Homework

Oxygen Containing Organic Compounds-II

Preparation of Aldehydes & Ketones

(A) General Methods :

1. Oxidation of alcohols
   (a) typical oxidation (b) PCC/ PDC (c) Jone's reagent
   (d) Cu/573K (e) MnO_2 (f) Oppenaur oxidation
2. From Alkenes
   (a) Ozonolysis (b) Oxo Process (only aldehydes)
   (c) Wacker Process (only ketones)
3. From Alkynes
   (a) Acid catalysed Hydration (b) HBO-DBO (c) Hydroxylation
4. Hydrolysis of Gem-halides
5. From Diols (glycols)
   (a) Cleavage (b) Acid catalysed rearrangement (c) Oxidation
6. Pyrolysis (heating) Calcium Salts of Acids

(B) Exclusively for Aldehydes & Benzaldehyde

7. Rosenmund Reduction (From Acid Chlorides)
8. Stephen Reduction (From Cyanides)
9. Use of DIBAL-H (Reduction of Esters & Cyanides)
10. Etard Reaction (From Toluene)
11. Gattermann Koch Reaction
12. Gattermann Aldehyde Synthesis
13. From Benzyl Chloride
14. From Organo-metallic compunds
    (a) Using Grignard Reagent (b) Using Gilman Reagent

Note : From Alkanes (Mainly Lower Aldehydes)

(C) Exclusively for Ketones & Aromatic ketones

15. From Organo-metallic compunds
    (a) Using Grignard Reagent
    (b) Using Gilman Reagent
    (c) Using Dialkyl Cadmium
16. Friedel Crafts Acylation
17. Fries Rearrangement

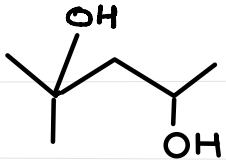
Class-2-OCOC-II

Reactions of Aldehydes & Ketones

I. Typical (Direct) Nucleophilic Addition :

1. Of Hydride ion (H^-) : $LiAlH_4$ /ether or $NaBH_4/H_2O$
2. Of Alkynide ion ($R-C\equiv\bar{C}-\overset{+}{N}a$)
3. Of H_2O/H^+ (Hydration)
4. (a) Of ROH/H^+ (b) Of Glycols (c) Of 1,3 Diols
5. Of HCN/KOH
6. Of $NaHSO_3$ (Bisulphate addition)
7. Of Grignard Reagent
8. Of Ylides (Wittig Reaction)
9. Of Ammonia & it's derivatives
   (a) of ammonia (b) of Amines (RNH^2 & RNHR)
   (c) of special derivatives (NH_2Y) (d) Reductive amination

Identify the products & reagents (R).

1.  $\xrightarrow[Py]{CrO_3}$ A $\xrightarrow[\Delta]{H^+}$ B

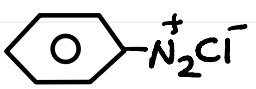
2.  $\xrightarrow[H_2O]{LiAlH_4}$ X $\xrightarrow{(O)}$ Y $\xrightarrow[2.\ (R)\ ?]{1.\ PCl_5}$ Z

 $\xrightarrow{DIBAL\text{-}H}$ Z

3. $CH_3C\equiv CH$ $\xrightarrow[2.\ H_2O_2/\bar{O}H]{1.\ BH_3/THF}$ A $\xrightarrow[Acetone,\ 25°C]{H_2CrO_4}$ B $\xrightarrow{SOCl_2}$ C $\xrightarrow[BaSO_4]{Pd}$ D $\xrightarrow[2.\ H_2O]{1.\ PhMgBr}$ E

4. A ($C_5H_{10}Br_2$) $\xrightarrow{KOH\ aq}$ B (an aldehyde with No α-H)

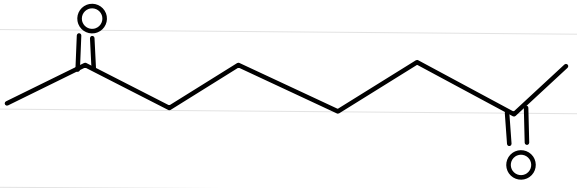
5. $Me_2Cd + PhCOCl \longrightarrow A \xrightarrow[2.\ H_3O^+]{1.\ MeMgBr} B \xrightarrow[573K]{Cu} C$

6.  $\xrightarrow[HCN]{CuCN} A \xrightarrow[2.\ H_2O]{1.\ SnCl_2} B \xrightarrow{(O)} C \xrightarrow{Ca(OH)_2} D \xrightarrow{\Delta} E$

7. $PhCH=CH_2$

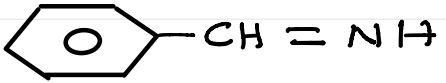
$\xrightarrow[\text{oxo process}]{CO/H_2} A \xrightarrow{(O)} D$

$\xrightarrow[H_2O]{PdCl_2}$ Wacker Process $B \xleftarrow{PhMgBr} C\ (C_3H_6O_2)$

8. 

