Oxygen Containing Organic Compounds - II

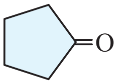
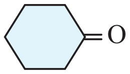
ALDEHYDES AND KETONES Section - 1

The compounds which contain a carbonyl group, > C = O with two valence of carbon satisfied by H or two alkyl (phenyl) groups are known as aldehydes and ketones. Aldehydes have alkyl or aryl, alkenyl group on one side of >C = O and H atom to the other side : whereas in ketones, the carbonyl group is situated between two carbon atoms (alkyl or aryl).

Important Aldehydes :

HCHO	(Formaldehyde)	C_6H_5CHO	(Benzaldehyde)
CH_3CHO	(Acetaldehyde)	$CH_2=CHCHO$	(Acrolein)
$(CH_3)_2CHCHO$	(Isobutyraldehyde)	$CH_3CH=CHCHO$	(Crotonaldehyde)
$C_6H_5CH_2CHO$	(Benzyl aldehyde)	$C_6H_5CH=CHCHO$	(Cinnamaldehyde)

Important Ketones :

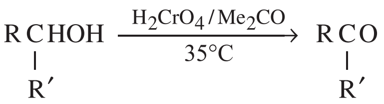
CH_3COCH_3	(Acetone)	$CH_3COCH = CH_2$	(Methyl vinyl ketone)
$CH_3COC_2H_5$	(Methyl ethyl ketone)	$C_6H_5CH = CHCOCH_3$	(Benzal acetone)
$C_6H_5COCH_3$	(Acetophenone)		(Cyclopentanone)
$C_6H_5COC_6H_5$	(Benzophenone)		
$C_6H_5CH_2COCH_3$	(Benzyl methyl ketone)		(Cyclohexanone)

Preparation :

1. Oxidation of alcohols :

By controlled oxidation of alcohols using $K_2Cr_2O_7$ at low temperature, alcohols are oxidised to aldehydes.

$$RCH_2OH \xrightarrow[K_2Cr_2O_7]{(O)} RCHO \xrightarrow[K_2Cr_2O_7]{(O)} RCOOH \text{ (Not a good method for aldehydes)}$$



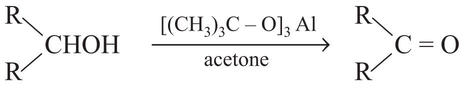
$$\underset{\displaystyle R'}{R\,\overset{}{C}HOH} \xrightarrow[35°C]{H_2CrO_4 / Me_2CO} \underset{\displaystyle R'}{R\,CO}$$

(Jones Oxidation)

The oxidation of primary alcohols can be brought by using Pyridinium chlorochromate, $C_5H_5NH^+CrO_3Cl^-$ (PCC) to aldehydes. PCC does not oxidise aldehydes to acids.

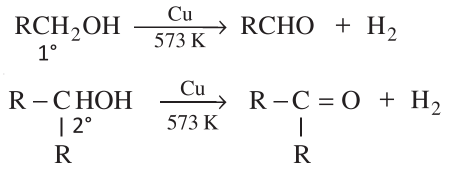
$$R-CH_2OH \xrightarrow[CH_2Cl_2]{PCC} R-CHO \xrightarrow[CH_2Cl_2]{PCC} \text{No oxidation}$$

Oppenauer oxidation : Using a specific oxidising agent like Aluminium tert. Butoxide, i.e., $[(CH_3)_3C-O]_3Al$ in presence of Acetone, secondary alcohols can be oxidised to ketones.



$$R_2CHOH \xrightarrow[\text{acetone}]{[(CH_3)_3C-O]_3Al} R_2C=O$$

2. Dehydrogenation of Alcohols :



$$\underset{1^\circ}{RCH_2OH} \xrightarrow[573\text{ K}]{Cu} RCHO + H_2$$

Aldehyde

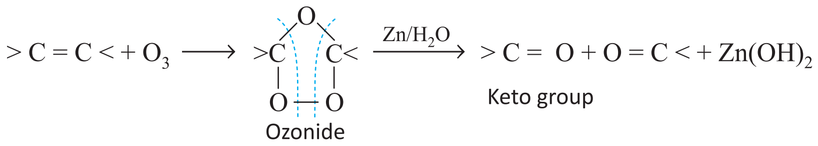
$$\underset{R}{\underset{|\,2^\circ}{R-CHOH}} \xrightarrow[573\text{ K}]{Cu} \underset{R}{\underset{|}{R-C=O}} + H_2$$

