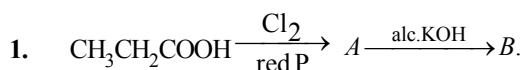


## CHAPTER

## 26

## Aldehydes, Ketones and Carboxylic Acids



What is B?

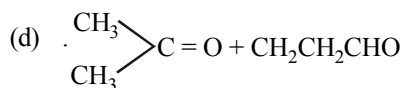
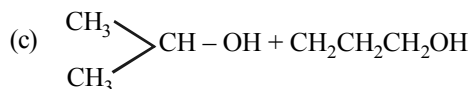
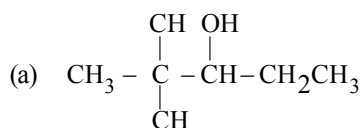
[2002]

- (a)  $\text{CH}_3\text{CH}_2\text{COCl}$  (b)  $\text{CH}_3\text{CH}_2\text{CHO}$   
(c)  $\text{CH}_2=\text{CHCOOH}$  (d)  $\text{ClCH}_2\text{CH}_2\text{COOH}$

2. On vigorous oxidation by permanganate solution.

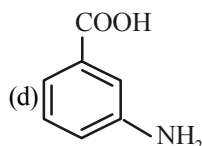
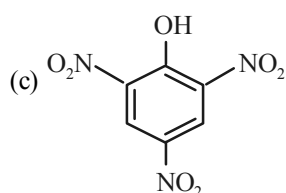
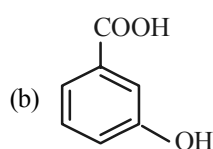
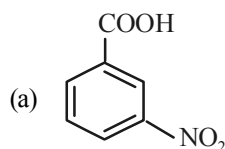
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CHO}$  gives

[2002]



3. Picric acid is:

[2002]



4. When  $\text{CH}_2=\text{CH}-\text{COOH}$  is reduced with  $\text{LiAlH}_4$ , the compound obtained will be

[2003]

- (a)  $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$   
(b)  $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$   
(c)  $\text{CH}_3-\text{CH}_2-\text{CHO}$   
(d)  $\text{CH}_3-\text{CH}_2-\text{COOH}$

5. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is

[2004]

- (a)  $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$   
(b)  $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$   
(c)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$   
(d)  $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$

6. Acetyl bromide reacts with excess of  $\text{CH}_3\text{MgI}$  followed by treatment with a saturated solution of  $\text{NH}_4\text{Cl}$  gives

[2004]

- (a) 2-methyl-2propanol  
(b) acetamide  
(c) acetone  
(d) acetyl iodide

7. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?

[2004]

- (a) Acetamide (b) Acetic acid  
(c) Ethyl acetate (d) Butan-2-one

8. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?

[2004]

- (a) Butanal (b) Benzaldehyde  
(c) Phenol (d) Benzoic acid

9. Among the following acids which has the lowest  $\text{pK}_a$  value?

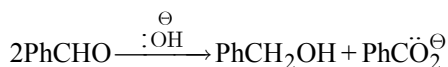
[2005]

- (a)  $\text{CH}_3\text{CH}_2\text{COOH}$   
(b)  $(\text{CH}_3)_2\text{CH}-\text{COOH}$

