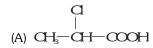
SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

- 1. Acids have much higher boiling points than isomeric esters because :-
 - (A) Acids form dimers by H-Bonding
 - (B) Acids are volatile in steam
 - (C) Ester are non-volatile
 - (D) Acids can ionise to give protons in aqueous solution
- 2. Which of the following acids have the lowest pK_a value :-



(C) CCl₃COOH

- (D) CHCl2COOH
- 3. The reaction of an amide with bromine and alkali to form a primary amine is called :-
 - (A) Hunsdiecker reaction

- (B) Hofmann mustard oil reaction
- (C) Hoffmann degradation of amides
- (D) Hell-Volhard-Zelinski reaction
- The regents A and B in the reaction sequence 4.

$$\begin{array}{c} \text{CH}_{2}\text{COOC}_{2}\text{H}_{2} \xrightarrow{A} \text{CH}_{3}\text{COOC}(\text{CH}_{3})_{3} \\ \\ \stackrel{\square}{\sqsubseteq} \text{CH}_{3}\text{CONHNH}_{2} \end{array}$$

are given by the set :-

(A) Isopropyl alcohol, hydrazine

(B) Isopropyl alcohol, hydroxylamine

(C) t-butyl alcohol, hydrazine

- (D) t-butyl alcohol, hydroxylamine
- 5. The carboxylic acids react with hydrazoic acid in presence of $\mathrm{H_2SO_4}$ to form a primary amine. This reaction is called as :-
 - (A) Curtius rearrangement

(B) Lossen rerrangement

(C) Schmidt reaction

- (D) Schotten-Boumann reaction
- Ethyl acetate $\xrightarrow{\text{CH}_3\text{MgBr}} \xrightarrow{\text{H}_3\text{O}^+} P$ 6.

The product P will be :-

$$(A) \begin{array}{c} H_3C & CH_1 \\ H_3C & OH_2 \end{array}$$

$$(B)$$
 H C C_2H

(C)
$$H_1C_2$$
 C_2H_1 C_2 C_2H_2

- 7. HVZ reaction is specific for -
 - (A) Replacement of β -hydrogens
- (B) Replacement of α -hydrogens

(C) Replacement of β - carbons

- (D) Replacement of α carbons
- 8. Decreasing order of acidity of p-methoxy benzoic acid (A), p-nitrobenzoic acid (B) and benzoic acid (C) is-
 - (A) B, C, A
- (B) A, B, C
- (C) C, A, B
- (D) None