Ketone

Note : 3° alcohols undergo dehydration (alkene formation)

3. From Alkenes :

(a) Ozonolysis : (refer to alkenes)



$$>C=C<+O_3 \longrightarrow \text{Ozonide} \xrightarrow{Zn/H_2O} >C=O+O=C<+Zn(OH)_2$$

Ozonide

Keto group

(b) Oxo-process : (only for Aldehydes)

It is an industrial method for formation of aldehydes from alkenes, where the catalyst, cobalt carbonyl at high temperature and pressure is used.

$$RCH=CH_2 + CO + H_2 \xrightarrow{[Co(CO)_4]_2} RCH_2CH_2CHO$$

(c) Wacker Process :

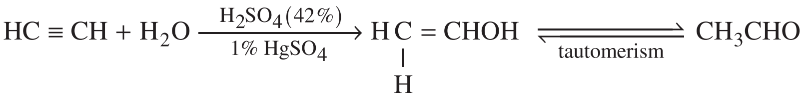
$$CH_2=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3CHO + Pd + 2HCl$$

aldehyde

$$CH_3CH=CH_2 + PdCl_2 + H_2O \xrightarrow{CuCl_2} CH_3COCH_3 + Pd + 2HCl$$

ketone

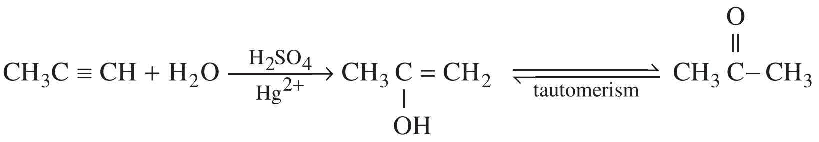
4. Hydration of Alkynes :



$$HC\equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{H_2SO_4(42\%)} \underset{H}{\underset{|}{HC=CHOH}} \underset{\text{tautomerism}}{\rightleftharpoons} CH_3CHO$$

enol form

keto form



$$CH_3C\equiv CH + H_2O \xrightarrow[Hg^{2+}]{H_2SO_4} \underset{OH}{\underset{|}{CH_3C=CH_2}} \underset{\text{tautomerism}}{\rightleftharpoons} CH_3\overset{O}{\overset{\|}{C}}-CH_3$$

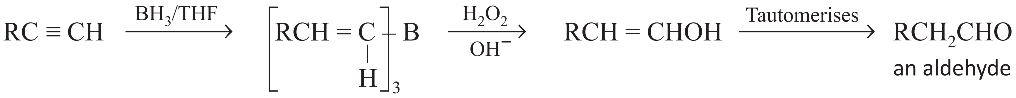
enol form

keto form

Note : Keto form is more stable than enol form.

5. Hydroboration-oxidation of Alkynes : *Syn, Anti-Markovnikov and free from any rearrangement.*

Hydroboration of terminal alkynes gives aldehydes.

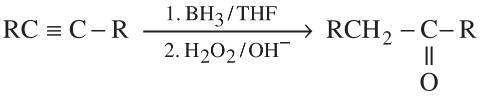


$$RC\equiv CH \xrightarrow{BH_3/THF} \left[RCH=\underset{\displaystyle H}{\overset{}{C}}-\right]_3 B \xrightarrow[OH^-]{H_2O_2} RCH=CHOH \xrightarrow{\text{Tautomerises}} RCH_2CHO$$

Trialkenyl borane

an aldehyde

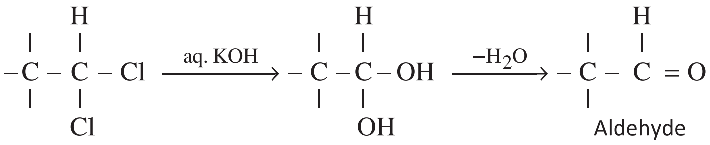
However, if non-terminal alkynes are used, ketones are formed.



$$RC\equiv C-R \xrightarrow[2.\ H_2O_2/OH^-]{1.\ BH_3/THF} RCH_2-\underset{\displaystyle \overset{\|}{O}}{C}-R$$

6. Hydrolysis of gem – dihalides

(i)