**Aldehydes, Ketones and Carboxylic Acids**

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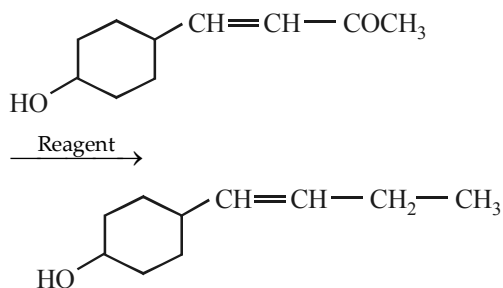
- (c)  $\text{HCOOH}$   
(d)  $\text{CH}_3\text{COOH}$
10. Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known [2005]  
(a) an amine (b) an imine  
(c) an anemine (d) a Schiff's base
11. The increasing order of the rate of HCN addition to compound A – D is [2006]  
(A)  $\text{HCHO}$  (B)  $\text{CH}_3\text{COCH}_3$   
(C)  $\text{PhCOCH}_3$  (D)  $\text{PhCOPh}$   
(a)  $\text{D} < \text{C} < \text{B} < \text{A}$  (b)  $\text{C} < \text{D} < \text{B} < \text{A}$   
(c)  $\text{A} < \text{B} < \text{C} < \text{D}$  (d)  $\text{D} < \text{B} < \text{C} < \text{A}$
12. The correct order of increasing acid strenght of the compounds [2006]  
(A)  $\text{CH}_3\text{CO}_2\text{H}$  (B)  $\text{MeOCH}_2\text{CO}_2\text{H}$   
(C)  $\text{CF}_3\text{CO}_2\text{H}$  (D)  $\text{Me}_2\text{C}(\text{Me})\text{CO}_2\text{H}$   
is  
(a)  $\text{D} < \text{A} < \text{B} < \text{C}$  (b)  $\text{A} < \text{D} < \text{B} < \text{C}$   
(c)  $\text{B} < \text{D} < \text{A} < \text{C}$  (d)  $\text{D} < \text{A} < \text{C} < \text{B}$
13. A liquid was mixed with ethanol and a drop of concentrated  $\text{H}_2\text{SO}_4$  was added. A compound with a fruity smell was formed. The liquid was : [2009]  
(a)  $\text{HCHO}$  (b)  $\text{CH}_3\text{COCH}_3$   
(c)  $\text{CH}_3\text{COOH}$  (d)  $\text{CH}_3\text{OH}$
14. Which of the following on heating with aqueous KOH, produces acetaldehyde? [2009]  
(a)  $\text{CH}_3\text{CH}_2\text{Cl}$  (b)  $\text{CH}_2\text{ClCH}_2\text{Cl}$   
(c)  $\text{CH}_3\text{CHCl}_2$  (d)  $\text{CH}_3\text{COCl}$
15. In Cannizzaro reaction given below



the slowest step is : [2009]

- (a) the transfer of hydride to the carbonyl group  
(b) the abstraction of proton from the carboxylic group  
(c) the deprotonation of  $\text{PhCH}_2\text{OH}$   
(d) the attack of  $:\text{OH}^-$  at the carboxyl group

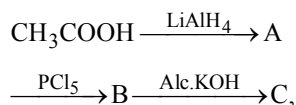
16. Iodoform can be prepared from all except: [2012]  
(a) Ethyl methyl ketone  
(b) Isopropyl alcohol  
(c) 3-Methyl 2-butanone  
(d) Isobutyl alcohol
17. In the given transformation, which of the following is the most appropriate reagent ? [2012]



- (a)  $\text{NH}_2\text{NH}_2, \text{OH}^-$  (b)  $\text{Zn} - \text{Hg} / \text{HCl}$   
(c)  $\text{Na}, \text{Liq NH}_3$  (d)  $\text{NaBH}_4$
18. An organic compound A upon reacting with  $\text{NH}_3$  gives B. On heating B gives C. C in presence of KOH reacts with  $\text{Br}_2$  to give  $\text{CH}_3\text{CH}_2\text{NH}_2$ . A is : [2013]

- (a)  $\text{CH}_3\text{COOH}$   
(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
(c)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{COOH}$   
(d)  $\text{CH}_3\text{CH}_2\text{COOH}$

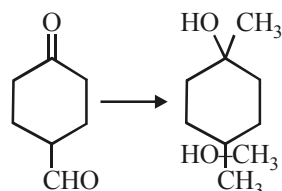
19. In the reaction,



the product C is:

[2014]

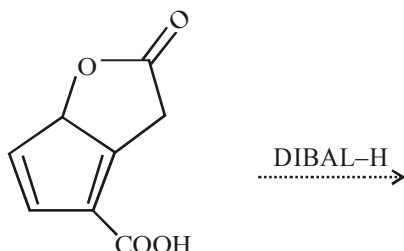
- (a) Acetaldehyde (b) Acetylene  
(c) Ethylene (d) Acetyl chloride
20. The correct sequence of reagents for the following conversion will be :



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Chemistry

- (a)  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{H}^+/\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{MgBr}$   
 (b)  $\text{CH}_3\text{MgBr}$ ,  $\text{H}^+/\text{CH}_3\text{OH}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$   
 (c)  $\text{CH}_3\text{MgBr}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{H}^+/\text{CH}_3\text{OH}$   
 (d)  $[\text{Ag}(\text{NH}_3)_2]^+ \text{OH}^-$ ,  $\text{CH}_3\text{MgBr}$ ,  $\text{H}^+/\text{CH}_3\text{OH}$
21. Sodium salt of an organic acid 'X' produces effervescence with conc.  $\text{H}_2\text{SO}_4$ . 'X' reacts with the acidified aqueous  $\text{CaCl}_2$  solution to give a white precipitate which decolourises acidic solution of  $\text{KMnO}_4$ . 'X' is :
- (a)  $\text{C}_6\text{H}_5\text{COONa}$  (b)  $\text{HCOONa}$   
 (c)  $\text{CH}_3\text{COONa}$  (d)  $\text{Na}_2\text{C}_2\text{O}_4$
22. The major product obtained in the following reaction is :

