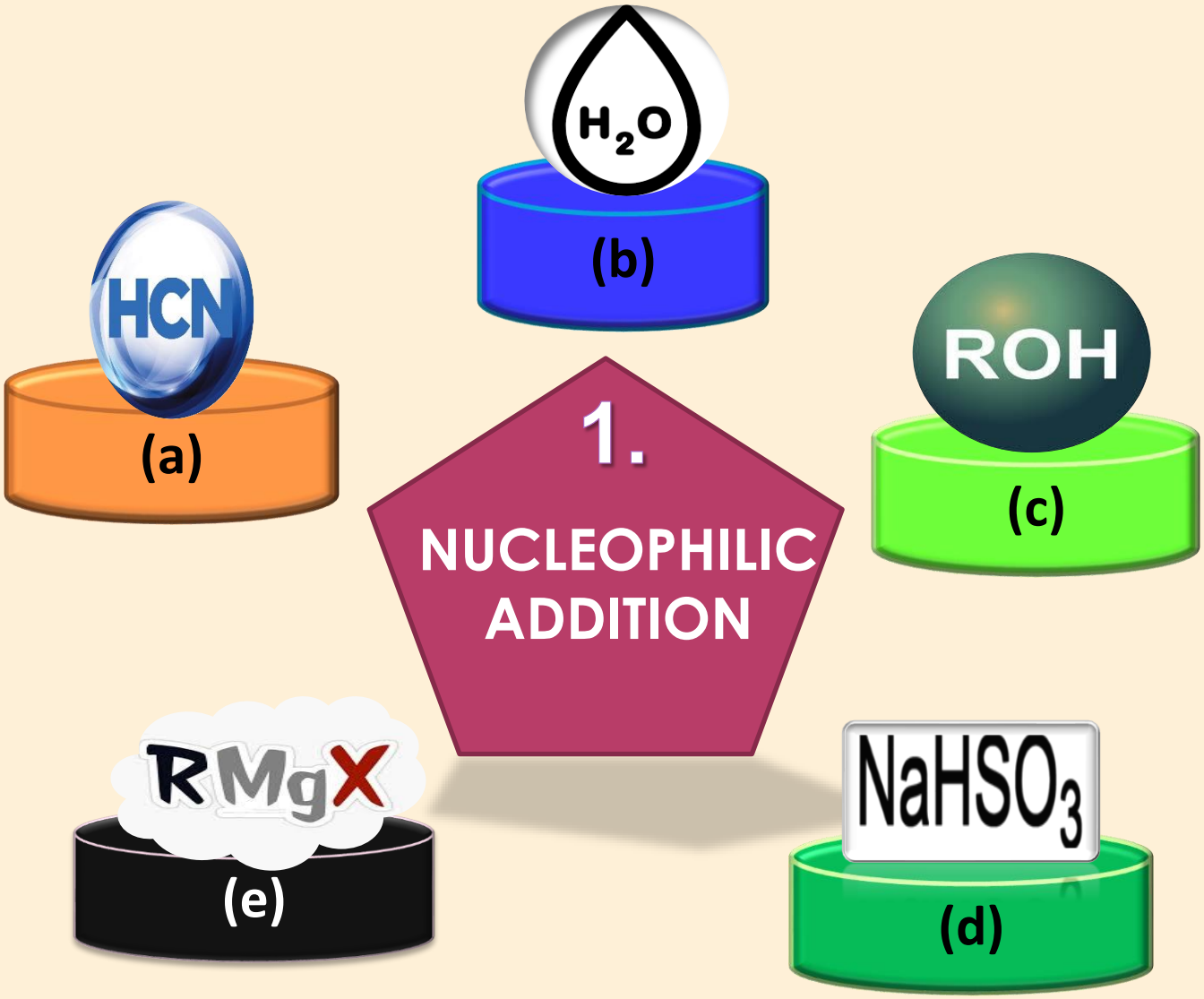
In C=O, the electron density is drawn more towards the O atom making the *C atom deficient in electrons*.

Thus, the **C atom** becomes the **site for Nu- attack**.



When carbonyl C is attacked by Nu^-, the carbonyl π bond is broken and a tetrahedral intermediate is formed.

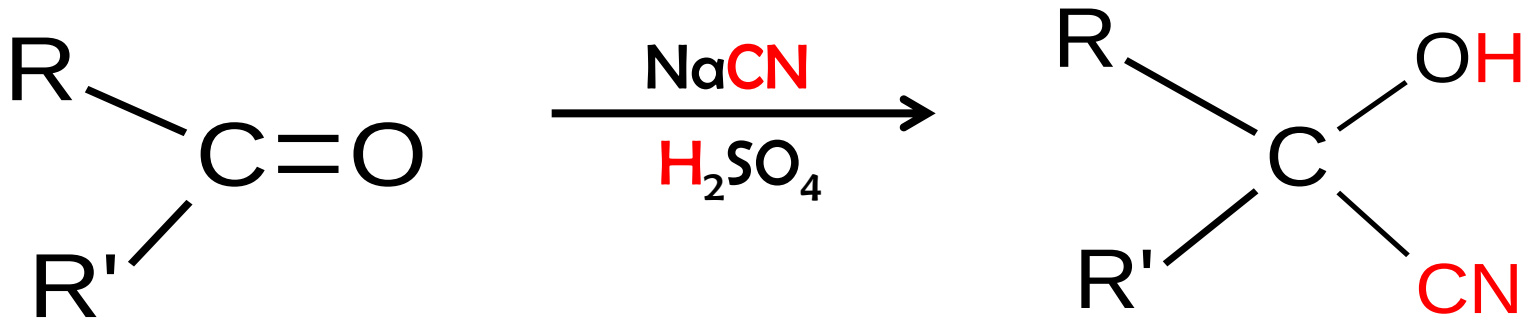
Hybridization of sp^2 C atom changes to sp^3.


1.
NUCLEOPHILIC ADDITION
HCN
(a)
H_2O
(b)
ROH
(c)
$NaHSO_3$
(d)
RMgX
(e)

Addition of HCN

(a)

General reaction:



Aldehyde or **ketone** and

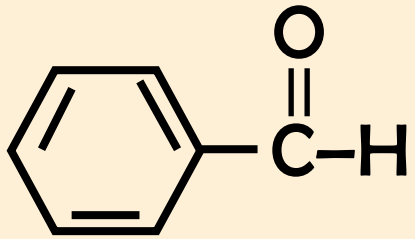
HCN (**'in situ' preparation**).

HCN : mixture of **KCN** or **NaCN** with **H_2SO_4** @ **HCl**

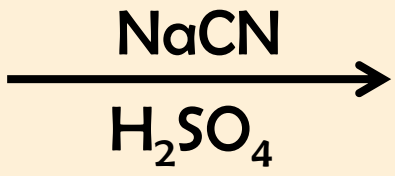
Product:

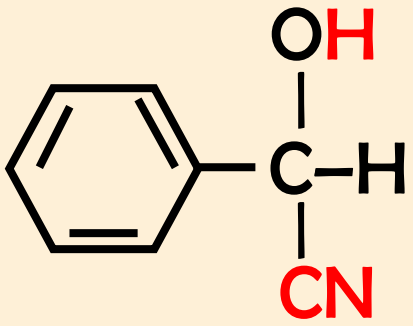
Cyanohydrin

Example :

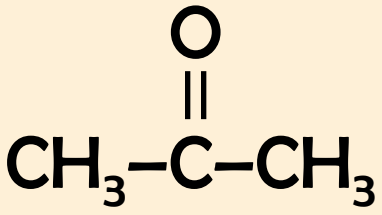


benzaldehyde

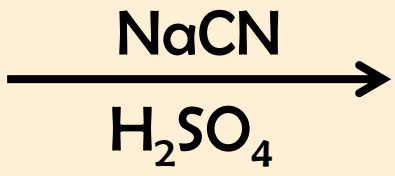


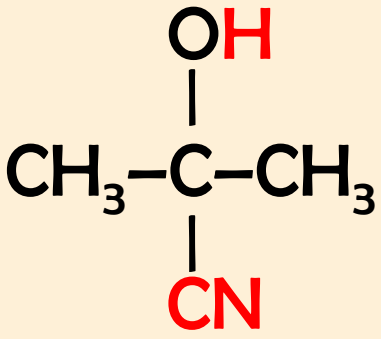


Cyanohydrin



propanone



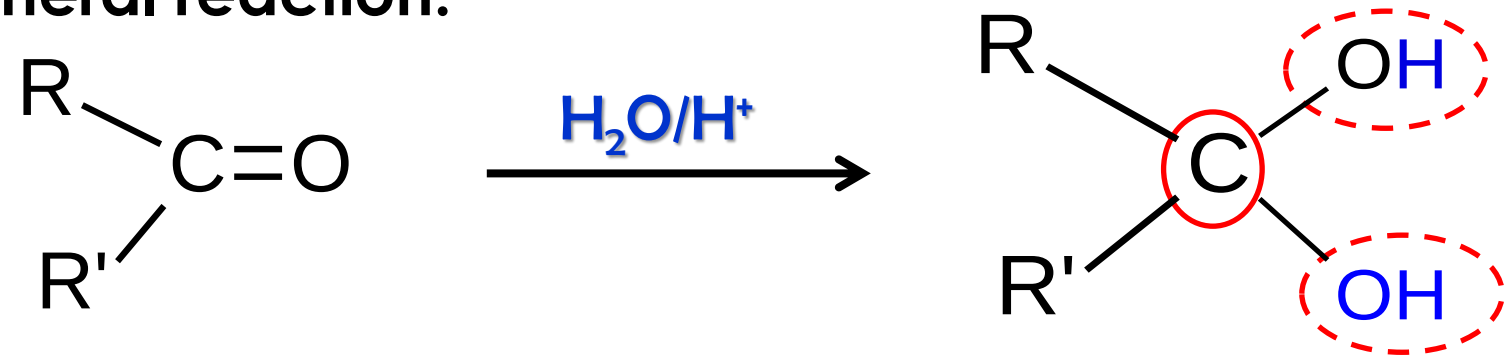


Cyanohydrin

Addition of Water

(b)

General reaction:



Aldehyde or **ketone** and **Water**

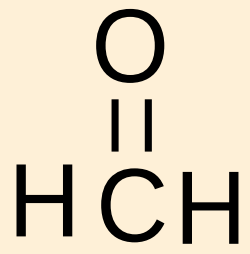
Product:

Hydrate

(gem-diols)

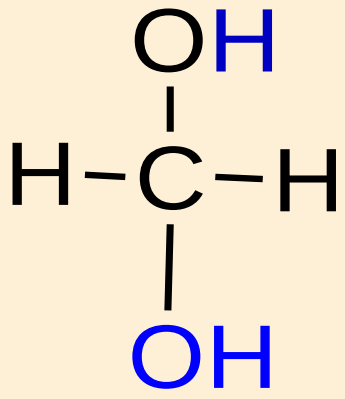
***gem = geminal (two OH or X bonded to the same C)

Example :

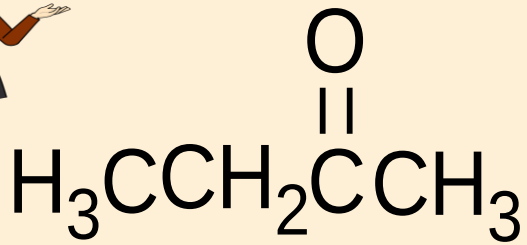


Methanal

H_2O/H^+

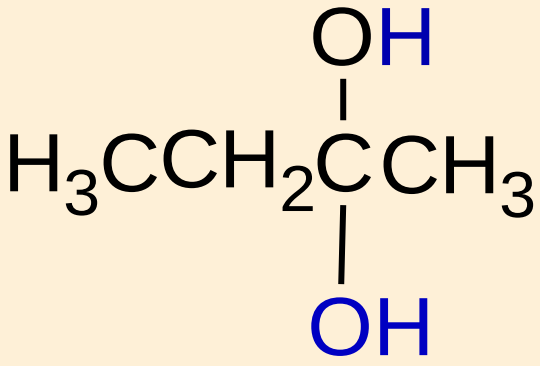


Hydrate (gem-diols)



Butanone

H_2O/H^+



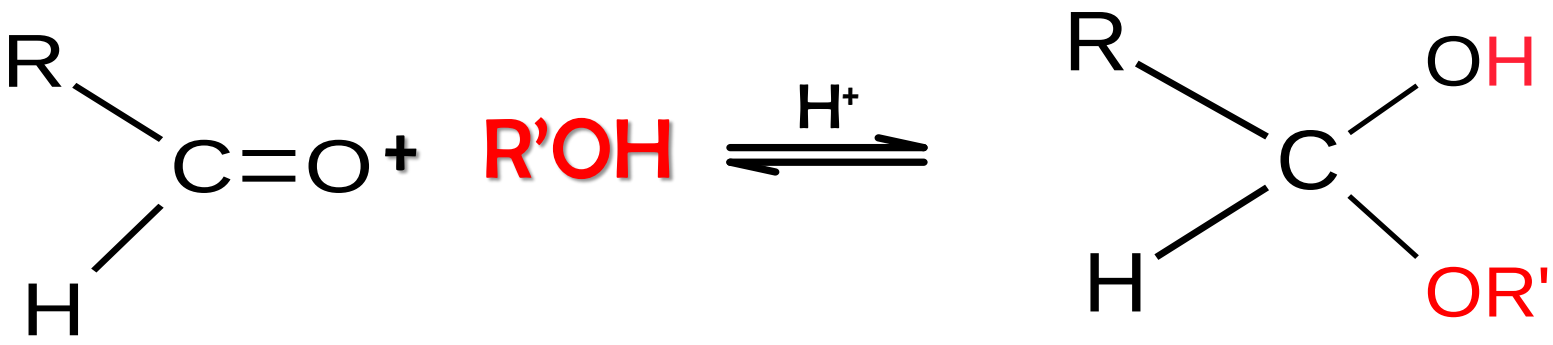
Hydrate (gem-diols)