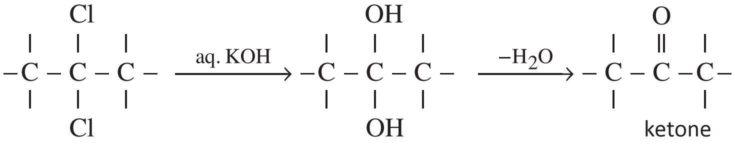


$$-\underset{|}{\overset{|}{C}}-\underset{\displaystyle Cl}{\overset{\displaystyle H}{C}}-Cl \xrightarrow{\text{aq. KOH}} -\underset{|}{\overset{|}{C}}-\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}-OH \xrightarrow{-H_2O} -\underset{|}{\overset{|}{C}}-\overset{\displaystyle H}{C}=O$$

(Terminal)

Aldehyde

(ii)



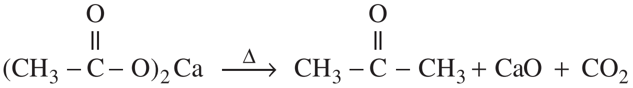
$$-\underset{|}{\overset{|}{C}}-\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{C}}-\underset{|}{\overset{|}{C}}- \xrightarrow{\text{aq. KOH}} -\underset{|}{\overset{|}{C}}-\underset{\displaystyle OH}{\overset{\displaystyle OH}{C}}-\underset{|}{\overset{|}{C}}- \xrightarrow{-H_2O} -\underset{|}{\overset{|}{C}}-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{|}{\overset{|}{C}}-$$

(Non-Terminal)

ketone

7. Pyrolysis (heating) of Calcium Salts of acids :

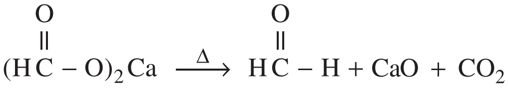
(i)



$$(CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3+CaO+CO_2$$

Calcium acetate

(ii)



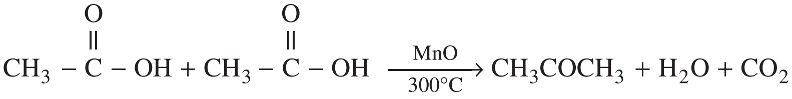
$$(H\overset{\displaystyle O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} H\overset{\displaystyle O}{\overset{\|}{C}}-H+CaO+CO_2$$

(iii)

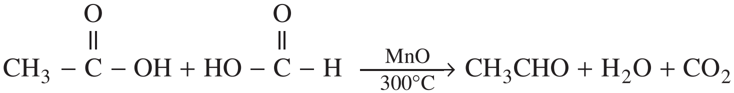
$$(CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-O)_2Ca+(H-\overset{\displaystyle O}{\overset{\|}{C}}-O)_2Ca \xrightarrow{\Delta} \underset{\text{major product}}{CH_3CHO}+\underset{\text{minor products}}{(CH_3COCH_3+HCHO)}+2CaO+2CO_2$$

(Cross product)

8. Catalytic decomposition of Acids :



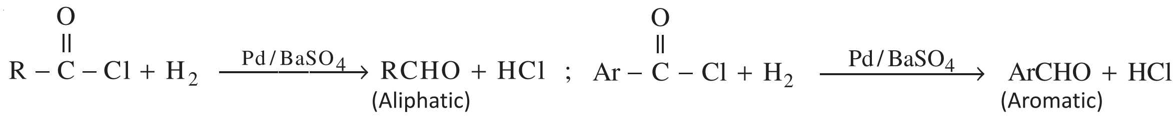
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH+CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH \xrightarrow[300^\circ C]{MnO} CH_3COCH_3+H_2O+CO_2$$



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH+HO-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow[300^\circ C]{MnO} CH_3CHO+H_2O+CO_2$$

(Cross product)

9. Reduction of Acid Chloride : (only Aldehydes are prepared by this method)

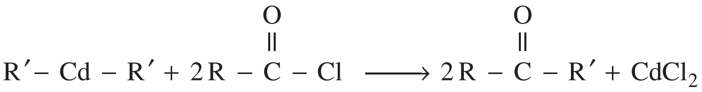


$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl \;;\; Ar-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} ArCHO + HCl$$

(Aliphatic) (Aromatic)