9.	Benzoic acid reacts with $Ca(OH)_2$. The produc	t obtained on dry distillation	gives-
	(A) Benzophenone (B) Acetophenone	(C) Benzaldehyde	(D) None of these
10.	In a set of the given reactions, acetic acid yie	elded a product C.	
	$CH_3COOH+PCl_5 \longrightarrow A \xrightarrow{C_6H_6} B \xrightarrow{(i) C_2H_5M_6} (ii) H_5$	$C : \operatorname{Br/ether} \to C : \operatorname{product} C : \operatorname{would} C$	d be:-
			CH
	(A) $CH_3CH(OH)C_2H_5$ (B) $CH_3COC_6H_5$	(C) CH ₃ CH(OH)C ₆ H ₅	(D) CH;—Q(OH)C;H;
11.	The correct reactivity order with the nucleophile	is:	
	(A) CH ₃ COCl > CH ₃ CONH ₂ > CH ₃ COOCH ₃		
	(B) $CH_3COCl > CH_3COOCH_3 > CH_3CONH_2$		
	(C) CH ₃ CONH ₂ > CH ₃ COOCH ₃ > CH ₃ COCl		
	(D) CH ₃ COOCH ₃ > CH ₃ COCl > CH ₃ CONH ₂		
12.	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$I_2 \xrightarrow{B} CH_3-CH_2-OH$	
	In the above sequence A & B respectively are -		
	(A) Br ₂ /KOH, NaOH (B) Br ₂ /KOH, HNO ₂	(C) KMnO ₄ , KOH	(D) HNO ₂ , Br ₂ / KOH
13.	Ethyl acetate on treatment with hydrazine gives		2 2
	(A) CH ₃ -C-NH.NH ₂ (B) CH ₃ -C-OC ₂ H ₄ 0 N.NH ₃	(C) CH3-C-ONH.NH 0	I, (D) CH3-C-NH2
14.	Among the following, which is the strongest acid?		
14.			YOOH
	(A) CHF ₂ - CH ₂ - CH ₂ -COOH (C) CH ₂ F -CHF - CH ₂ -COOH	(B) $CH_3 - CH_2 - CF_2 - C$	
15.	In the Rosenmund reduction, the catalyst used is:	(D) $CH_3 - CF_2 - CH_2 - C$	
10.	(A) Pd/ BaSO ₄ (B) Raney Ni	(C) Sn/HCl	(D) Zn/HCl
16.	Which of the following carboxylic acids undergoe		
	(A) $C_6H_5COCH_2COOH$ (B) $C_6H_5COCOOH$	(C) C,H,CH—COOH 	(D) C ₁ H ₂ CHCCOH
		ÓН	NH ₂
17.	The reactivities of acid halides (I), anhydrides (II), e	sters (III) and amides (IV) with n	ucleophilic reagents follow the
	(A) $I > II > III > IV$ (B) $IV > III > I > I$	(C) I > III > II > IV	(D) $III > II > IV$
18.	In the following sequence of reactions		
	$+ CH_3CH_2COCI \xrightarrow{AlCl_3} A \xrightarrow{conc.}$	Zn (Hg) HCl, Heat B	
	the product (B) is:		
	(A) PhCOCH ₂ CH ₃ (B) PhCHOHCH ₂ CH ₃	(C) PhCH ₂ CH ₂ CH ₃	(D) PhCH= CHCH ₃

19. Consider the following reaction.

The product (A) is:

20. Which of the following orders regarding the base strength of a leaving group in a reaction of an acid derivative with a nucleophile is correct:

(A)
$$Cl^{\Theta} > RCOO^{\Theta} > RO^{\Theta}$$

(B)
$$Cl^{\Theta} > RO^{\Theta} > RCOO^{\Theta}$$

(C)
$$RO^{\Theta} > RCOO^{\Theta} > Cl^{\Theta}$$

(D)
$$RO^{\Theta} > Cl^{\Theta} > RCOO^{\Theta}$$

21. The correct sequence of decreasing order of reactivity of hydrolysis of acid chlorides is:

(A)
$$PhCOCl > p-O_2NC_6H_4COCl > p-CH_3OC_6H_4COCl$$

(B)
$$PhCOCl > p-CH_3OC_6H_4COCl > p-O_2NC_6H_4COCl$$

(C)
$$p-O_2NC_6H_4COCl > PhCOCl > p-CH_3OC_6H_4COCl$$

(D)
$$p-O_2NC_6H_4COCl > p-CH_3OC_6H_4COCl > PhCOCl$$

22. Kolbe electrolysis of potassium succinate gives CO₂ and:

(D)
$$CH_4$$
, C_2H_6 and C_2H_4

23. In the following reaction identify compounds A, B, C and D:

$$PCl_5 + SO_2 \longrightarrow A + B$$
;

$$A + CH_3COOH \longrightarrow C + SO_2 + HCl$$

$$2C + (CH_3)_2 Cd \longrightarrow D + CdCl_2$$

- (A) SOCl₂, POCl₃, CH₃COCl, CH₃COCH₃
- (B) SOCl₂, HCl, CH₃Cl, CH₃CHO
- (C) SO₂, Cl₂, C₂H₅Cl, CH₃COCH₃
- (D) None of these