ROH

(c)

Addition of Alcohols

General reaction: Formation of hemiacetal



Aldehyde and **alcohols**

Product:

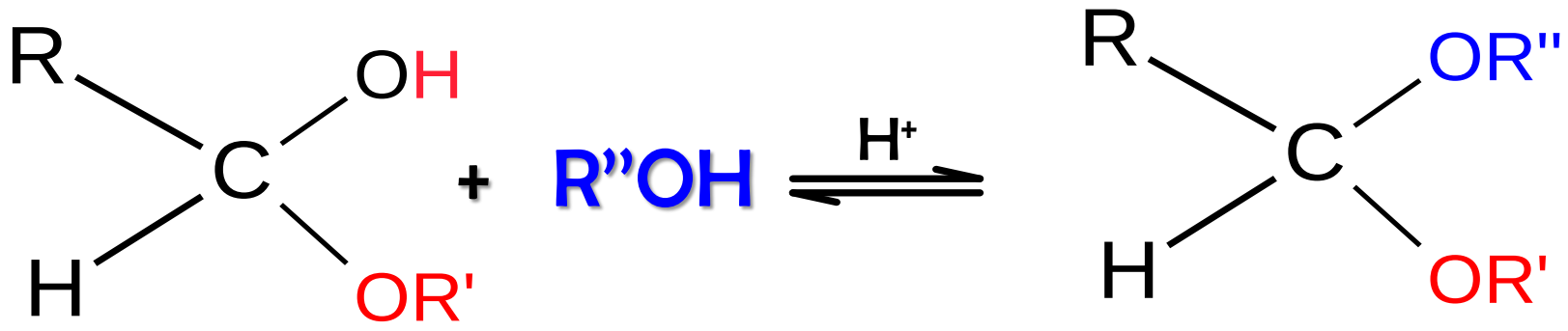
Hemiacetal

ROH

(c)

Addition of Alcohols

General reaction: Formation of acetal



Hemiacetal

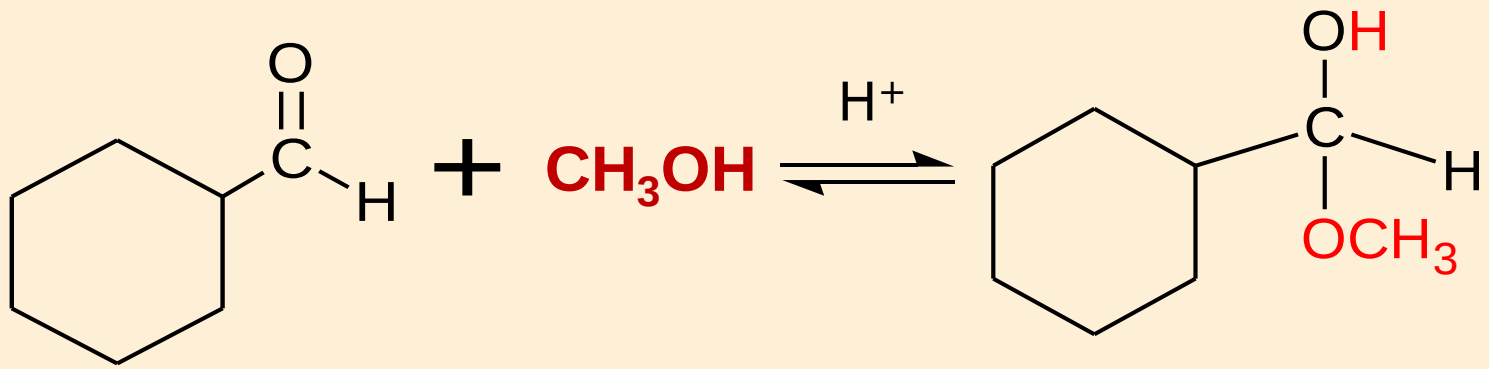
In **acidic catalyst**

Further react with **alcohols**

Product:

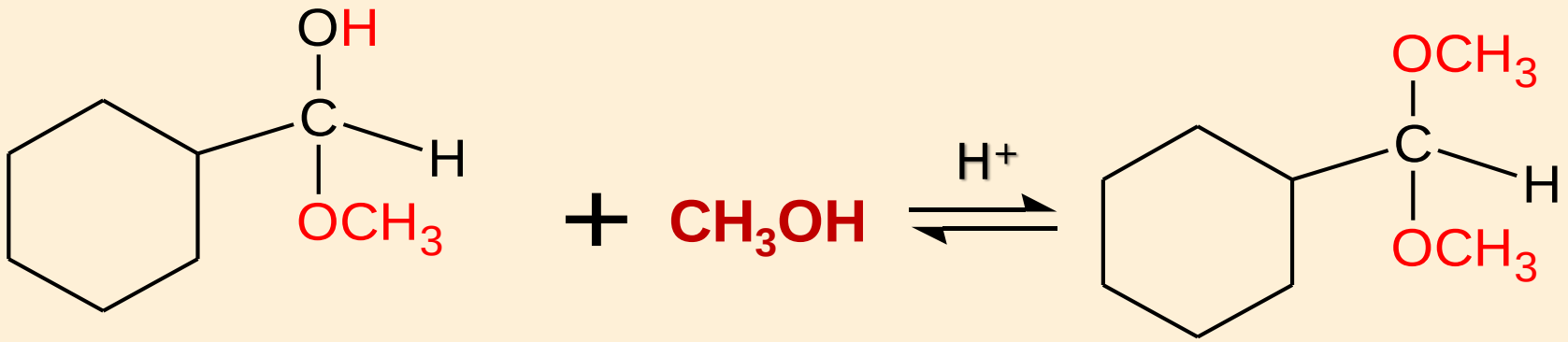
Acetal

Example :



cyclohexanecarbaldehyde

cyclohexyl(methoxy)methanol

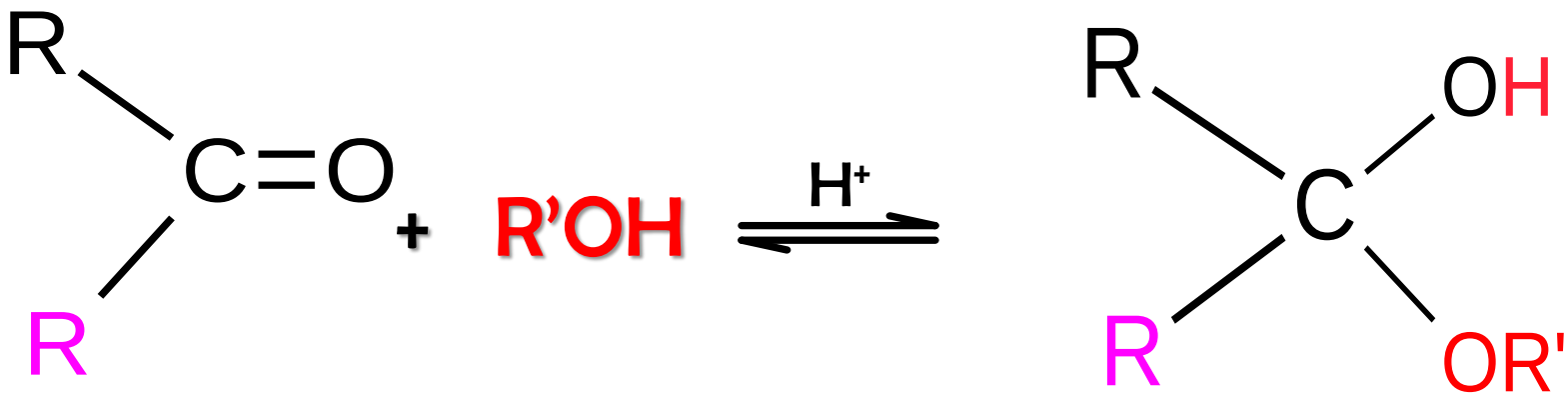


ROH

(c)

Addition of Alcohols

General reaction: Formation of hemiketal



Ketone and **alcohols**

Product:

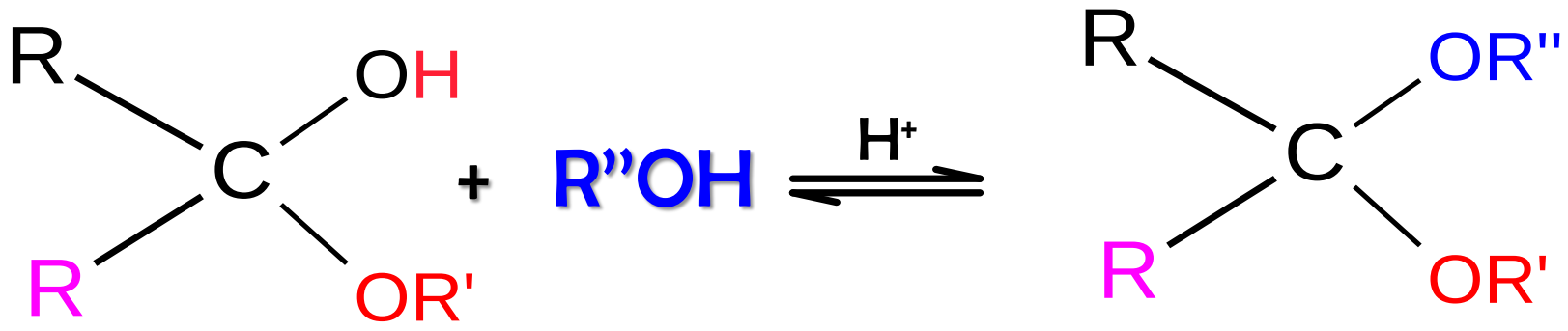
Hemiketal

ROH

(c)

Addition of Alcohols

General reaction: Formation of ketal



Hemiketal

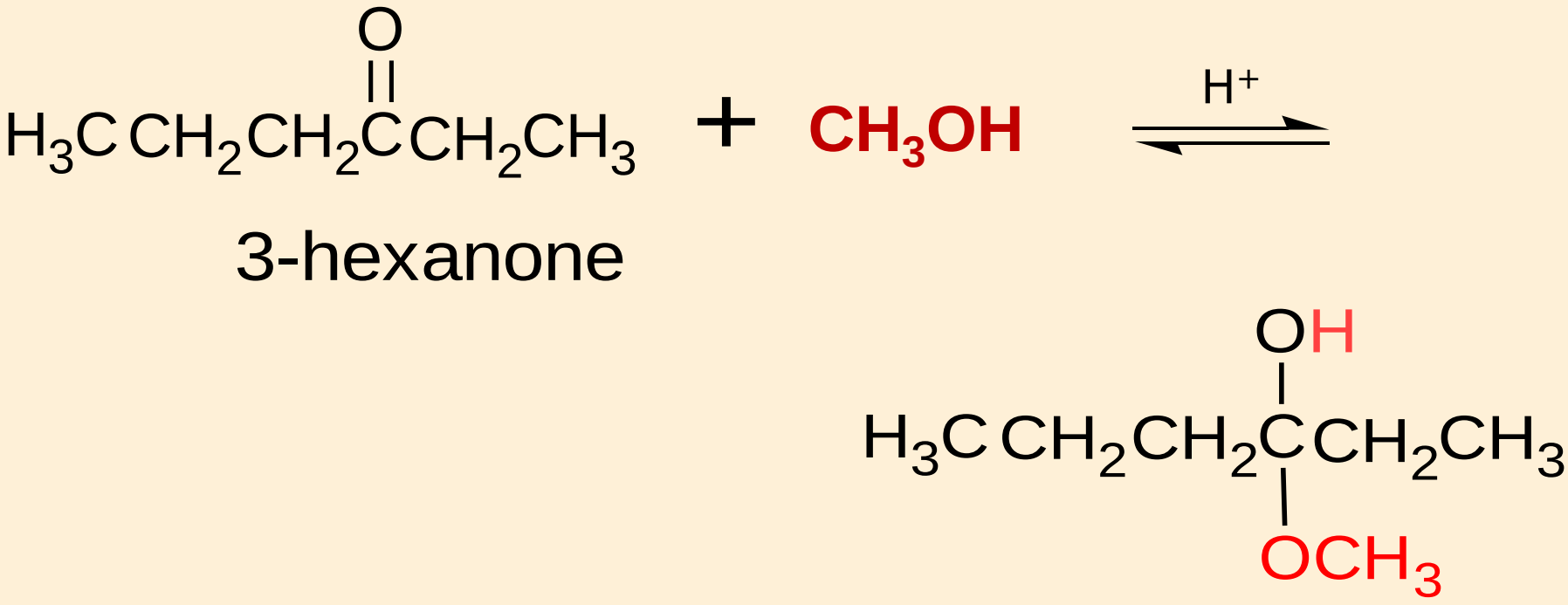
In **acidic catalyst**

Further react with **alcohols**

Product:

Ketal

Example :