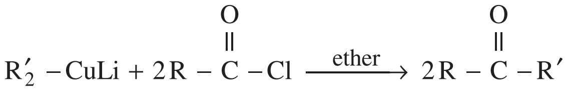
Note : The above reduction is known as *Rosenmund Reduction.*

10. From Dialkyl Cadmium : (only Ketones can be prepared by this method)



$$R'-Cd-R' + 2R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-R' + CdCl_2$$

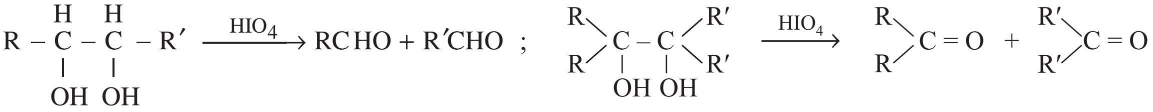
11. From Lithium Dialkylcuprates : (only Ketones are prepared by this method)



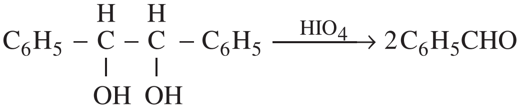
$$R'_2-CuLi + 2R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{ether} 2R-\overset{O}{\overset{\|}{C}}-R'$$

12. Cleavage of Diols :

By oxidative cleavage of 1, 2–diols (glycols) by periodic acid (HIO_4) or by lead tetra acetate, both aldehydes and ketones may be produced.



$$R-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-R' \xrightarrow{HIO_4} RCHO + R'CHO \;;\; R_2\underset{OH}{C}-\underset{OH}{C}R'_2 \xrightarrow{HIO_4} R_2C=O + R'_2C=O$$

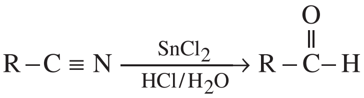


$$C_6H_5-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-C_6H_5 \xrightarrow{HIO_4} 2C_6H_5CHO$$

(Benzaldehyde)

13. Stephan Method : (only Aldehydes can be prepared by this method)

An alkyl cyanide is dissolved in ether or ester and reduced with stannous chloride and HCl and finally distilled to give aldehydes.



$$R-C\equiv N \xrightarrow[HCl/H_2O]{SnCl_2} R-\overset{O}{\overset{\|}{C}}-H$$

Note :

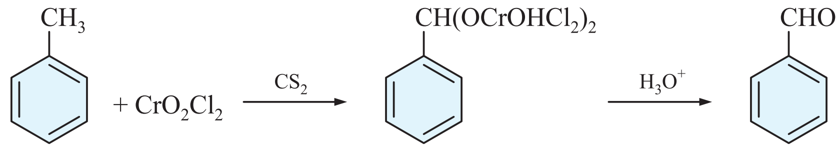
- Using Grignard reagent with ester, cyanides and acid chlorides under proper conditions, one can prepare aldehydes and ketones. Refer to reactions of Grignard Reagent in Halogen derivatives.
- Nitriles are selectively reduced by di-isobutyl aluminium hydride (DIBAL-H) to imines and then to aldehydes by hydrolysis. It is also called as (DIBAH). $RCN \xrightarrow[2.\ H_2O]{1.\ AlH(iso-Bu)_2} R-CHO$
- DIBAL-H also reduces acid halides to aldehydes.
- Esters can also be reduced to aldehydes using DIBAL-H. $RCOOR' \xrightarrow[2.\ H_2O]{1.\ AlH(iso-Bu)_2} RCHO + R'OH$

Preparation of Benzaldehyde : C_6H_5CHO

(a) Gattermann – Koch Reaction : $C_6H_6 + CO + HCl \xrightarrow[\text{or CuCl}]{AlCl_3} C_6H_5CHO$

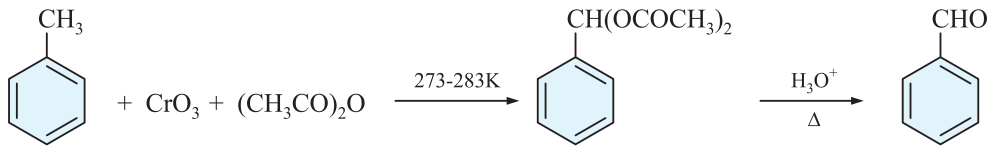
> **Note :** *Gattermann Aldehyde Synthesis :* $C_6H_6 + HCN + HCl \xrightarrow[H_2O]{AlCl_3} C_6H_5CHO + NH_4Cl$

(b) Etard Reaction :



Toluene Chromium complex Benzaldehyde

Note : The above reaction can also be brought by CrO_3/acetic anhydride followed by acidic hydrolysis.