24. What are A and B in the following sequence of reactions:

(i)
$$CH_3CH_2COOH \xrightarrow{P \ Br_2} A$$
 ; (ii) $A \xrightarrow{\text{(ii)Alc.KOH excess}} B$

(A)
$$CH_3$$
— CH COOH, CH_2 = CH COOH Pr

(B)
$$CH_3CH_2COBr$$
, $CH_2 = CHCOOH$

25. Which of the following compound would be expected to decarboxylates when heated:

CHECK YOUR GRASP					A	ANSWER KEY				EXERCISE -1										
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	А	С	С	С	С	Α	В	Α	Α	D	В	В	Α	В	Α	Α	Α	С	С	С
Que.	21	22	23	24	25															
Ans.	С	С	Α	Α	Α															

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

- 1. Which of the following reactions involve a decrease in the length of the carbon chain :-
 - (A) Schmidt reaction

(C) Hofmann's bromamide reaction

(C) Hell-Volhard-Zelinski reaction

- (D) All of these
- 2. Dry distillation of a mixture of calcium formate and the calcium acetate gives -
 - (A) HCHO
- (B) CH₃CHO
- (C) CH₃COCH₃

(D) None

 CH_0CH

3. Consider the following sequence of reactions.

$$\frac{1. \text{ LiAlH}_{4}, \text{Et}_{2}O}{\text{H}} \Rightarrow A \xrightarrow{2. \text{H}_{3}O^{\dagger}} B$$

$$\frac{1. \text{ LiAlH}_{4}, \text{Et}_{2}O}{2. \text{H}_{3}O^{\dagger}} \Rightarrow B$$

The products (A) and (B) are, respectively,

4. Consider the following reaction.

CCCCH₃

$$\begin{array}{c} \text{CH}_2\text{COOH} \\ \hline \\ \text{C}_2\text{N} \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_2\text{COOH} \\ \hline \\ \text{C}_2\text{N} \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_2\text{COOH} \\ \hline \\ \text{C}_2\text{N} \end{array}$$

 $CH_{0}CH$

The product (A) is

- 5. Which of the following methods are used for the conversion of carboxylic acids into acid chlorides $(RCOOH \longrightarrow RCOCI)$?
 - (A) RCOOH + $SOCl_2 \longrightarrow$

(B) RCOOH + $PCl_5 \longrightarrow$

(C) RCOOH + $Cl_2 \longrightarrow$

- (D) RCOOH + P + $Cl_2 \longrightarrow$
- 6. Which of the following statements are correct for benzoic acid?
 - (A) Nitration gives o-and p-nitrobenzoic acid.
 - (B) Bromination (Br₂/FeBr₃) gives m-bromobenzoic acid.
 - (C) The Friedel-Crafts reaction with CH3COCl/AlCl3 gives m-carboxyacetophenone.
 - (D) The reaction with concentrated sulphuric acid gives 3-carboxybenzenesulphonic acid.
- 7. Which of the following compounds react with aniline to give acetanilide:

Which of the following compounds react with aniline to give acetanilide.

Aniline

Acetanilide

8. What is the final product (B) of this sequence :

$$\begin{array}{c}
CH_3 \\
\hline
Br_2 \\
\hline
 light
\end{array}
A \xrightarrow{1.KON} A \xrightarrow{2.H_3O^{\dagger}, Heat} B$$

9. What is compound Z:

$$CH_3CH_2CH_2Br \xrightarrow{NaCN} X \xrightarrow{H_3O^+} Y \xrightarrow{CH_3CH_2OH} Z$$

(C) CH₃CH₂CH₂CH(OCH₂CH₃)₂

- 10.