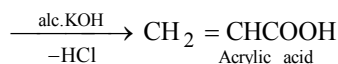
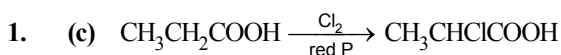


- (a)
- (b)
- (c)
- (d)

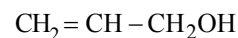
## Answer Key

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(c)	(b)	(c)	(a)	(c)	(a)	(d)	(b)	(c)	(c)	(a)	(a)	(c)	(c)	(a)
16	17	18	19	20	21	22								
(d)	(a)	(d)	(c)	(a)	(d)	(b)								

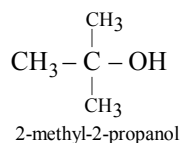
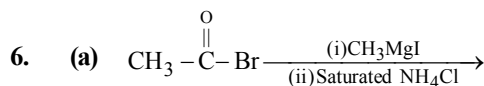
## SOLUTIONS



2. (b) Aldehydic group gets oxidised to carboxylic group. Double bond breaks and carbon gets oxidised to carboxylic group.  
 3. (c) 2,4,6-Trinitrophenol is also known as picric acid.  
 4. (a)  $\text{LiAlH}_4$  can reduce  $\text{COOH}$  group and not the double bond.



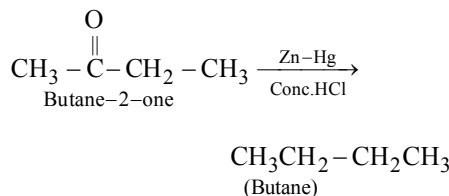
5. (c) There is no reaction hence the resultant mixture contains  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$ .



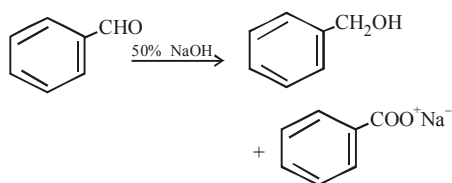
**Aldehydes, Ketones and Carboxylic Acids**

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7. (d) It is Clemmensen's reduction

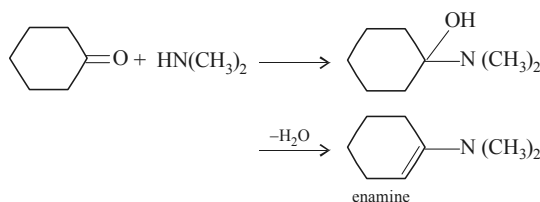


8. (b) This reaction is known as Cannizzaro's reaction. In this reaction benzaldehyde in presence of 50% NaOH undergoes disproportionation reaction and form one mol of Benzyl alcohol (Red. product) and one mole of sod. benzoate (ox. product)



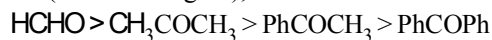
9. (c)  $pK_a = -\log K_a$ ; HCOOH is the strongest acid and hence it has the highest  $K_a$  or lowest  $pK_a$  value.

10. (c)



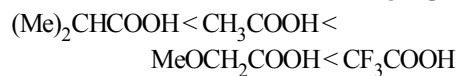
11. (a) **NOTE** Addition of HCN to carbonyl compounds is nucleophilic addition reaction. The order of reactivity of carbonyl compounds is

Aldehydes (smaller to higher) Ketones (smaller to higher), Then



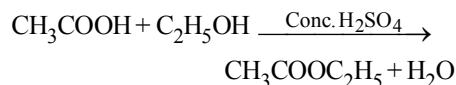
**NOTE** The lower reactivity of Ketones is due to presence of two alkyl group which shows +I effect. The reactivity of Ketones decreases as the size of alkyl group increases.

12. (a) The correct order of increasing acid strength



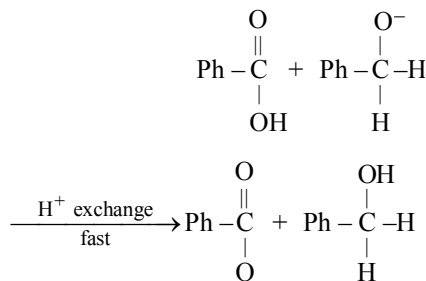
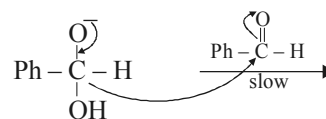
[**NOTE** Electron withdrawing groups increase the acid strength and electron donating groups decrease the acid strength.]

13. (c) Fruity smell is due to ester formation which is formed between ethanol and acid.