Toluene Benzylidene diacetate Benzaldehyde

(c) From Benzyl Chloride :

By boiling benzyl chloride in aqueous solution of copper or lead nitrate in a current of CO_2 benzaldehyde can be prepared.

$$C_6H_5CH_2Cl \xrightarrow[CO_2]{Pb(NO_3)_2} C_6H_5CHO + HNO_2 + PbCl_2$$

> **Note :** Benzaldehyde can also be prepared by Rosenmund reduction, Stephan method and Grignard reagent with formates.
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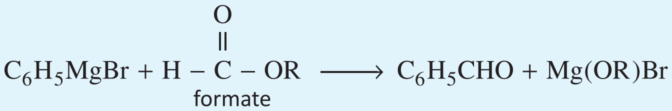
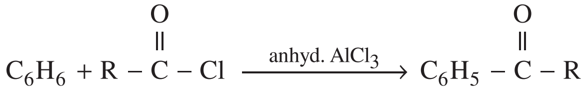
> 
>
> $$C_6H_5MgBr + \underset{\text{formate}}{H-\overset{\overset{\displaystyle O}{\|}}{C}-OR} \longrightarrow C_6H_5CHO + Mg(OR)Br$$

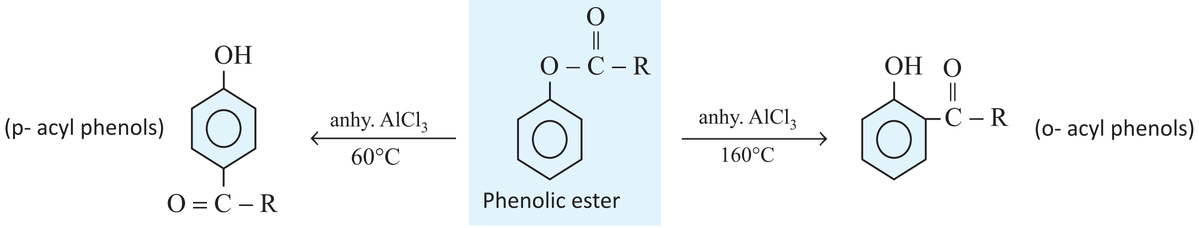
Preparation of Aromatic Ketones :

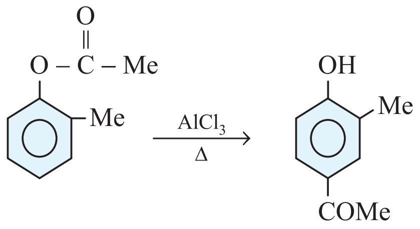
(a) Friedel-Craft Acylation reaction : Aromatic ketones can be formed by acylation of Benzene.



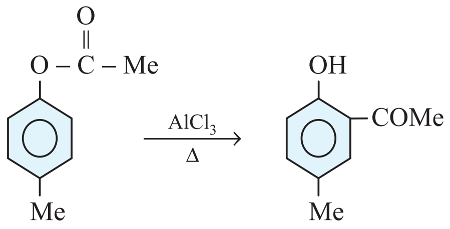
$$C_6H_6 + R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{\text{anhyd. }AlCl_3} C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-R$$

(b) Fries rearrangement : It is an important method for the preparation of aromatic ketones from phenolic esters.

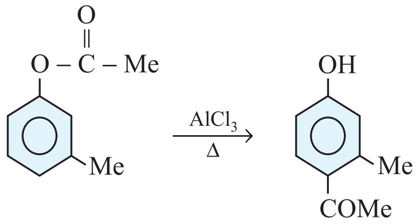




(Major) ;



(Major)



Note **:** Observe that phenolic group (–OH attached to benzene) can be reduced by zinc dust to give ketones.