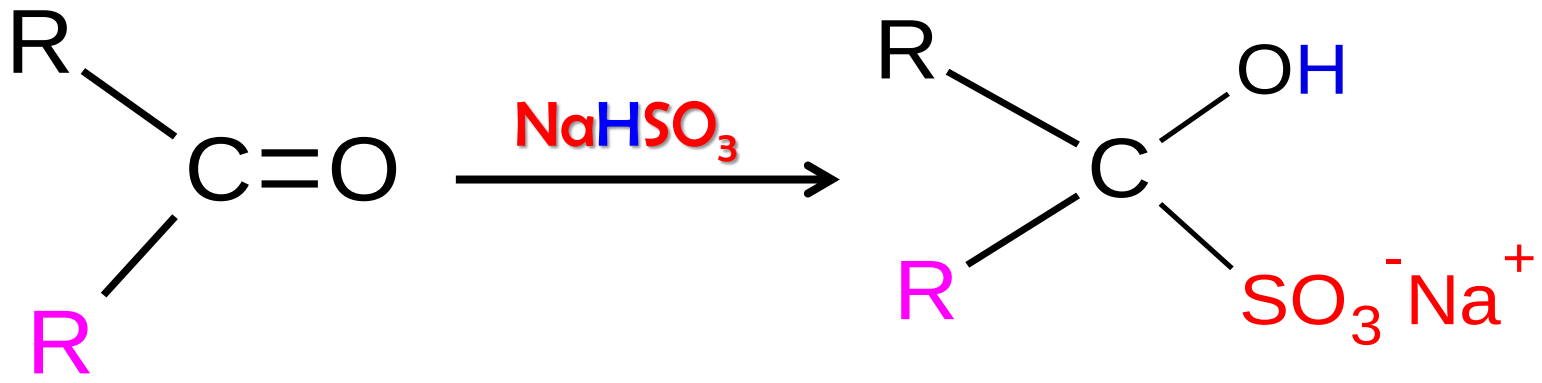

O
H3C CH2CH2C CH2CH3
+
CH3OH
H+
3-hexanone
OH
H3C CH2CH2C CH2CH3
OCH3
3-methoxy-3-hexanol

NaHSO$_3$

(d)

Addition of Sodium bisulphite, NaHSO$_3$

General reaction:



Aldehyde Or Ketone

And NaHSO$_3$

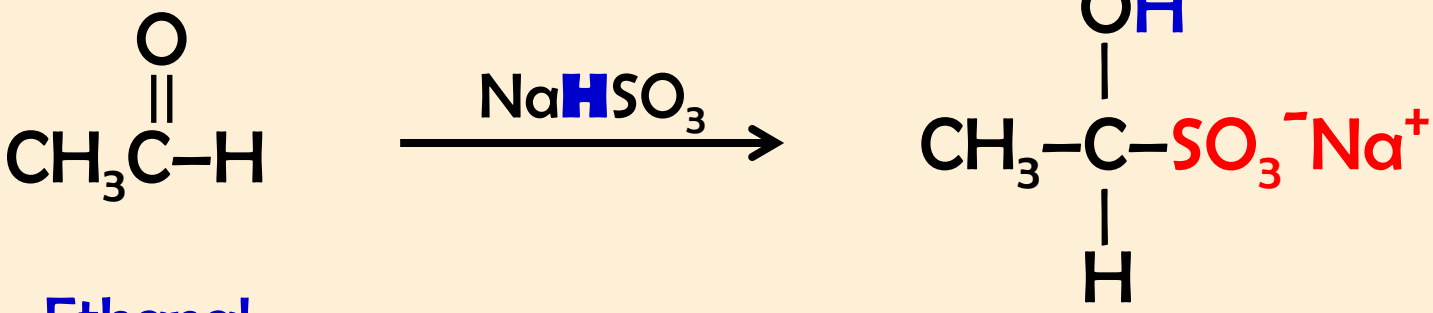
Product:

Bisulphate salt

Uses of Reaction

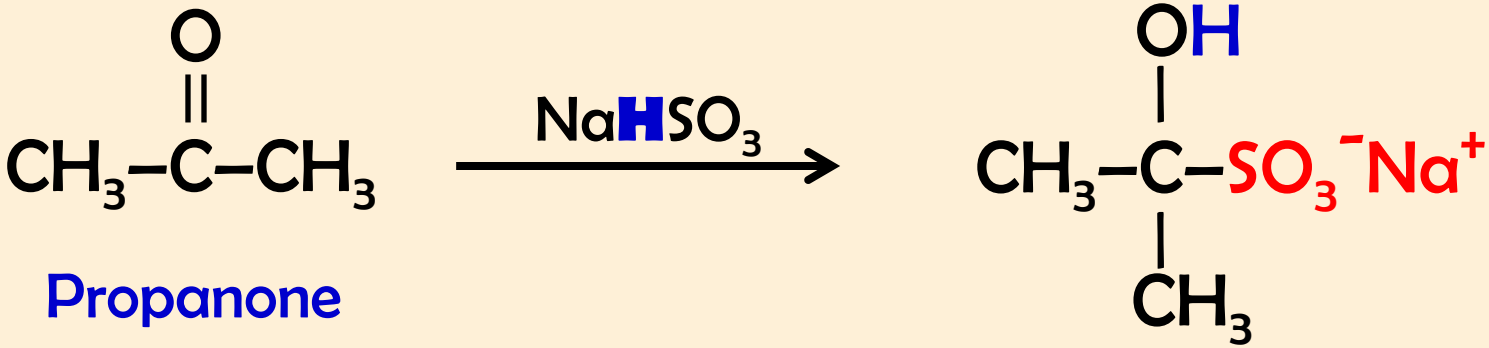
for purification of aldehyde @ ketone from other non-soluble organic compounds.

Example :