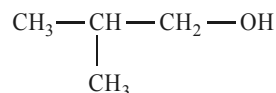


14. (c)  $\text{CH}_3\text{CHCl}_2 \xrightarrow{\text{aq. KOH}} \text{CH}_3\text{CH}(\text{OH})_2 \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CHO}$

15. (a)  $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} + \text{OH}^- \xrightleftharpoons{\text{fast}}$



16. (d) Iodoform test is given by methyl ketones, acetaldehyde and methyl secondary alcohols.



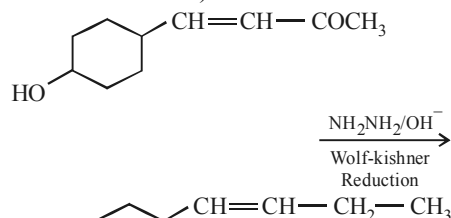
isobutyl alcohol is a primary alcohol hence doesn't give positive iodoform test.

17. (a) Aldehydes and ketones can be reduced to hydrocarbons by the action (i) of amalgamated zinc and concentrated hydrochloric acid (Clemmensen reduction), or (b) of hydrazine ( $\text{NH}_2\text{NH}_2$ ) and a strong base like NaOH, KOH or potassium *tert*-butoxide in a high-boiling alcohol like

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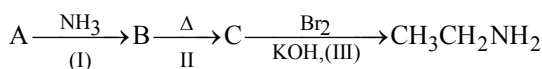
Chemistry

ethylene glycol or triethylene glycol (Wolf-Kishner reduction)



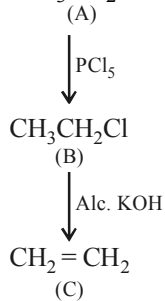
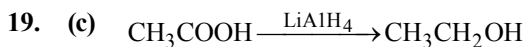
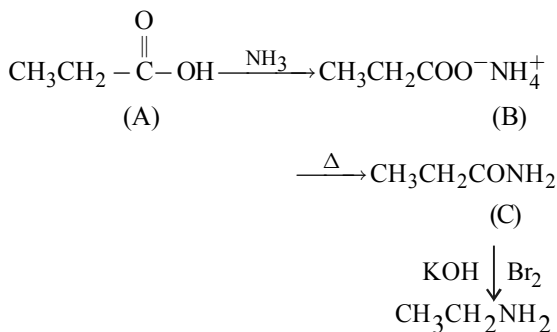
-OH group and alkene are acid-sensitive groups so clemmensen reduction can not be used. Acid sensitive substrate should be reacted in the Wolf-Kishner reduction which utilise strongly basic conditions.

18. (d)



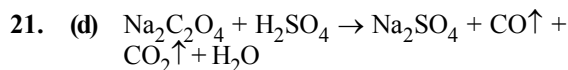
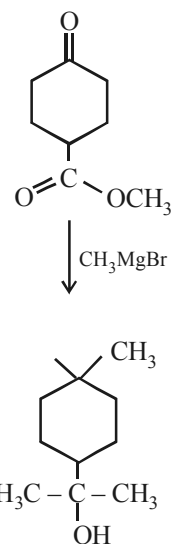
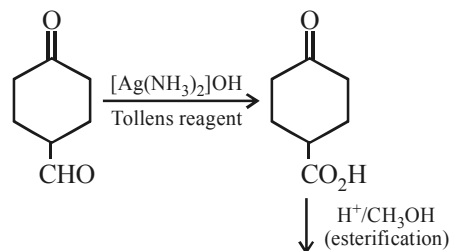
Reaction (III) is a Hofmann bromamide reaction. Now formation of  $\text{CH}_3\text{CH}_2\text{NH}_2$  is possible only from a compound  $\text{CH}_3\text{CH}_2\text{CONH}_2$  (C) which can be obtained from the compound  $\text{CH}_3\text{CH}_2\text{COO}^- \text{NH}_4^+$  (B).

Thus (A) should be  $\text{CH}_3\text{CH}_2\text{COOH}$

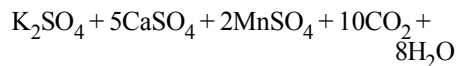
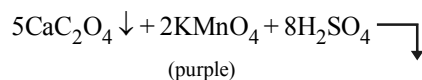
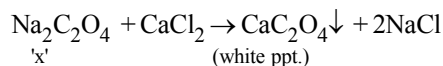


Hence the product (C) is ethylene.

20. (a)



'x' (conc.)



(colourless)

22. (b) DIBAL-H is an electrophilic reducing agent. It reduces both ester and carboxylic group into an aldehyde at low temperature.