Mechanism :

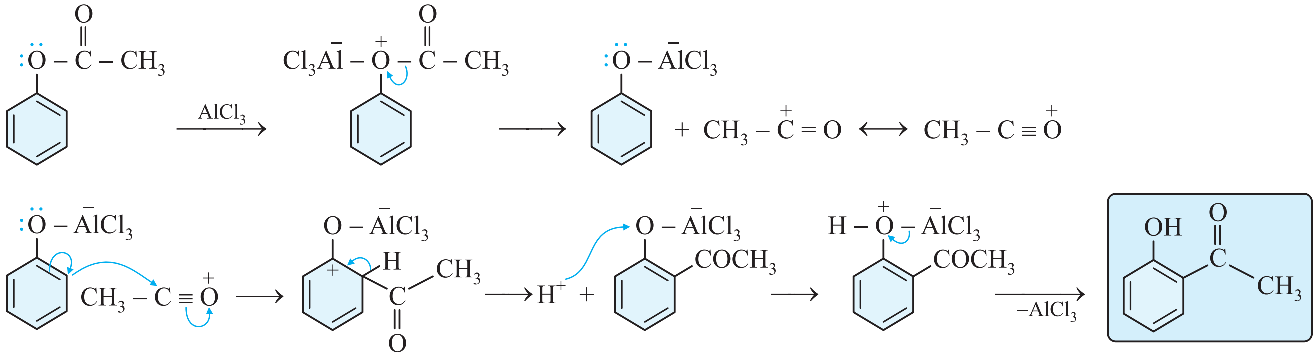
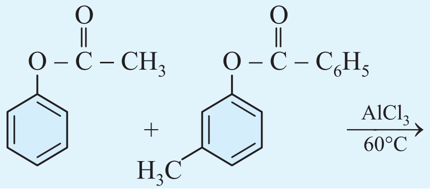


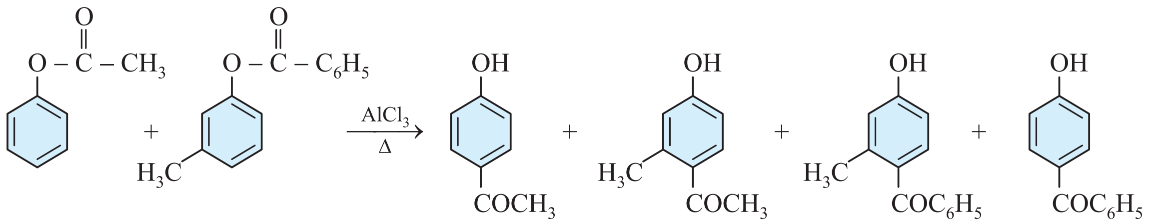
Illustration - 1

Visualise the formation of four products in the given reaction :



SOLUTION :

Observing the mechanism illustrated above, acyl carbocation is separated during rearrangement. This will result in S_E reaction in both the rings.



IN-CHAPTER EXERCISE-A

Choose the correct alternative. Only One choice is Correct. However, questions marked with '*' may have More than One correct option.

***1.** *Which of the following reactions will give acetophenone as product ?*

(A) *Acid catalysed hydration of styrene followed by oxidation with hot alkaline* $KMnO_4$

(B) *Phenyl acetylene* $\xrightarrow{\text{dil } H_2SO_4 / Hg^{2+}}$

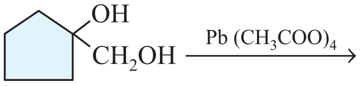
(C) *Reaction of benzoyl chloride with dimethyl cadmium*

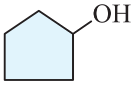
(D) *Dry distillation of a mixture of calcium acetate and calcium benzoate*

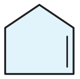
***2.** *Which of the following reactions give aldehyde as a product ?*

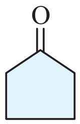
(A) $CH_3 - COOC_2H_5 \xrightarrow[\text{2. } H_2O]{\text{1. DIBAL-H}}$ **(B)** $C_6H_6 \xrightarrow[AlCl_3 / CuCl]{CO + HCl_{(g)}}$

(C) $C_6H_6 \xrightarrow[\text{2. } H_2O]{\text{1. HCN + } HCl_{(g)}}$ **(D)** $CH_3 - CH_2 - CN \xrightarrow[\text{2. } H_2O]{\text{1. } CH_3MgBr}$

***3.**  *Products. The possible product(s) obtained in the above reaction is(are) :*

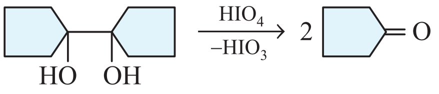
(A) 