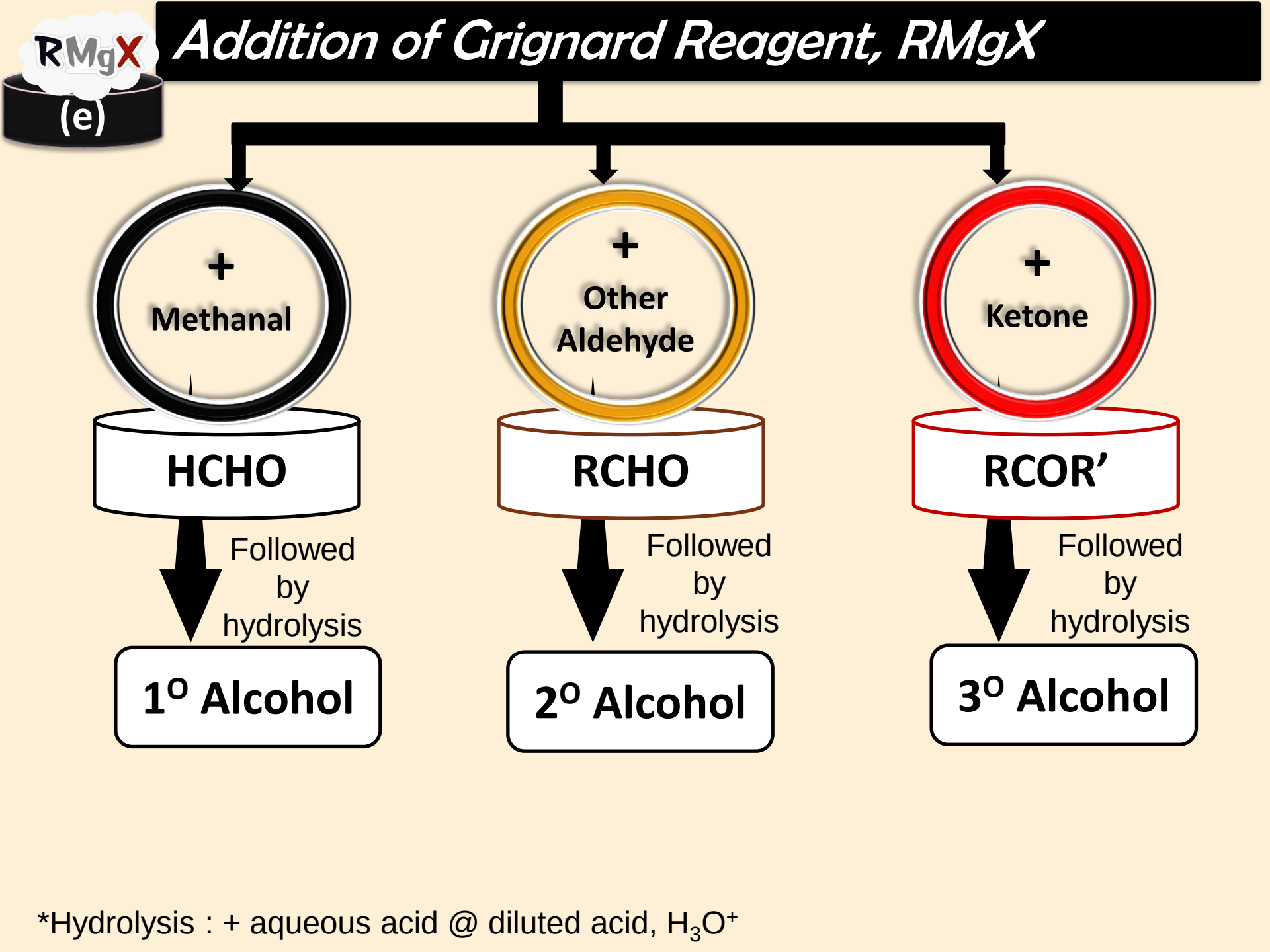
Ethanal

Bisulphate salt



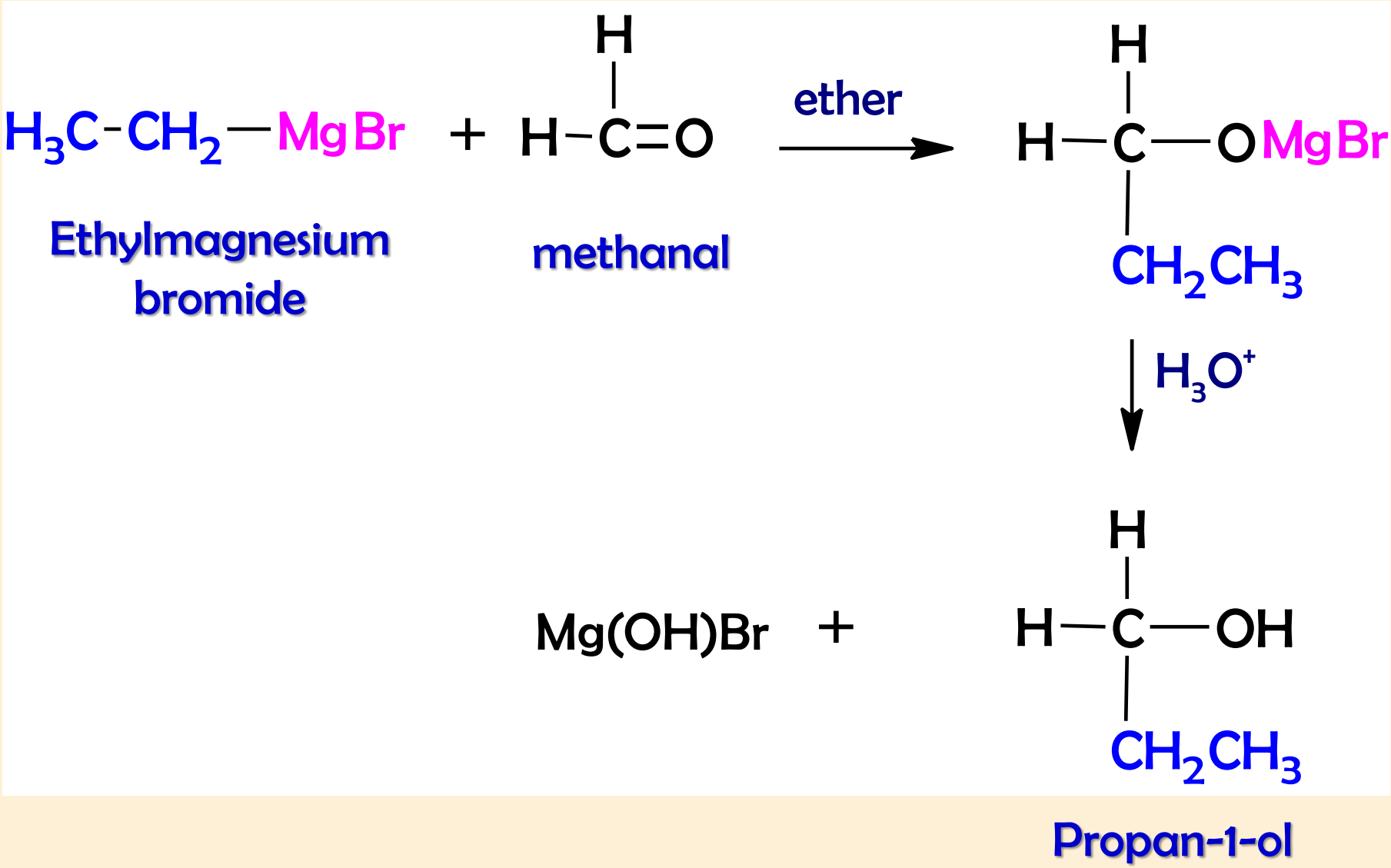
Propanone

Bisulphate salt

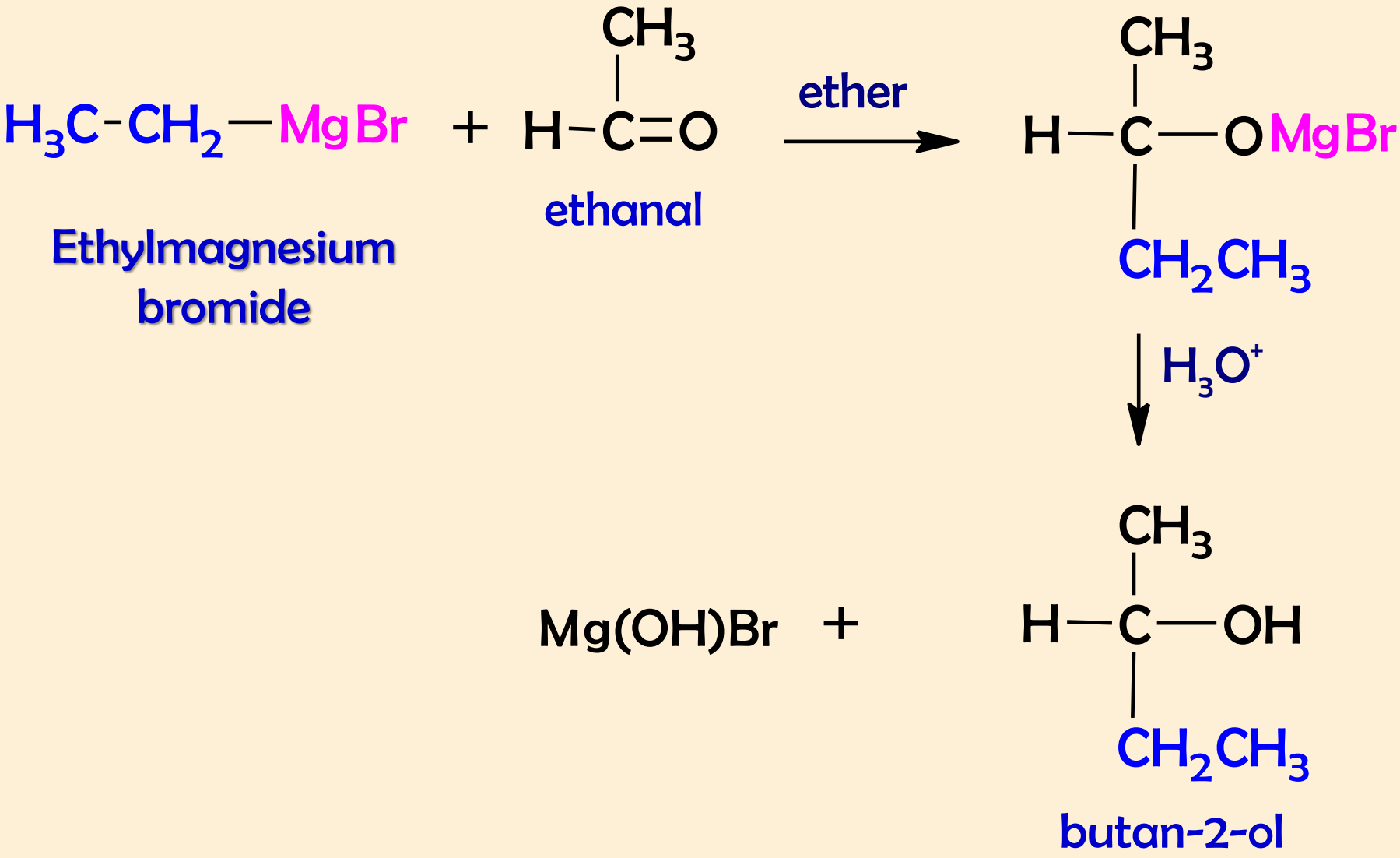


*Hydrolysis : + aqueous acid @ diluted acid, H_3O^+

Example :


H3C-CH2—MgBr
+
H
H—C=O
ether
H
H—C—OMgBr
CH2CH3
Ethylmagnesium bromide
methanal
H3O+
Mg(OH)Br
+
H
H—C—OH
CH2CH3
Propan-1-ol

Example :

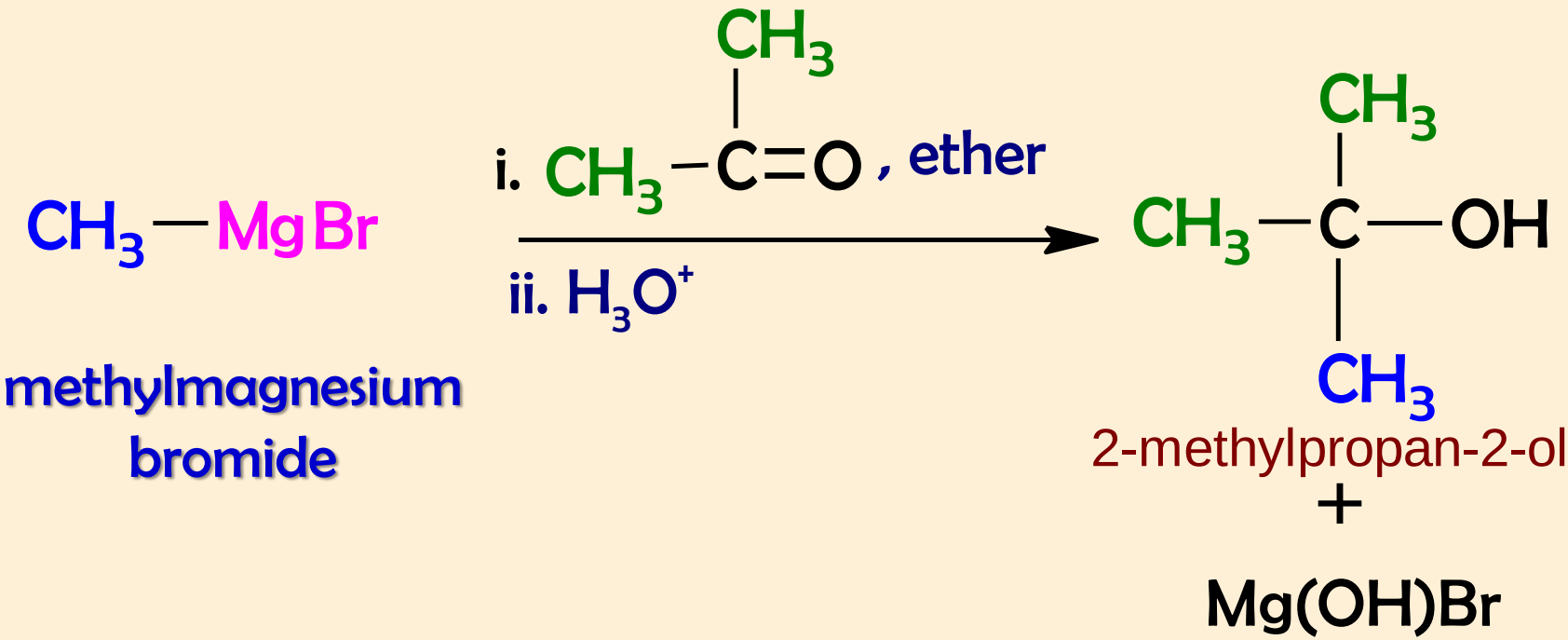


Ethylmagnesium bromide

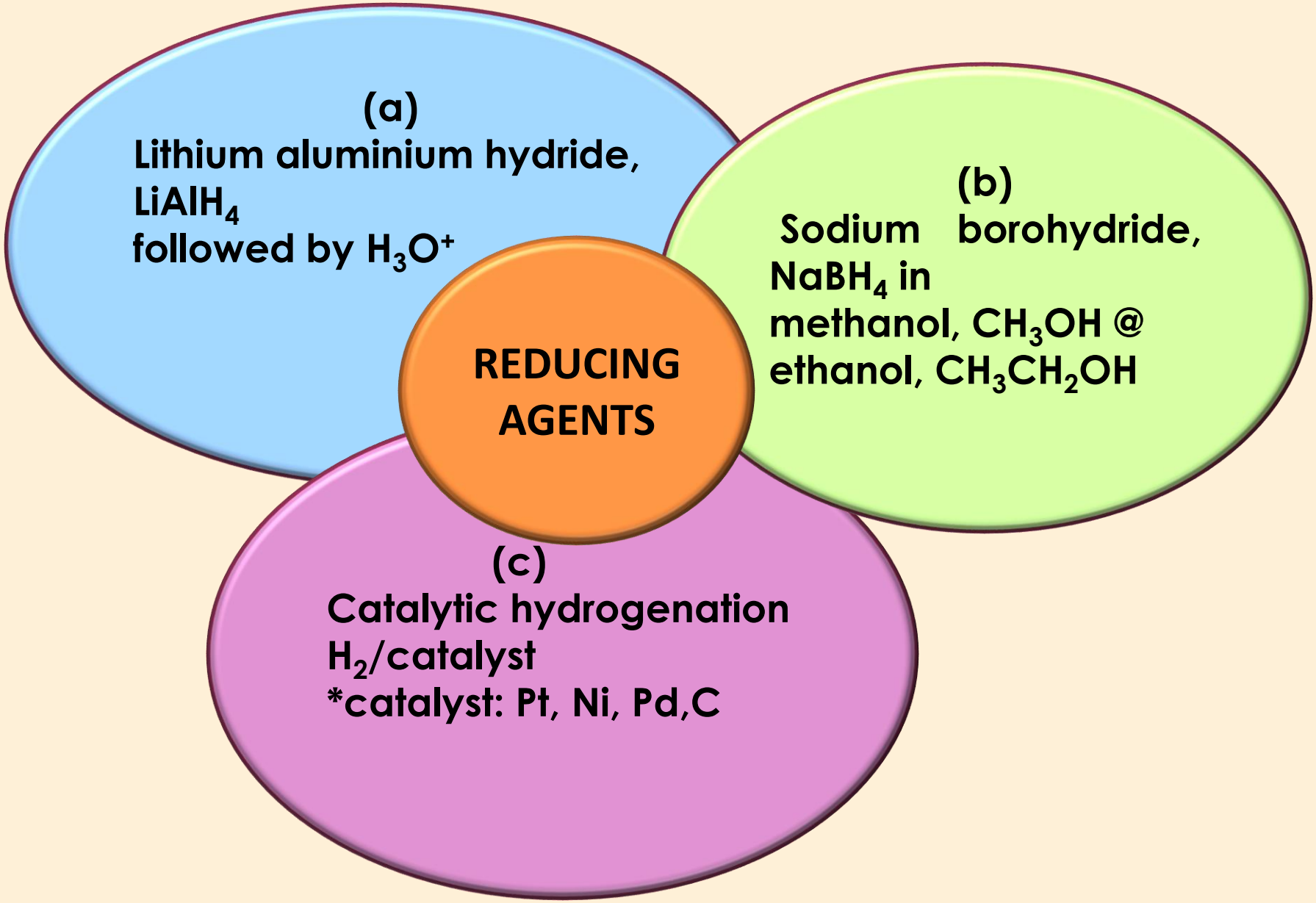
ethanal

butan-2-ol

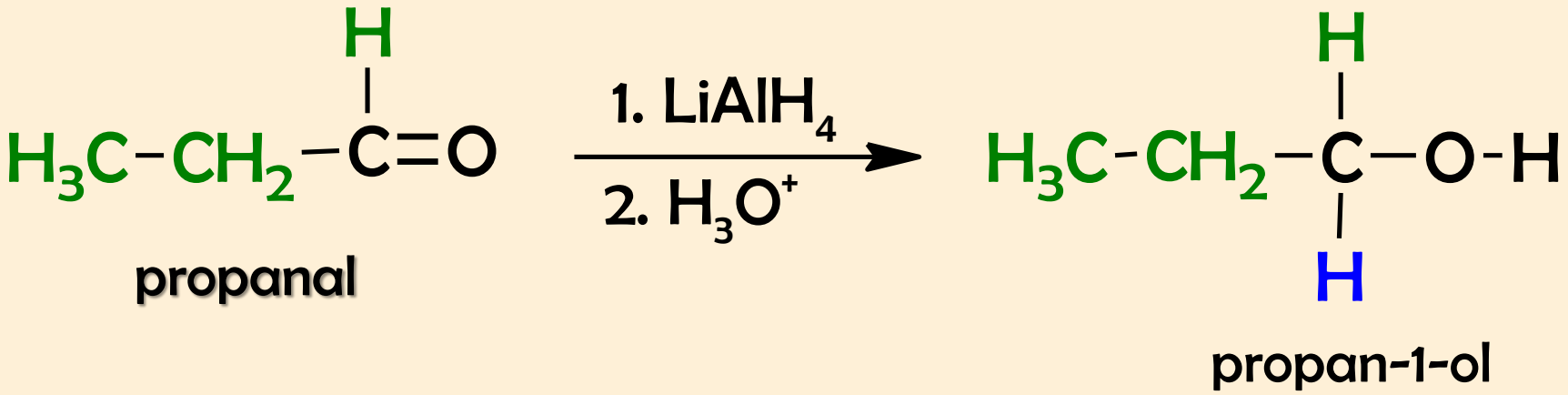
Example :


CH3—MgBr
methylmagnesium bromide
i. CH3—C(=O)—CH3 , ether
ii. H3O+
CH3—C(CH3)2—OH
2-methylpropan-2-ol
+
Mg(OH)Br

ii) Reduction of Carbonyl, C=O to Alcohol

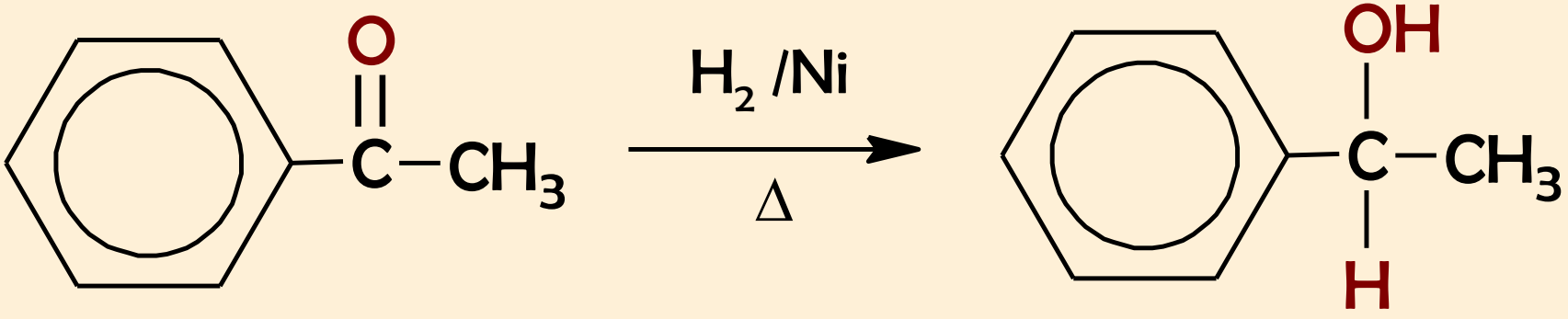


Example :