 - (A) CH₂-CH₂ (B) CH₂-CH₂ OH COOCH₂ COOH OCH
 - (C) Both are correct (D) None is correct

- 11. Which of the following orders of acid strength is correct:
 - (A) RCOOH > ROH > HOH > HC≡CH
- (B) RCOOH > HOH > ROH > HC≡CH
- (C) RCOOH > HOH > HC≡CH > ROH
- (D) RCOOH > HC≡CH > HOH > ROH

- 12. The relative order of esterification of alcohols is :-
 - (A) 1 < 2 < 3
- (B) 1 > 2 > 3
- (C) 1 > 3 > 2
- (D) 1 < 3 < 2
- 13. The treatment of CH_3CH_2COOH with chlorine in the presence of phosphorus gives :
 - (A) CH₃CH₂COCH₃
- (B) CH₂CH₂CH₂Cl
- (C)CH₃CH(Cl)COOH
- (D) ClCH₂CH₂COOH
- **14.** Which of the following sequences of rate of alkaline hydrolysis of esters is correct:
 - (A) $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
 - (B) $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$
 - (C) $CH_3CH_2COOCH_3 > (CH_3)_2CHCOOCH_3 < (CH_3)_3CCOOCH_3$
 - (D) $CH_3CH_2COOCH_3 < (CH_3)_2CHCOOCH_3 > (CH_3)_3CCOOCH_3$
- **15**. Which of the following is used to perform following transformation :

- (A) SOCl₂
- (B) PCl₅
- (C) PCl₃
- (D) SO₂Cl₂

- **16.** Which of the following does not give iodoform :
 - (A) Acetic acid
- (B) lactic acid
- (C) Actophenone
- (D) propionic acid

- 17. One can distinguish between HCOOH and CH₃COOH with:
 - (A) NaHCO₃
- (B) H₂SO₄
- (C) tollens reagent
- (D) fehling's solution
- 18. Which of the following reagents are involved in the following transformation?

- (A) H_3O^+
- (B) LiAlH₄
- (C) Ethylene glycol
- (D) Acetone

Identify the correct statement(s) about the above sequence of reactions :

- (A) Compound (A) is formed through S_N reaction
- (B) Compound (C) on reduction with $LiAIH_4$ forms a product which on dehydration given cyclohexene.
- (C) compound (A) requires two moles of hydrogen for complete reduction.
- (D) Compound (C) on Schmidt's reaction gives a product which reacts with ${\rm HNO_2}$ to give (D) as major product. Compound (D) on dehydration gives cyclopentene
- 20. Which of the following on reduction with $LiAIH_4$ will give ethyl alcohol?
 - (A) (CH₂CO)₂O
- (B) CH₃COCl
- (C) CH₃CONH₂
- (D) CH₃COOC₂H₅

BRAIN TEASERS					A	ANSWER KEY				EXERCISE -2					
Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	A,B	A,B,C	С	Α	A,B,D	B,D	A,B,D	D	D	Α	В	В	С	В	A,B,C
Que.	16	17	18	19	20										
Ans.	A,D	C,D	A,B,C	A,B,D	A,B,D										

TRUE OR FALSE:

1. \bigcirc Concept, cannot undergoes claisen condensation.

2. Heating of β -hydroxy acid gives lactones.

3. Hunsdiecker reaction involve free redical in intermediate steps.

4. Benzoic acid is stronger than methanoic acid but weaker than ethanoic acid.

5. Acid halides are more reactive than acid amides towards the hydrolysis.

FILL IN THE BLANKS:

1. When sodium benzoate is heated with sodalime, it gives......

2. pK_a and K_a of an acid are connected by the relation.....

3. Benzoic acid does not undergo Friedel-Crafts reaction due toof the benzene ring by the effect of -COOH group.

4. Hell-Volhard-Zelinsky reaction involves the replacement of anatom from the alkyl group of a monocarboxylic acid by a atom.