$\xrightarrow[Ca(OH)_2]{I_2} A + B\ (salt)$

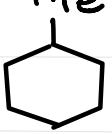
$B \xrightarrow{\Delta} C$

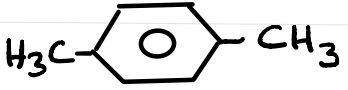
9.  $\xrightarrow[H_2O^{18}]{H^+}$ A $\xrightarrow[2.\ H_2O]{1.\ NaBD_4}$ B

10. $Me-C\equiv CH \xrightarrow[2.\ CO_2/H_3O^+]{1.\ EtMgBr}$ A $\xrightarrow[H_2O]{H^+/Hg^{2+}}$ B

11. $CH_3CH=CH_2 \xrightarrow[2.\ DBO]{1.\ HBO}$ A $\xrightarrow{(O)}$ B $\xrightarrow[2.\ \triangle]{1.\ Ca(OH)_2}$ C

12. $PhC\equiv CH \xrightarrow[2.0eq]{HCl}$ A $\xrightarrow{KOH_{aq}}$ B $\xrightarrow[I_2]{NaOH}$ C + D

13.  $\xrightarrow[h\nu]{Br_2}$ $\xrightarrow[KOH]{alc.}$ A $\xrightarrow[2.\ DBO]{1.\ HBO}$ B $\xrightarrow[Me_2CO]{[Me_3C-O]_3Al}$ C

14.  $\xrightarrow[(CH_3CO)_2O\ 2.0eq]{CrO_3}$ $\xrightarrow{H_3O^+}$ A $\xrightarrow[H_2O]{NaBH_4}$ B

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45 min

Organic Chemistry	Aldehydes & Ketones	Class Test-1

For each question choose the correct alternative Only One choice is correct. However, questions marked with '*' may have More than One correct option :

1. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.
I. Ethanal **II.** Propanal **III.** Propanone **IV.** Butanone
(A) III < II < I < IV **(B)** II < I < III < IV **(C)** IV < III < II < I **(D)** I < II < III < IV

***2.** Acetone can be obtained from :
(A) Hydrolysis of isopropylidene chloride **(B)** Hydration of propyne
(C) Dehydrogenation of isopropyl alcohol **(D)** Hydrolysis-deboration of propyne

3. Ethyl alcohol $\xrightarrow[300°C]{Cu} A + B$. What are A & B ?
(A) Acetadehyde, Acetone **(B)** Acetone, Water
(C) Acetaldehyde, H_2 **(D)** Acetone, H_2

***4.** For the given conversion which reagent can be used ? $CH_2 = CH - CH_2OH \xrightarrow{?} CH_2 = CH - CHO$:
(A) MnO_2 **(B)** PCC/CH_2Cl_2 **(C)** $HgSO_4 / H^+$ **(D)** H_2CrO_4 / acetone / 35°C

***5.** Grignard reagent can give a ketone with :
(A) CO_2 **(B)** RCOCl **(C)** RCN **(D)** RCOOR

6. The medium in which ethanol is oxidised to ethanal using PCC or PDC is :
(A) Any alcohol **(B)** Nitro benzene
(C) Methylene dichloride **(D)** Ether

7. Addition of water to alkynes occurs in acidic medium and in the presence of Hg^{2+} ions as a catalyst. Which of the following product will be formed on addition of water to but-1-yne under these conditions ?
(A) $CH_3 - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - H$ **(B)** $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - CH_3$
(C) $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - OH + CO_2$ **(D)** $CH_3 - \overset{O}{\overset{\|}{C}} - OH + H - \overset{O}{\overset{\|}{C}} - H$

8. When But-1-yne is subjected to hydroboration-deboration reaction, it results in formation of :
(A) $(n-Bu)_3B$ **(B)** Butanol **(C)** Butanal **(D)** Butanone