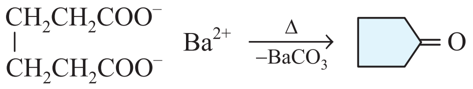
(B) 

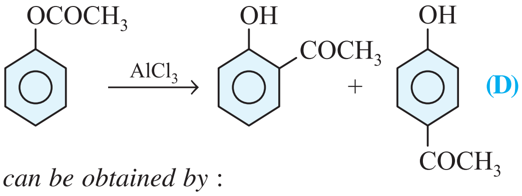
(C) 

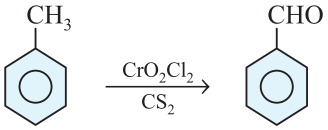
(D) *HCHO*

***4.** *Which of the following reactions are represented correctly ?*

(A) 

(B) 

(C) 

(D) 

***5.** *Acetone can be obtained by :*

(A) *alkaline hydrolysis of 2, 2-dichloropropane*

(B) *passing vapours of isopropyl alcohol over red hot copper*

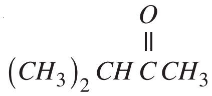
(C) *acid catalyzed hydration of methyl acetylene*

(D) *ozonolysis of 2, 3-dimethylbut-2-ene*

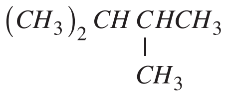
(E) *acid catalyzed hydrolysis of cumene hydroperoxide*

6. $(CH_3)_2C = CH_2 + CO + H_2 \xrightarrow[\text{High T \& P}]{[Co(CO)_4]_2} A$

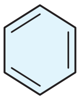
A formed is :

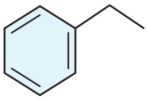
(A) $(CH_3)_2CHCH_2CHO$ **(B)** 

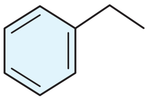
$(CH_3)_2CH\overset{\overset{\large O}{\|}}{C}CH_3$

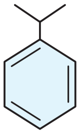
(C) $(CH_3)_2CHCH_2CH_3$ **(D)** 

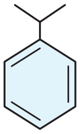
$(CH_3)_2CH\underset{\underset{\large CH_3}{|}}{C}HCH_3$

7.  $\xrightarrow[AlCl_3]{CH_3-CH_2-CH_2-Cl}$ [P] $\xrightarrow[2.\ H_3O^+]{1.\ O_2/\Delta}$ [Q] + Phenol, P and Q are :

(A)  and $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

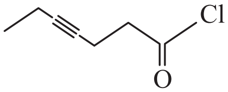
(B)  and $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(C)  and $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(D)  and $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

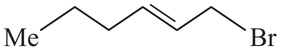
Paragraph for Questions 8 - 10

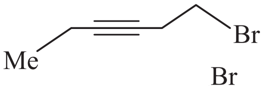
In the following reaction sequence, products I, J and L are formed and K represents a reagent.

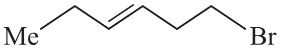
Hex-3-ynal $\xrightarrow[2.\ PBr_3]{1.\ NaBH_4}$ I $\xrightarrow[3.\ H_3O^+]{1.\ Mg/ether \quad 2.\ CO_2}$ J $\xrightarrow{K}$ 

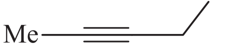
$\xrightarrow[Pd/BaSO_4,\ quinoline]{H_2}$ L

8. The structure of the product I is:

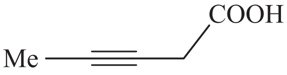
(A) 

(B) 

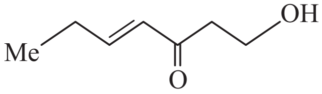
(C) 

(D) 

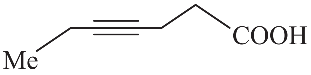
9. The structures of compounds J and K, respectively, are :

(A) 

and $SOCl_2$

(B) 

and SO_2Cl_2

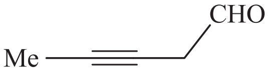
(C) 

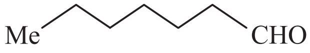
and $SOCl_2$

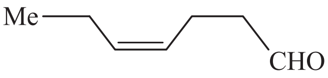
(D) 

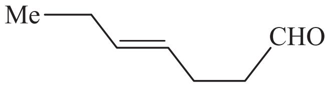
and CH_3SO_2Cl

10. The structure of product L is :

(A) 

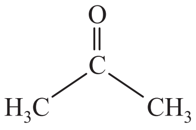
(B) 

(C) 

(D) 

Paragraph for Questions 11 - 12

An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in the which Q is an intermediate organic compound.