5. Carboxylic acids may be prepared by the reaction of Grignard reagents with

MATCH THE COLUMN

1. Match the column I with column II.

	Column-I (Reaction)	\sum	Column-II (Possible products)
(A)	Arndt Eistert synthesis	(p)	Carbanion
(B)	Hunsdiecker reaction	(q)	Carbocation
(C)	Claisen condensation	(r)	Ketene
(D)	Esterification reaction	(s)	Free radical

2. Match the column I with column II.

	Column-I (Acid)		Column-II (K _a)
(A)	Benzoic acid	(p)	$3.3 10^{-5}$
(B)	0 ₂ N-(O)-000H	(q)	$10.2 10^{-5}$
(C)	а—(<u>)</u> —соон	(r)	30.6 10 ⁻⁵
(D)	H300-(O)-000H	(s)	$6.4 10^{-5}$
(E)	H³C-\(\bigc\)-\(\com\)H	(t)	4.2 10 ⁻⁵

3. Match the column I with column II.

	Column-I	\sum	Column-II
(A)	Schimdt reaction	(p)	$RCOOH \xrightarrow{NaOH/CaO} RH$
(B)	Curtius reaction	(q)	$R-CH_2COOH \xrightarrow{\text{Red P/X}_2} R-CH-COOH$
(C)	Decarboxylation	(r)	$RCOC1 \xrightarrow{NaN_3} RNH_2$
(D)	HVZ reaction	(s)	$RCOOH \xrightarrow{N_3H} RNH_2$

ASSERTION & REASON QUESTION:

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
- 1. Statement-I: Unlike the >C=O group of aldehydes and ketones, the >C=O of R-C-OH does not undergo nucleophilic addition reactions.

Because

Statement-II: Carboxylic acids exist as dimers due to intermolecular hydrogen bonding in aprotic medium.

2. Statement-I: CH₃COCH₂COOC₂H₅ will give iodoform test.

Because

Statement-II : It contains CH_3C — group linked to a carbon atom.

3. Statement-I: Acetic acid does not undergo haloform reaction.

Because

Statement-II : Acetic acid has no α hydrogen.

4. Statement-I: Benzoic acid on nitration will give m- Nitro benzoic acid.

Because

Statement-II: -COOH group will increase e density on meta position.

5. Statement-I: Acyl halide are more reactive than acid substance amide towards nucleophillic substitution.

Because

 $\textbf{Statement-II} \ : \ X^- \ \text{are better leaving group than} \ \ NH_2 \ .$

COMPREHENSION BASED QUESTIONS:

Comprehension # 1

Amides undergo hydrolysis to yield carboxylic acid plus amine on heating in either aqueous acid or aqueous base. The conditions required for amide hydrolysis are more severe than those required for the hydrolysis of esters, anhydrides or acid chlorides, but the mechanism is similar (nucleophilic acyl substitution). Nucleophilic

acyl substitutions involve a tetrahedral intermediate, hence these are quite different from alkyl substitution $(RCH_2Br \xrightarrow{NaCN} RCH_2CN)$ which involves a pentavalent intermediate or transition state.

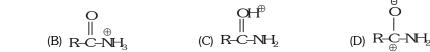
One of the important reactions of esters is their reaction with two equivalent of Grignard reagent to give tertiary alcohols.

- 1. The mechanism involved during the hydrolysis of acid derivatives is :
 - (A) elimination-addition

- (B) addition-elimination
- (C) nucleophilic addition elimination
- (D) electrophilic addition elimination
- 2. Which of the following constitutes the best substrate during the acidic hydrolysis of amides?







- 3. For which functional derivative of carboxylic acids, acidic hydrolysis is avoided?
 - (A) Acid chlorides
- (B) Acid amides
- (C) Acid anhydrides
- (D) Esters
- O is treated with two equivalent of methyl magnesium iodide and the product acidified 4. the final product will be

Comprehension # 2

Ester gives nucleophilic addition reaction followed by elimination reaction with carbon nucleophile. When carbon nucleophile is of an ester then the reaction is known as Claisen condensation reaction. This reaction is also carried out between ester and a ketone. A successful Claisen condensation requires an ester with two α -hydrogens and an equivalent amount of base rather than a catalytic amount of base.