propanal

propan-1-ol

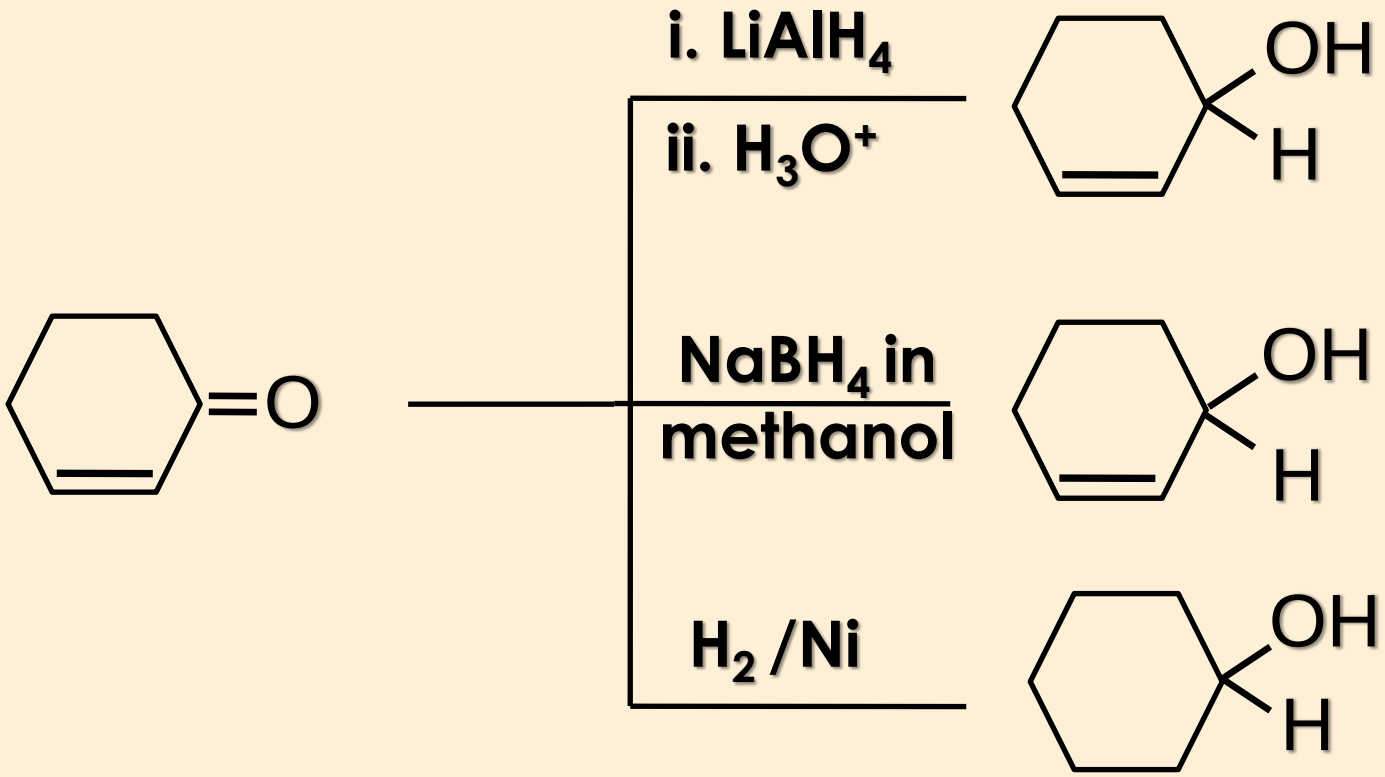


acetophenone

1-phenylethanol

KEEP IN MIND!

When a compound contains both C=O and C=C, selective reduction of one functional group by proper choice of reducing agent :



iii) Condensation with Ammonia Derivatives

Condensation Process: Addition reaction

Followed by dehydration reaction (elimination smaller molecule)

Ammonia : NH_3

Ammonia Derivaties : YNH_2

} **Act as nucleophile**

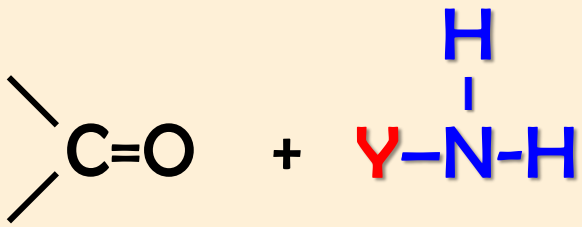
Example : $R\text{-}NH_2$ (1^0 amine)

$HO\text{-}NH_2$ (hydroxylamine)

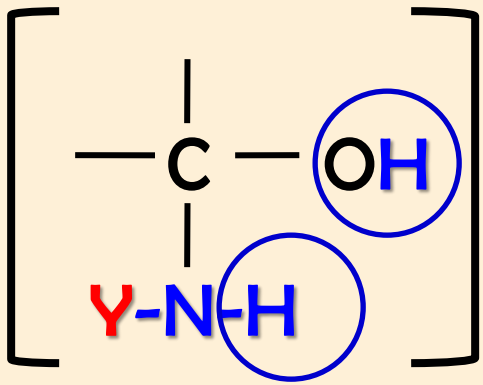
$NH_2\text{-}NH_2$ (hydrazine)

iii) Condensation with Ammonia Derivatives

A condensation reaction



addition ⇌

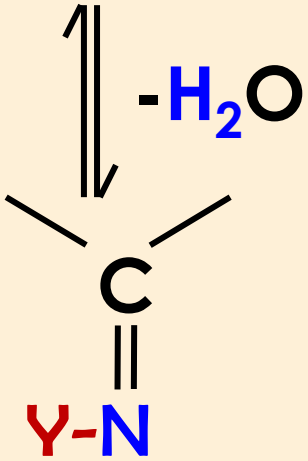


Carbinolamine

'Unstable intermediate'

which two molecules combine to form a larger molecule

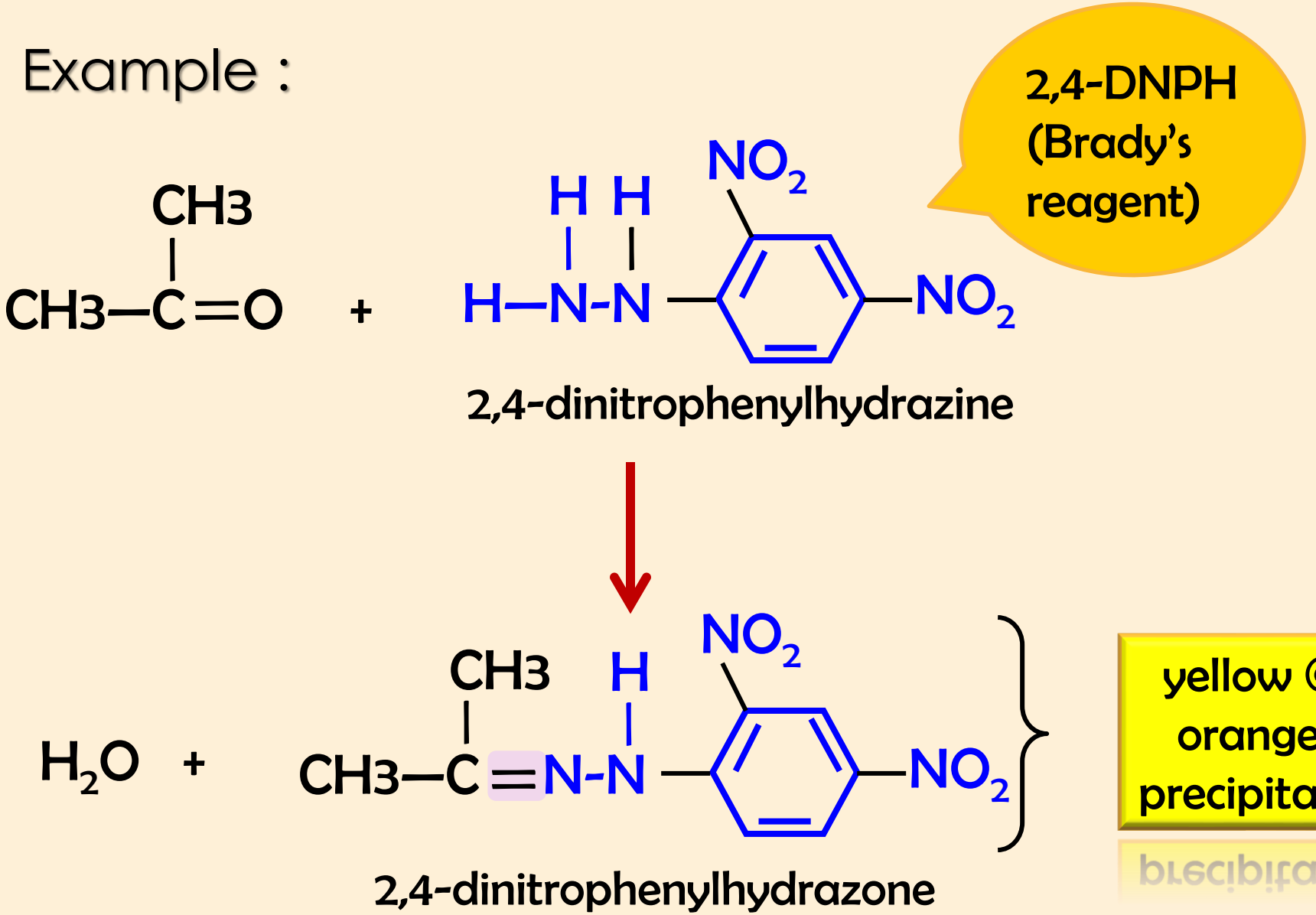
the *elimination of a* ***smaller molecule***



Compound with imine group (C=N)

Smaller molecule :water, H_2O ammonia, NH_3 or HCl.

Example :


2,4-DNPH (Brady's reagent)
CH3
CH3—C=O
+
H H
H—N-N
NO2
NO2
2,4-dinitrophenylhydrazine
H2O
+
CH3
H
CH3—C=N-N
NO2
NO2
2,4-dinitrophenylhydrazone
yellow @ orange precipitate

iii) Condensation with Ammonia Derivatives

NH_3 derivatives	Name	Product	Name
$R\text{-}NH_2$ or $Ar\text{-}NH_2$	primary amine	$C{=}N\text{-}R$ or $C{=}N\text{-}Ar$	Imine
NH_2NH_2	hydrazine	$C{=}NNH_2$	Hydrazone
$NH_2\text{-}OH$	hydroxyl amine	$C{=}N\text{-}OH$	Oxime

NH_3 derivatives	Name	Product	Name
$NH_2NHC_6H_5$	phenyl hydrazine	$C{=}NNHC_6H_5$	phenyl hydrazone
$NH_2NHC(=O)NH_2$	semi carbazide	$C{=}NNHC(=O)NH_2$	semi carbazone

Carbonyl reacts with **hydrazine or phenylhydrazine** to form **yellow orange precipitate**.

iv) Oxidation

Oxidation reactions

- **Tollens'**
- **Fehlings'**
- **Schiff**

<u>Differentiation test</u> for aldehydes and ketones :

REMEMBER

Strong Oxiziding agent :

- $KMnO_4 / H^+, \Delta$
- $K_2Cr_2O_7 / H^+, \Delta$
- CrO_3/H^+

Can't be used as Differentiation test

iv) Oxidation

Aldehyde

→ **Strong oxidizing agent** → **Carboxylic Acid RCOOH**

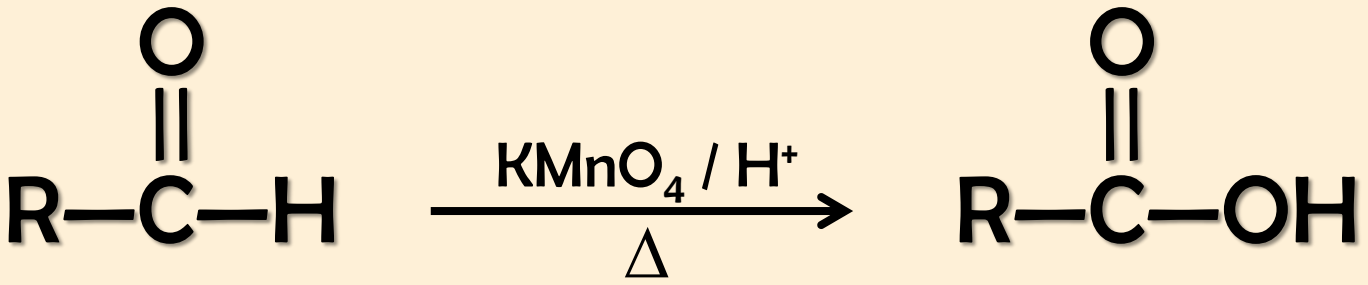
→ **Mild oxidizing agent** → **Carboxylate Ion $RCOO^-$**

Tollens',
Schiff,
Fehling's and
Benedict's solutions

Ketone → **resistant to oxidation**

because they **do not have hydrogen** attached to the carbonyl carbon atom.