9. The correct order of reactivity of given compounds towards MeMgBr is :
I. Acetophenone **II.** p-Nitrobenzaldehyde
III. Benzaldehyde **IV.** p-Tolylaldehyde
(A) I < IV < III < II **(B)** I < II < III < IV **(C)** I > IV > III < II **(D)** III < I < II < IV

10. Oxidation of toluene with CrO_3 in presence of $(CH_3CO)_2O$ gives a product (A) which on hydrolysis forms Benzaldehyde. A is :

(A) Chromium complex **(B)** Benzylidene diacetate

(C) Benzophenone **(D)** Benzal chloride

11. Which of the following on heating with aq. KOH produces n-butyraldehyde ?

(A) $CH_3CH_2CH_2CH_2Cl$ **(B)** $CCl_3CH_2CH_2CH_3$

(C) $CH_3CH_2CH_2CHCl_2$ **(D)** $CH_3CCl_2CH_2CH_3$

12. Find A in the given reaction : $CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[(ii)\ H_2O]{(i)\ DIBAL-H} A$:

(A) $CH_3-CH=CHCH_2CH_2COOH$ **(B)** $CH_3-CH_2-CH_2CH_2CH_2CHO$

(C) $CH_3-CH=CHCH_2CH_2CHO$ **(D)** $CH_3-CH(OH)-CH_2CH_2CH_2CHO$

13. Propanoyl chloride on reduction with Lindlar's catalyst forms compound (A). Product (A) is :

(A) Propanone **(B)** Propanoic acid **(C)** Propanol **(D)** Propanal

14. The increasing order of the rate of nucleophilic addition is :

I. HCHO **II.** CH_3COCH_3 **III.** $PhCOCH_3$ **IV.** PhCOPh

(A) I < II < III < IV **(B)** IV < II < III < I **(C)** IV < III < II < I **(D)** III < IV < II < I

***15.** Di-Isobutyl aluminium hydride (DIBAL-H) can be used to carry out which of the following conversions,

(A) Ester to aldehyde **(B)** Nitriles to imines

(C) Formates to formaldehyde **(D)** Aldehyde to Carboxylic acids

16. Two isomeric compounds 'A' and 'B' have the formula $C_3H_6Cl_2$. With aq. KOH solution 'A' gives propionaldehyde and 'B' gives acetone. Then 'A' and 'B' are :

(A) $CH_3-CCl_2-CH_3$ and $CH_3-CH_2-CHCl_2$

(B) $CH_3-CHCl-CHCl_2$ and $CH_3-CH_2-CHCl_2$

(C) $CH_3-CH_2-CHCl_2$ and $CH_3-CCl_2-CH_3$

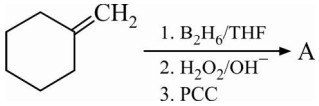
(D) $CH_3-CHCl-CHCl_2$ and $CH_3-CCl_2-CH_3$

17. The relative rate of hydride ion (a nucleophile) addition among given compound is :

I. HCHO **II.** CH_3CHO **III.** C_6H_5CHO

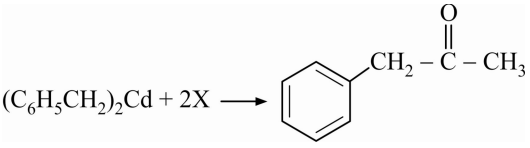
(A) I > III > II **(B)** III > II > I **(C)** I = II > III **(D)** I > II > III

18. Identify A in following :



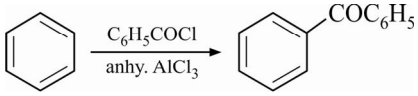
(A) cyclohexane carboxylic acid **(B)** methylcyclohexane

(C) cyclohexane carbaldehyde **(D)** methylcyclohexane carbaldehyde

19. 

Identify X :

(A) CO_2 **(B)** CH_3COCl **(C)** CH_3COOH **(D)** CH_3COOCH_3

20. 