1. Consider the given reaction

$$\text{CH}_3\text{-COOC}_2\text{H}_5 \xrightarrow[C_2\text{H}_5\text{OH}]{} \text{C}_2\text{H}_5\text{OH} \xrightarrow{} \text{enolate ion } \xrightarrow[\text{Claisen condensation}]{} \text{Product}$$

For the above reaction the most reactive ester is:

(B)
$$C_2H_5O-C-C-OC_2H_5$$

(D)
$$C_2H_5O - C - OC_2H_5$$

- 2. Intramolecular Claisen condensation given by diester is known as:
 - (A) Stobbe condensation

(B) Dieckmann condensation

(C) Mannich reaction

(D) Reformatsky reaction

3. In the given reaction :

$$\begin{array}{c} O \\ \parallel \\ C_2H_5O-C-(CH_2)_3-CH_2-COOC_2H_5 \end{array} \xrightarrow{\text{(i) } C_2H_5ONa/C_2H_5OH} \begin{array}{c} [X] \end{array}$$

[X] is :

4. In the given reaction

 $[X]\ is\ :$

(A)
$$_{\mathrm{H-C-Cl}}^{\mathrm{O}}$$
 (B) $_{\mathrm{HCl+CO}}^{\mathrm{COOC}_2\mathrm{H}_5}$ (C) $_{\mathrm{COOC}_2\mathrm{H}_5}^{\mathrm{COOC}_2\mathrm{H}_5}$

Comprehension # 3

The reactivity of acid derivatives in general follows the order :

The above order of reactivity can be explained in terms of the :

(i) Basicity of leaving group (ii) Resonance effect (iii) Inductive effect

Weaker is the basic character of leaving group, more is the reactivity of acid derivative. In general, all the acid derivatives show resonance as follows:

$$\begin{array}{c} R \\ C \\ C \end{array} \longrightarrow \begin{array}{c} R \\ C \\ C \end{array}$$

More is the stabilization, lesser is the reactivity and vice-versa.

- 1. Which among the following anions is the most basic?
 - (A) $\overline{N}H_2$
- (B) $\bar{O}R$

- (C) R COO
- (D) Cl-

- 2. Which of the most reactive acid derivative?
 - (A) R-COCl
- (B) (RCO)₂O
- (C) RCOOR
- (D) RCONH₂

- 3. Which among the following ester is most reactive towards nucleophilic attack?
 - (A) CH₃COOCH₃
- (B) HCOOCH₃
- (C) CH₃CH₂COOC₆H₅
- (D) All are equally reactive
- 4. Acid derivatives although contain -C— group, yet do not undergo the usual properties of carbonyl group. It is due to:
 - (A) inductive effect
- (B) resonance
- (C) eletromeric effect
- (D) all of these
- 5. Which of the following compounds will be most easily hydrolysed?
 - (A) Acid halide
- (B) Acid amide
- (C) Ester
- (D) Acid anhydride

MISCELLANEOUS TYPE QUESTION	ANSWER KEY	EXERCISE -3
• <u>True / False</u> 1. T 2. F 3. T	4 . F 5 . T	
• Fill in the Blanks		
1. Benzene	2. $pk_a = -log k_a$ 3	deactivation , electron withdrawing
4. α - Hydrogen, halogen	5 . CO ₂	
• Match the Column		
1. (A) \rightarrow r; B \rightarrow s; (C) \rightarrow p; (D) \rightarrow q	2. (A) \rightarrow s ; (B) \rightarrow r ; (C) \rightarrow	$q ; (D) \rightarrow p ; (E) \rightarrow t$
3. (A) \rightarrow s; (B) \rightarrow r; (C) \rightarrow p; (D) \rightarrow q		
• Assertion - Reason Questions		
1. C 2. D	3 . C 4 . C 5	. A
• Comprehension Based Question	<u>s</u>	
Comprehension #1 : 1. (C) 2. (o)
Comprehension #2 : 1. (B) 2. (•
Comprehension #3 : 1. (A) 2. (A) 3. (B) 4. (B	5. (A)