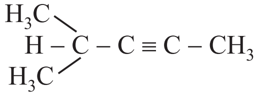
$\underset{(C_6H_{10})}{[P]}$ $\xrightarrow[2.\ NaBH_4/ethanol \quad 3.\ dil.\ acid]{1.\ dil.\ H_2SO_4/HgSO_4}$ [Q] $\xrightarrow[2.\ O_3 \quad 3.\ Zn/H_2O]{1.\ conc.\ H_2SO_4\ (Catalytic\ amount),\ -H_2O}$ 2 

11. *The structure of compound P is :*

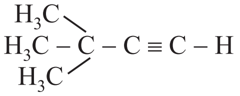
(A) $CH_3CH_2CH_2CH_2-C\equiv C-H$

(B) $CH_3CH_2-C\equiv C-CH_2CH_3$

(C)

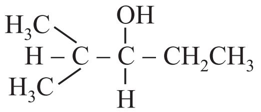


(D)

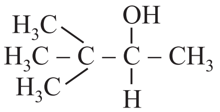


12. *The structure of the compound Q is :*

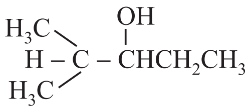
(A)



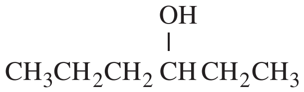
(B)



(C)



(D)



$CH_3CH_2CH_2\overset{OH}{\overset{|}{C}H}CH_2CH_3$

13. *An acid chloride on reaction with* $\xrightarrow[Pd-BaSO_4]{H_2}$ *gives* $(CH_3)_2CHCHO$. *It on reaction with* CH_3MgBr/H_3O^+ *will give :*

(A) $(CH_3)_2CHCOCH_3$

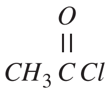
(B) CH_3CHO

(C) CH_3COCH_3

(D) CH_3CH_2CHO

14. *Grignard reagent can convert the following into carbonyl compounds except :*

(A)



$CH_3\overset{O}{\overset{||}{C}}Cl$

(B)

$H\overset{O}{\overset{||}{C}}OCH_3$

(C) $CH_3C\equiv N$

(D) CH_3CH_2OH

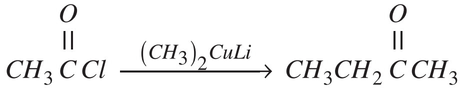
***15.** *Which is (are) the correct reaction(s) ?*

(A) $CH_3CH=CH_2 \xrightarrow{\text{Oxo method}} CH_3CH_2CH_2CHO$

(B) $RCN \xrightarrow{\text{DIBAL-H}} RCHO$

(C) $(HCOO)_2Ca \xrightarrow{\Delta} HCHO$

(D)



$CH_3\overset{O}{\overset{||}{C}}Cl \xrightarrow{(CH_3)_2CuLi} CH_3CH_2\overset{O}{\overset{||}{C}}CH_3$

***16.** CH_3CHO *can be prepared by :*

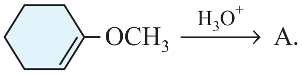
(A) *Oxidation of* CH_3CH_2OH *using* $Cr_2O_7^{2-}/H^+$

(B) *Oxidation of* $CH_2=CH_2$ *using* $PdCl_2 . CuCl_2/H_2O$

(C) *Reaction of* CH_3CN *with* $SnCl_2/HCl/H_2O$

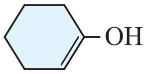
(D) *oxidation of* CH_3CH_2OH *using* PCC/CH_2Cl_2

17.

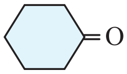


The structure of A is :

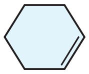
(A)



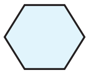
(B)



(C)



(D)



18. *Which one of the following can be oxidised to the corresponding carbonyl compound ?*

(A) *2-propanol* **(B)** *ortho-nitrophenol* **(C)** *Phenol* **(D)** *2-methyl-2-propanol*