General reaction :



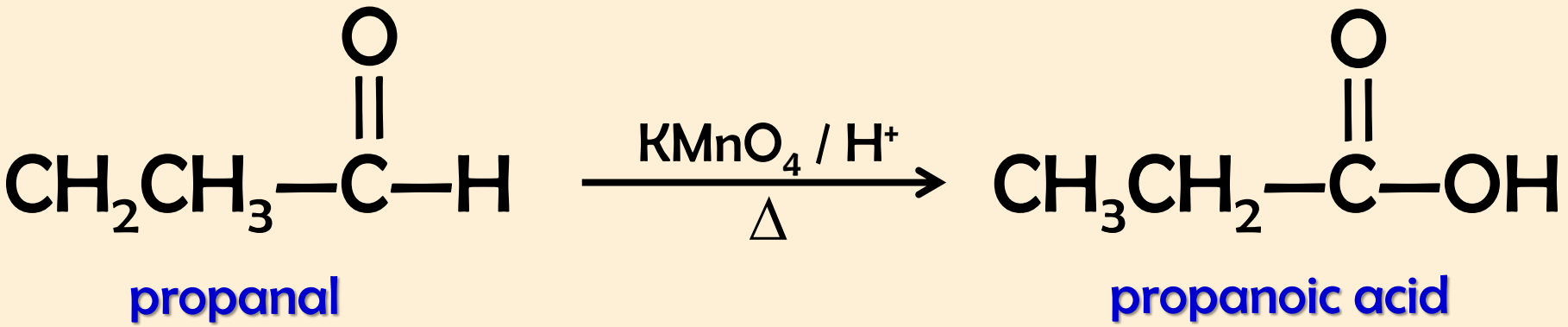
Aldehyde

Carboxylic acid

Other strong oxidizing agents:

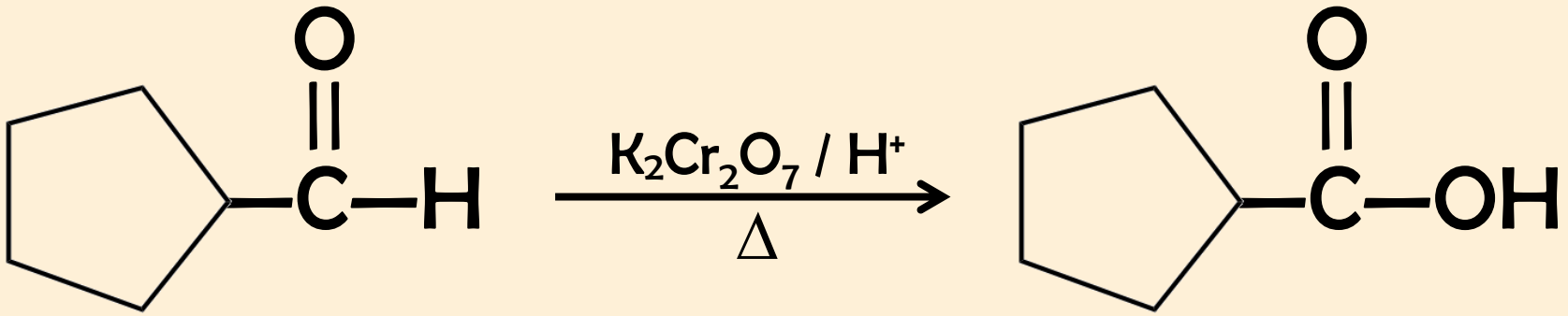
- Hot acidified $K_2Cr_2O_7$ @
- Hot acidified $Na_2Cr_2O_7$ @
- Acidified CrO_3

Example :



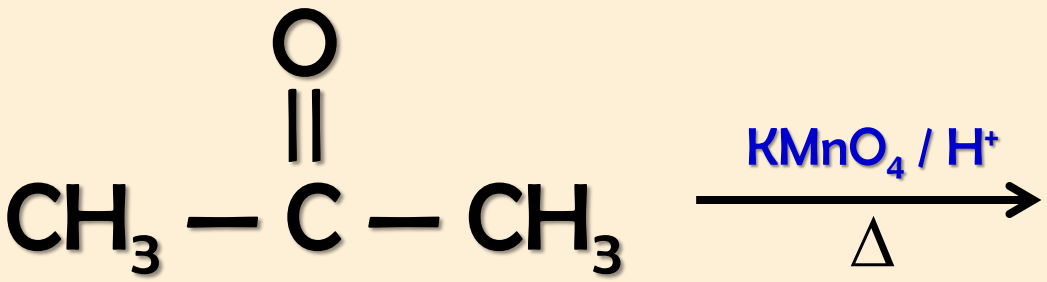
propanal

propanoic acid



cyclopentylmethanal

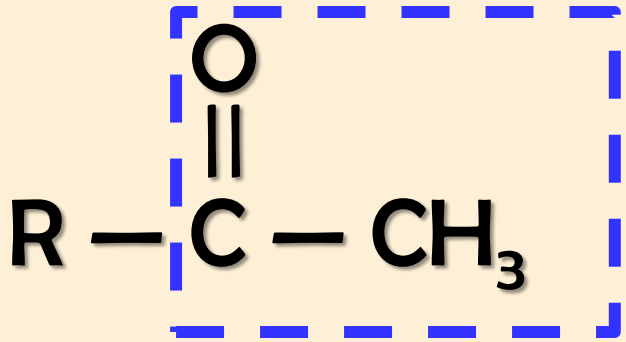
Cyclopentylmethanoic acid



Purple colour of acidified $KMnO_4$ remains

Propanone

(v) IODOFORM TEST

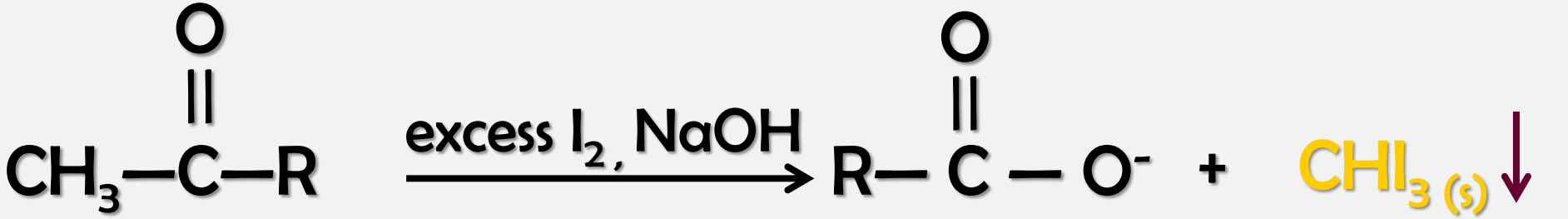


Identify methyl carbonyl group

Reagent : excess I_2 in $NaOH_{(aq)}$

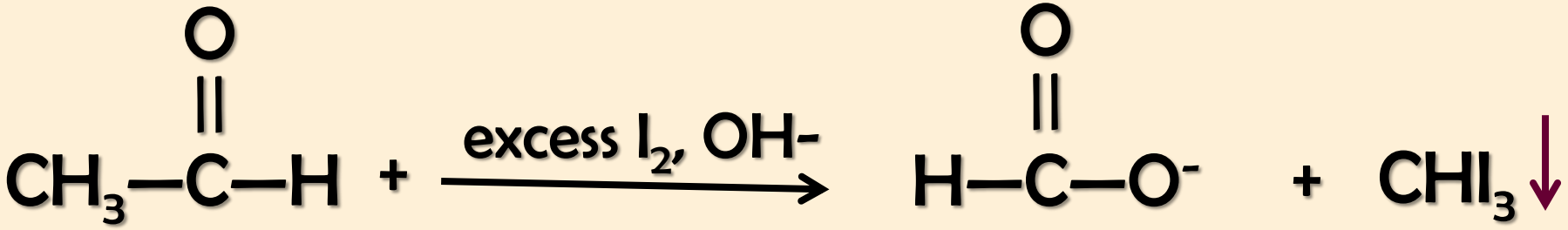
Observation : light yellow precipitate (CHI_3) is formed.

General reaction :



Triiodomethane (iodoform)

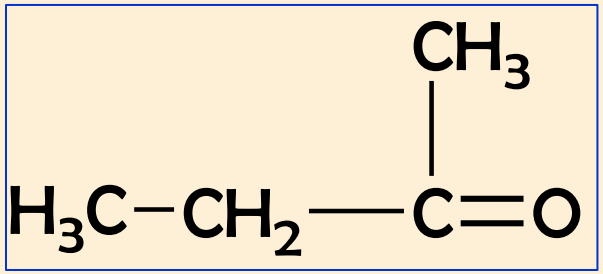
Example :



OBSERVATION: Light yellow precipitate (CHI_3) formed.

Which structures show the formation of yellow precipitate with excess iodine in NaOH?

1)



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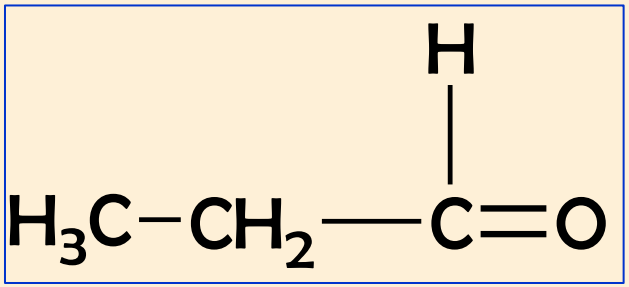

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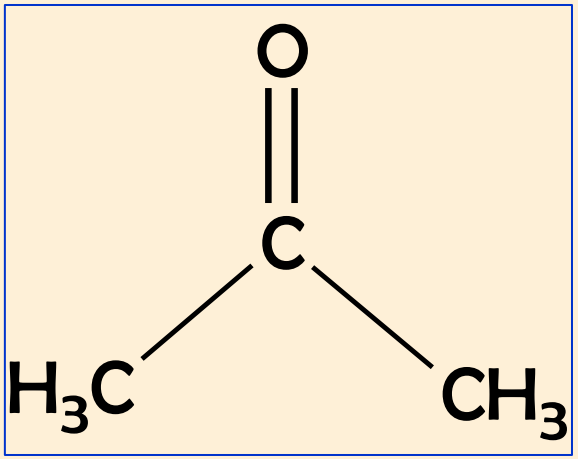

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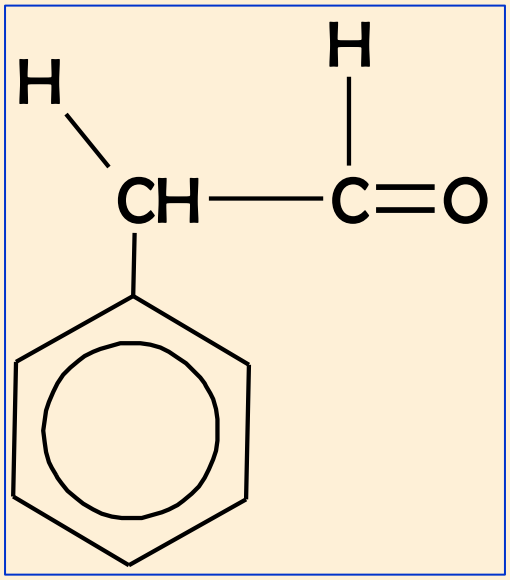
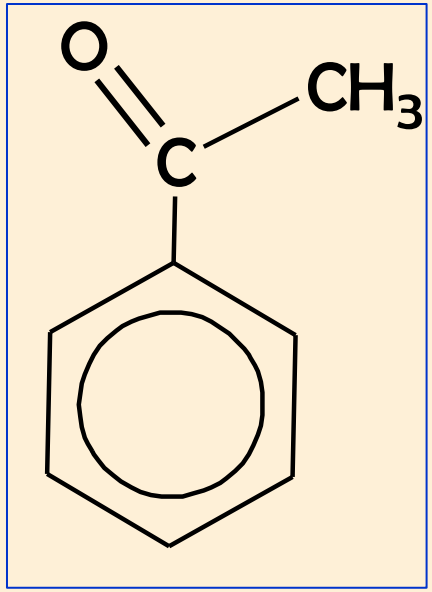
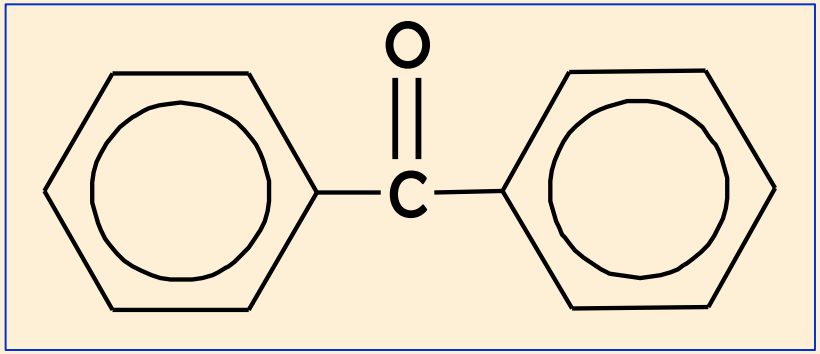


5)

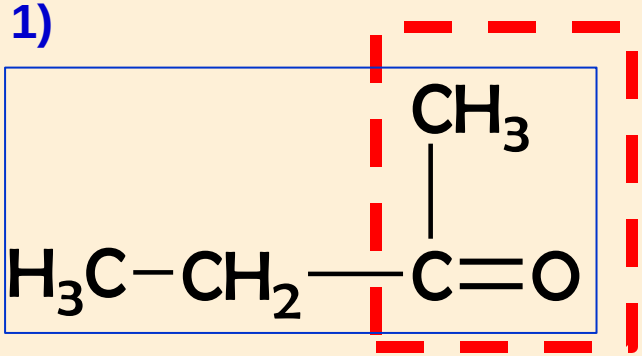


6)

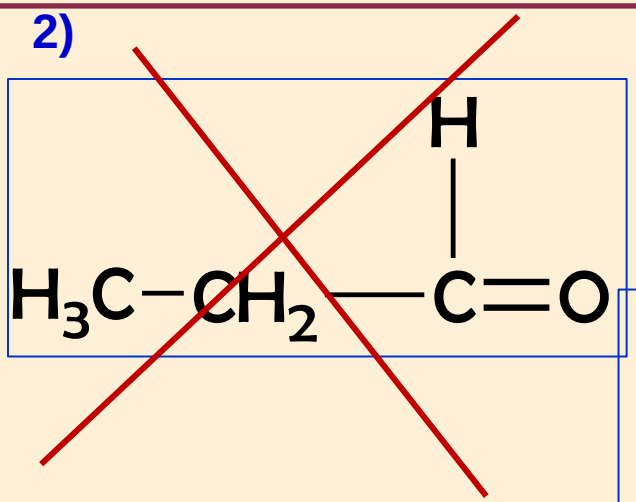


ANSWER :

1)



2)