Name of above reaction is :

(A) Wurtz reaction **(B)** Clemmenson reduction

(C) Wolf-Kishner reduction **(D)** Friedel-Craft's acylation

21. Which of the following on hydrolysis with dilute alkali followed by acidification gives benzaldehyde ?

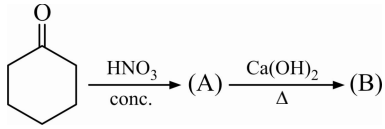
(A) Benzotrichloride **(B)** Benzal chloride

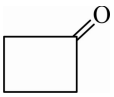
(C) Benzyl chloride **(D)** p-chlorotoluene

22. Compound-A (C_6H_6O) undergoes following reactions to form B and C. Identify A, B and C

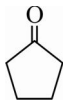
$$C \xleftarrow{Zn-Hg/HCl} \underset{A}{C_3H_6O(A)} \xrightarrow{I_2/NaOH} \underset{B}{B} \,.$$

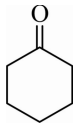
	A	B	C
(A)	$H_3C-\overset{\overset{O}{\|\|}}{C}-CH_3$	CHI_3	$H_3C-CH_2-CH_3$
(B)	$H_2C=CH-CH_2OH$	CH_3I	$H_3C-CH_2-CH_2-OH$
(C)	H_2C-CH_2-CHO	CH_3I	$H_3C-CH(OH)-CH_3$
(D)	$H_3C-\overset{\overset{O}{\|\|}}{C}-CH_3$	CHI_3	$H_3C-CH(OH)-CH_3$

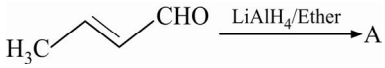
23. Identify the product (B) in given reaction. 

(A) 

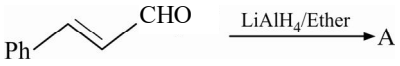
(B) 

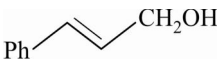
(C) 

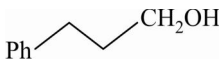
(D) 

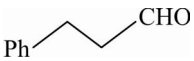
24. Identity (A) in the given reaction. 

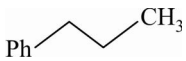
(A) Butanol **(B)** 2-butanol **(C)** But-2-en-1-ol **(D)** But-2-en-2-ol

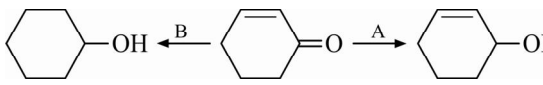
25. Identity (A) in the given reaction. 

(A) 

(B) 

(C) 

(D) 

26. 

. In the given reaction setup A and B respectively are :

(A) $H_2/Pt/\Delta$; $LiAlH_4/H_2O$ **(B)** $H_2/Pt/\Delta$; $H_2/Pt/\Delta$

(C) $LiAlH_4/H_2O$; $LiAlH_4/H_2O$ **(D)** $LiAlH_4/H_2O$; $H_2/Pt/\Delta$

***27.** In which of the following products will be a ketone ?

(A) $(CH_3)_2C=C(CH_3)_2 \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3}$ **(B)** $CH_3CH=CH_2 \xrightarrow[(ii)\ [Co(CO)_8]]{(i)\ CO/H_2}$

(C) $CH_3CH=CH_2 \xrightarrow[or\ CuCl_2]{PdCl_2,\ H_2O}$ **(D)** $CH_3-C\equiv CH \xrightarrow[H_2SO_4/H_2O]{HgSO_4}$

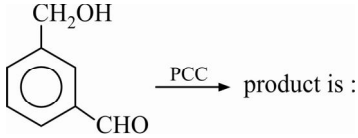
28. The product B in the reaction sequence is :

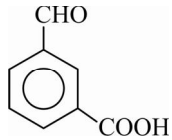
$$(CH_3COO)_2Ca \xrightarrow{distillation} A \xrightarrow{Zn-Hg/HCl} B$$

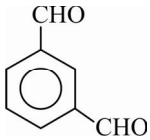
(A) $(CH_3)_2CHOH$ **(B)** $CH_3-CH_2-CH_3$

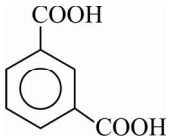
(C) CH_3CHO **(D)** $CH_3-CH_2-CH_2OH$

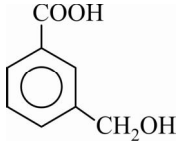
29.



(A) 

(B) 

(C) 

(D) 

30. Which one of the following is the most reactive towards nucleophilic addition on carbonyl group ?

(A) Benzaldehyde **(B)** p-Methoxybenzaldehyde

(C) p-Chlorobenzaldehyde **(D)** p-Ethylbenzaldehyde