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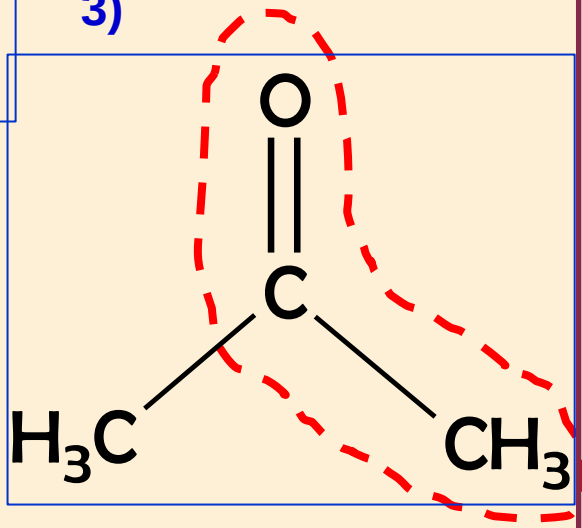

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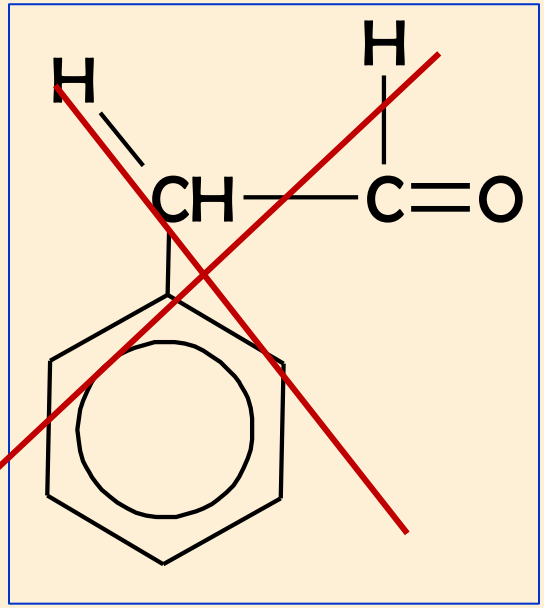

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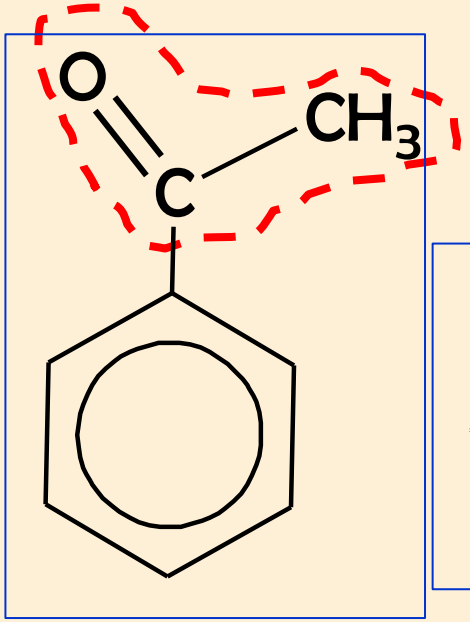
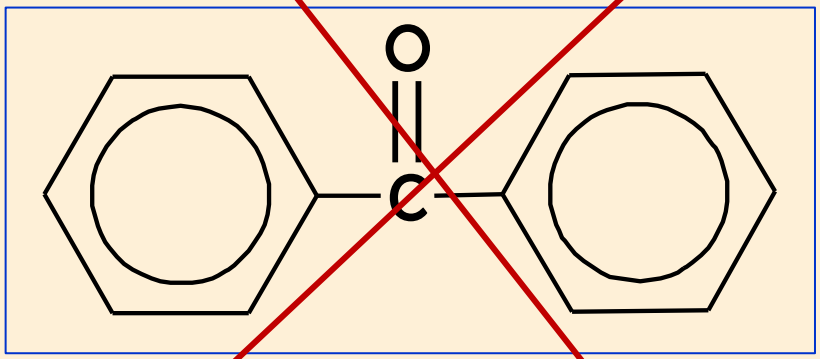


6)



Structure 1, 3 and 5.

Learning Outcomes:

9.3 Chemical Properties of Carbonyl Compounds

b) Explain the identification test for aldehyde & ketone using:

i. 2,4-dinitrophenylhydrazine (2,4-DNPH).

ii. Tollens', Fehlings' and Benedict's reagent

c) Differentiates between:

i. carbonyl & other compounds

ii. Aldehydes & ketone

Identification Tests

1.Brady's Test

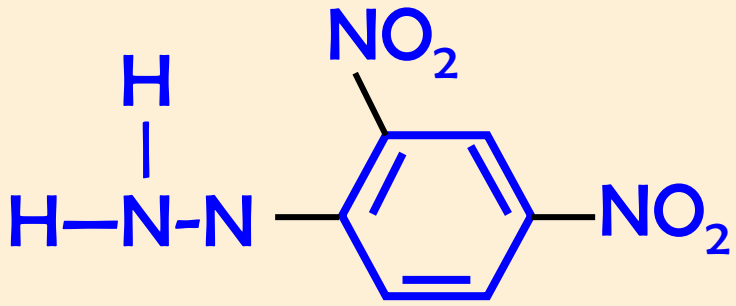
2.Tollens' Test

3.Fehlings' Test

4.Benedict's Test

Brady's Test

Identification Test	The presence of carbonyl group
Reagent :	2,4-DNPH (Brady's reagent)

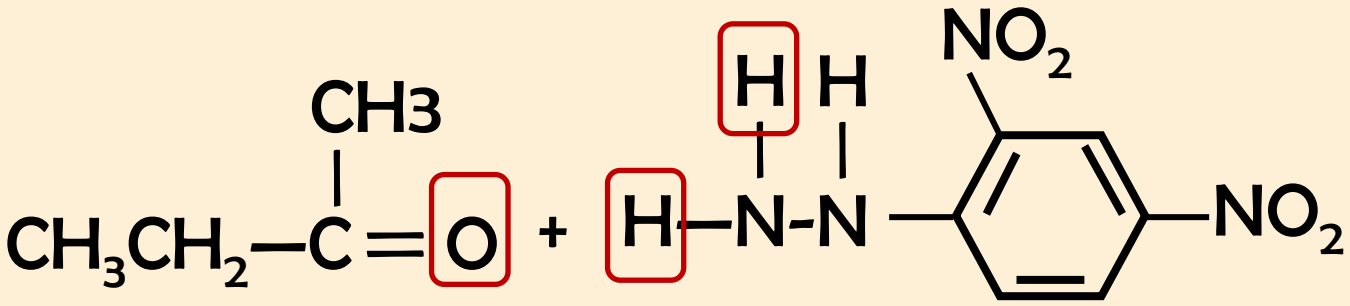


2,4-dinitrophenylhydrazine

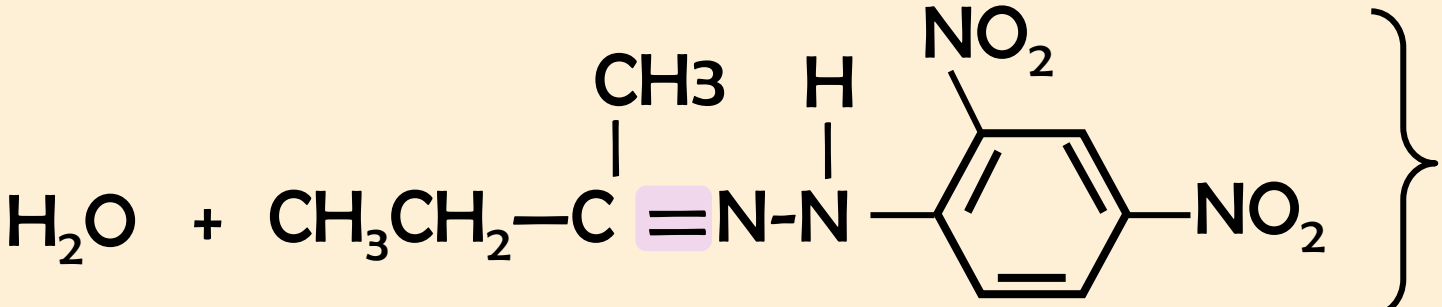
Observation:	Yellow @ Orange precipitate is formed.

1. Brady's Test

Example :



2,4-DNPH Brady's reagent



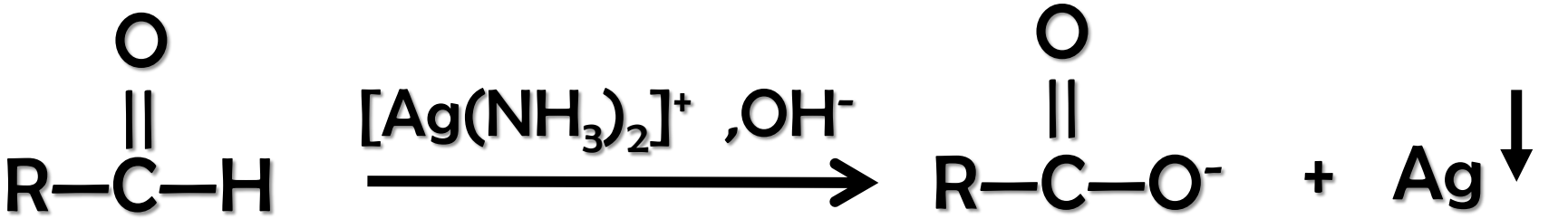
yellow @ orange precipitate

2-butanone-2,4-dinitrophenylhydrazone

2. Tollens' Test (Silver Mirror Test)

Identification Test	Differentiates aldehydes from ketones
Reagent :	➢ a mixture of aqueous silver nitrate and aqueous ammonia @ Tollens' reagent. ➢ Contains diamminosilver (I) ion, $Ag(NH_3)_2^+$.
Product :	**Carboxylate ion, RCOO- & silver, Ag(s)**
Observation:	**Silver is deposited on the wall of the test tube (Silver mirror)**

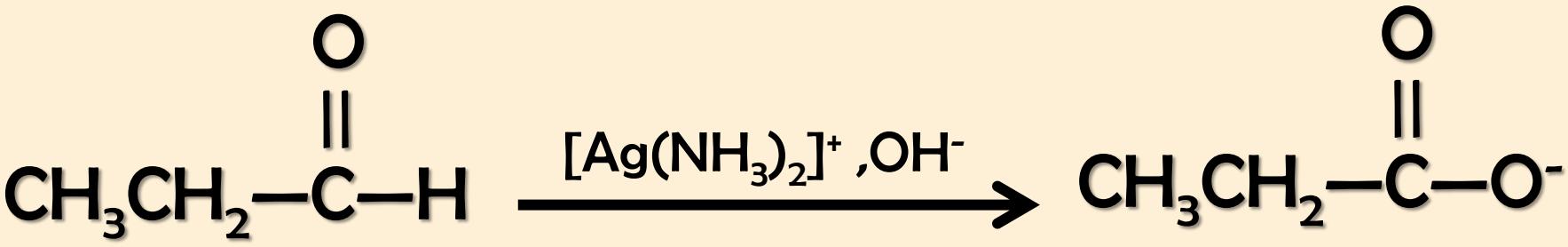
General reaction :



Aldehyde is **oxidised to carboxylate ion**.

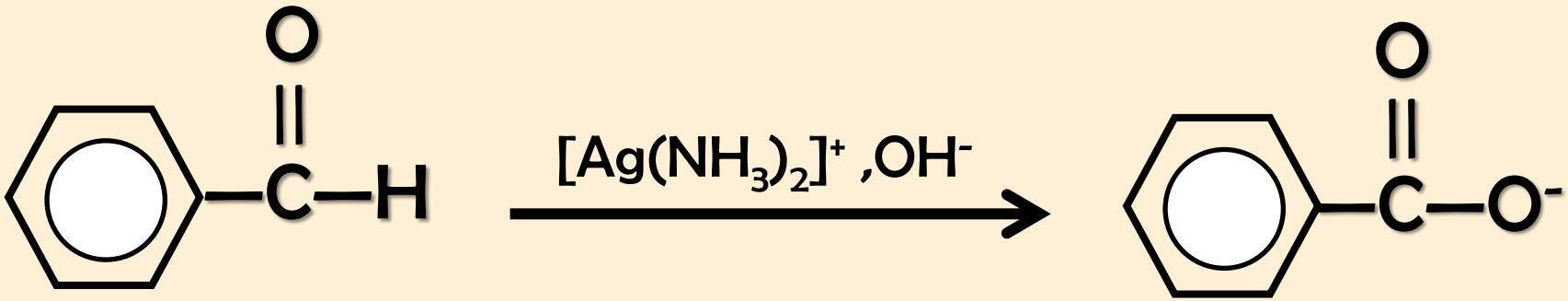
Ag^+ is reduced to Ag (silver)

Example :



propanal

Silver mirror

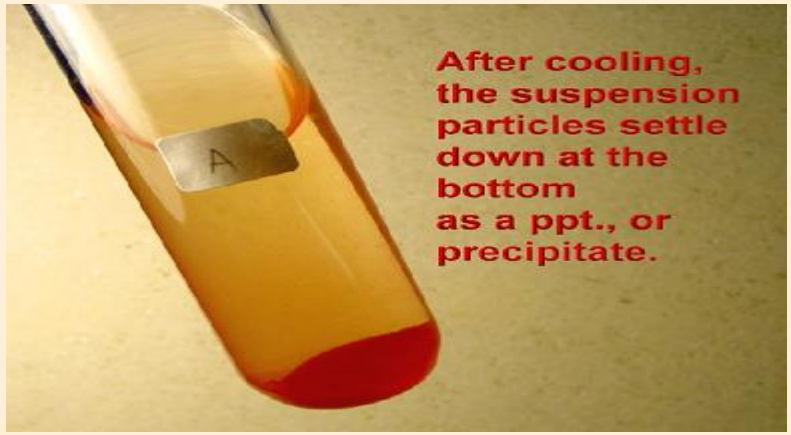


phenylmethanal

Silver mirror

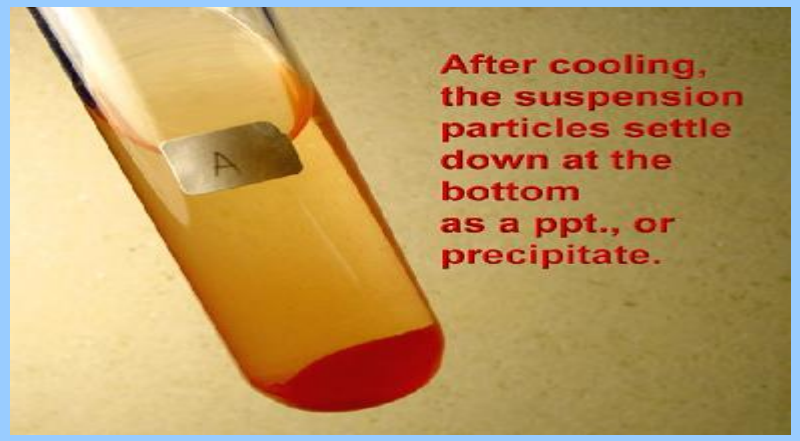
3. Fehlings' Test

Identification Test	to distinguish aliphatic aldehydes from aromatic aldehydes and ketones
Reagent :	➢ Cupric tartrate complex ion, Cu^{2+} (complex) ➢ Show the blue colour solution.
Product :	**Carboxylate ion, RCOO- &** **Copper (I) oxide, $Cu_2O(s)$**
Observation:	**Brick red precipitate is formed.**

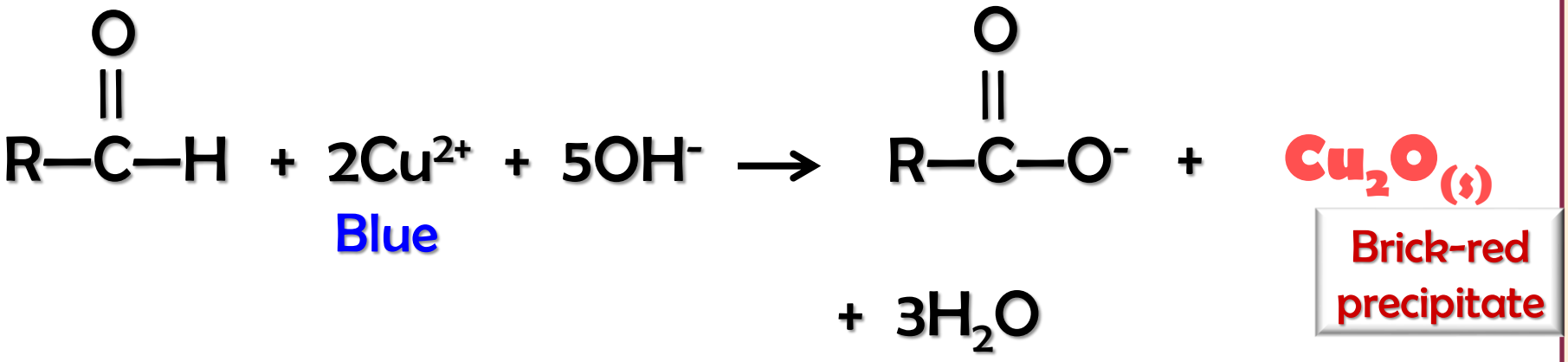


4. Benedict's Test

Identification Test	to distinguish aldehydes and ketones
Reagent :	➢ Cupric citrate complex ion, Cu^{2+} (complex) ➢ Show the blue colour solution.
Product :	**Carboxylate ion, RCOO- &** **Copper (I) oxide, $Cu_2O(s)$**
Observation:	**Brick red precipitate is formed.**



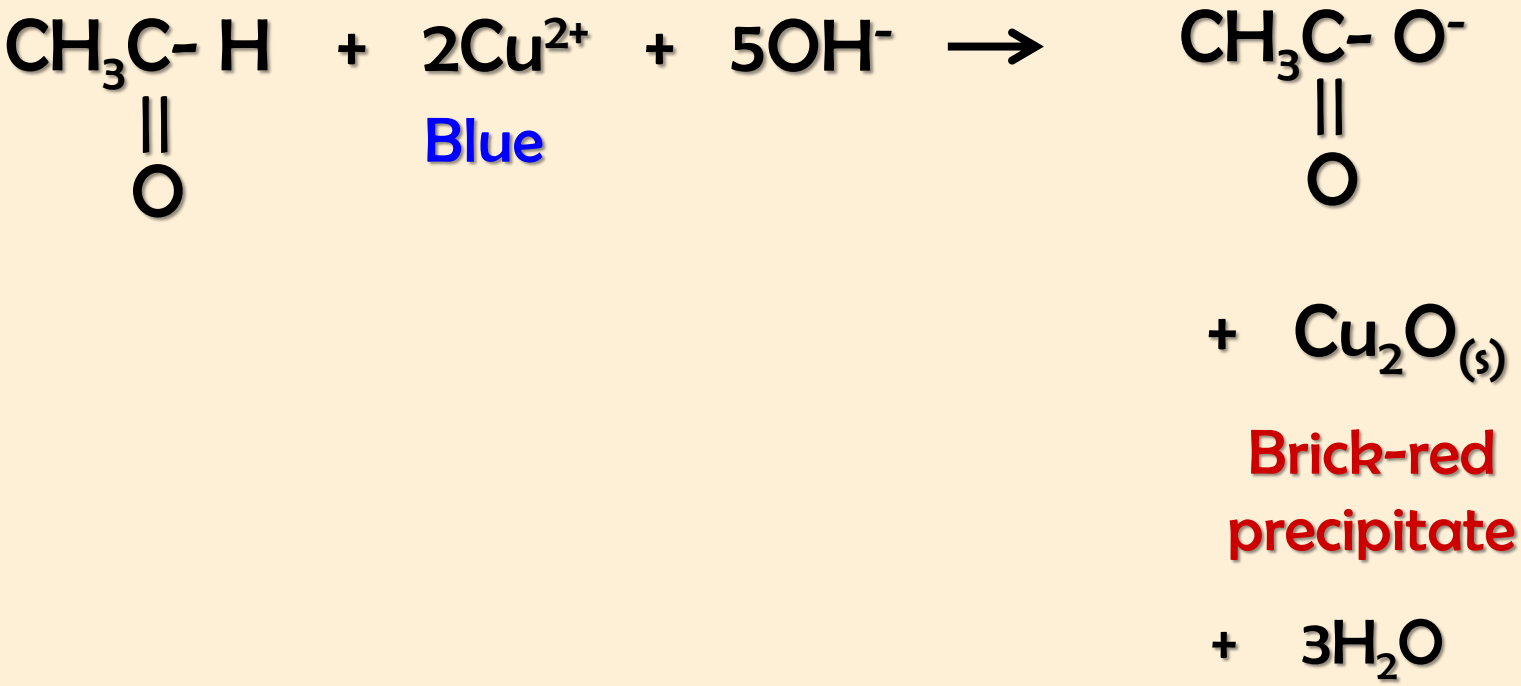
General reaction :



Aliphatic aldehyde is **oxidised to carboxylate ion**.

Copper (II) ion, Cu^{2+} is reduced to Copper (I) ion, Cu^{+}.

Example :



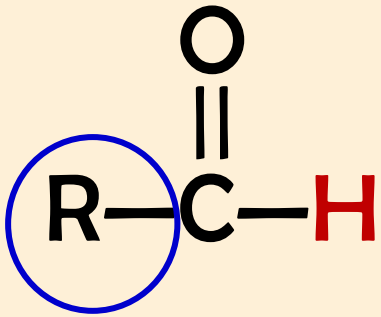
OBSERVATION: **Brick-red precipitate**

ALDEHYDE Vs KETONE

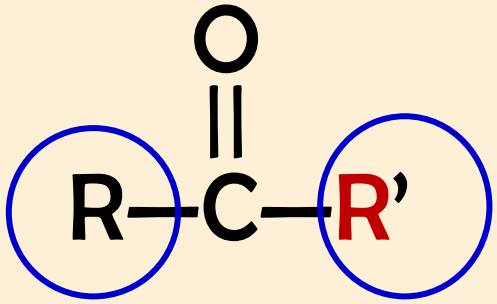
Aldehydes are **more reactive** than ketone in Nu^- addition reaction:

- **Steric factor**
- **Electronic factor**

Steric factor



- Only one alkyl group.
- More positively charged of the carbonyl C.
- Less steric effect.

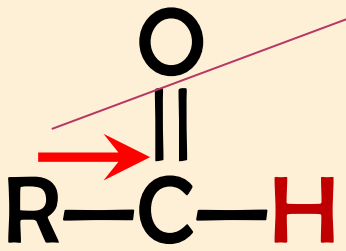


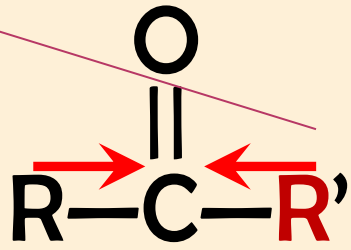
- Two alkyl groups.
- Less positively charged of the carbonyl C.
- More steric effect.

ALDEHYDE Vs KETONE

Electronic factor

Alkyl group, R = Electron Donating/Releasing group





Aldehyde has only ONE electron donating group.

Thus making the aldehyde carbonyl group slightly more **electron-poor** and electrophilic.

Refer : pg 832, Wade., Organic Chemistry, 17th Ed, Prentice Hall

Reduction of C=O

Selectivity of Reducing Agents

$LiAlH_4$ - does not reduce C=C and C≡C

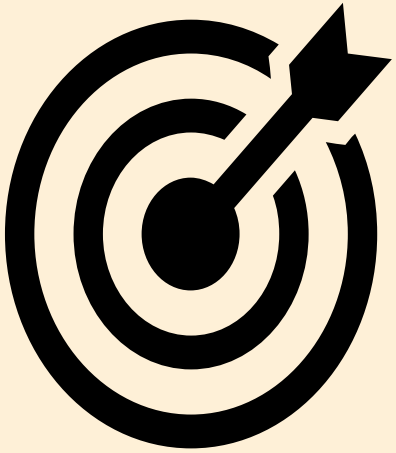
$NaBH_4$ - does not reduce C=C , C≡C and C=O in acid and esters

H_2/Pt - reduce C=C, C≡C and C=O

Hence, $NaBH_4$ is the best reducing agent for reduction of simple ketone and aldehyde.

Learning Outcomes:

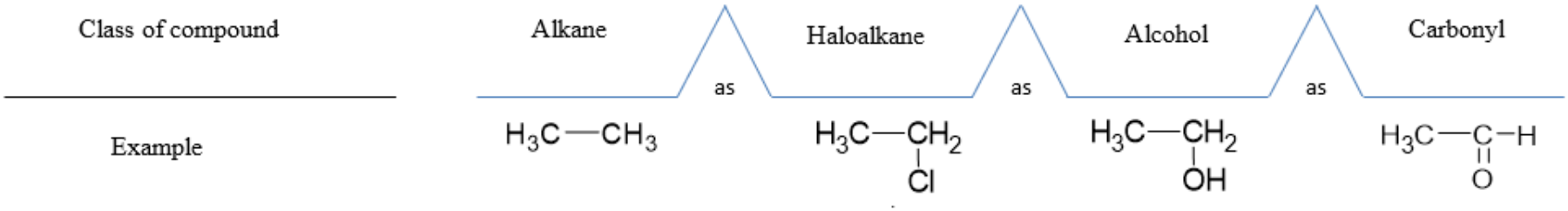
9.3 Chemical Properties of Carbonyl Compounds



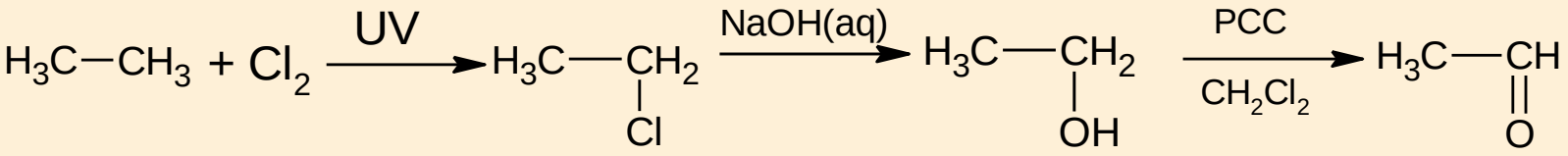
d) Outline the synthesis of compounds involving carbonyl compounds.

* Limit to maximum 4 steps only

Synthesis of carbonyl compounds.



Example :Outline the synthetic pathway of ethanal from ethane



GLOSSARY

BIL	TERM	SYMBOL/FORMULA	DEFINE
1.	**ALDEHYDE**	-	**Aldehye is named by substituting the letter –e of the corresponding alkane with -al.**
2.	**KETONE**	-	**Ketone is named by substituting the letter –e of the corresponding alkane with –one.**
3.	**GEM**	-	**Geminal (two OH or X bonded to the same C).**
4.	**HYDROLYSIS**	-	**Aqueous acid or diluted acid , H_3O^+.**

GLOSSARY

BIL	TERM	SYMBOL/FORMULA	DEFINE
5.	**OZONOLYSIS OF ALKENE**	-	**Oxidative cleavage of C=C to form aldehyde or ketone.**
6.	**TOLLENS' TEST**	-	**Contains the complex diaminesilver ion complex, $Ag(NH_3)_2^+$ prepared by mixing excess ammonia with silver nitrate solution.**
7.	**FEHLINGS' TEST**	-	**Contains basic complex of Cu^{2+} ion by mixing copper(II) sulphate with alkaline sodium potassium tartarate.**
8.	**IODOFORM TEST**	-	**Carbonyl compounds with methyl carbonyl group can react with iodine in warm alkaline solution, NaOH to form yellow precipititate of triiodomethane , CHI_3.**