- 1. Carbon-oxygen bond length in formic acid are 1.23 Å and 1.36Å but in sodium formate both the carbon-oxygen bonds have same value, i.e., 1.27Å. Explain.
- 2. The second dissociation constant of fumaric acid is greater than maleic acid. Explain.
- **3.** Which is stronger conjugate base in each pair?
 - (A) $\overline{O}H$ or $N\overline{H}_2$ (B) $\overline{C}H_3$ or CH_3COO^- (C) $HCOO^-$ or CH_3COO^-
 - (D) CF₃COO⁻ or CCl₃COO⁻
- 4. Which acid of each pair shown here would you expect to be stronger?
 - (A) CH₃CO₂H or CH₂FCO₂H
 - (B) CH_2CICO_2H or CH_2BrCO_2H
 - (C) CH₃CH₂CHFCO₂H or CH₃CHFCH₂CO₂H

5. What are A and B in the following?

$$\begin{array}{c}
O \\
\hline
OH
\end{array}$$

$$\xrightarrow{\text{NaBH}_4} A \xrightarrow{\text{H}_2O/\text{H}^+} B$$

6. In the following reaction, trace the position of isotopic O^{18} .

7. Write the reagents to carry out following conversions:

8.
$$\longrightarrow$$
 AlCl₃ A, What is A?

9.
$$+ NBS \longrightarrow X \xrightarrow{\text{(i)Mg/ether} \atop \text{(ii)CO}_2; \atop \text{(ii)H}_3O^+} Y$$

What are X and Y?

10. HN + Br₂
$$\xrightarrow{\text{O C}}$$
 A

Write down the structure of A? What is the use of A?

- 1. Formate in shows equivalent resonating structures while formic acid does not.
- **2.** After the first dissociation, maleate ion is more stabilised due to intramolecular H-bonding, whereas fumarate ion does not have intramolecular H-bonding.
- 3. (A) NH_2^-
- (B) CH_3^-
- (C) CH₃COO⁻
- (D) CCl₃COO-

4 (A) CH₂FCO₂H

(B) CH2ClCO2H

(C) CH₃CH₂CHFCO₂H

- 5. A: $\frac{3}{6}$ $\frac{3}{4}$ $\frac{3}{2}$ $\frac{3}{2}$ (NaBH₄ reduces keto group)

$$B: \frac{4}{3}$$
 (by intramolecular esterification)

- 6. O is in ester CH₃COCH₂CH₄
- 7. I : LiAlH₄ II : Pd/BaSO₄ (Rosenmund)
- 8. A is formed by Friedel-Crafts reaction A:

10.
$$+$$
 $Br_2 \xrightarrow{0 \text{ C}} Br - N + HBr$

1-Bromopyrrolidine-2, 5-dione or N-Bromosuccinimide (NBS)

It is used for brominating in allylic and benzylic hydrogen.

$$H_{1}C$$
 CH_{2}
 Br
 CH_{2}
 CH_{2}

1. Identify A, B, C, D and E in the following sequence of reactions:

$$CH_{3}COH \xrightarrow{PCl_{5}} A \xrightarrow{H_{2} Pd/BaSO_{4}} B \xrightarrow{dil. NaOH} C$$

$$\xrightarrow{red P, Br_{2}} D \xrightarrow{NaOH} E$$

When the compound shown was heated in refluxing hydrochloric acid, a compound with the molecular formula $A(C_5H_6O_3)$ was isolated. Identify this product. Along with this product, three other carbon-containing substances are formed. What are they ?

What happens when $A(C_5H_6O_3)$ reacts with

(A) HCN follwed by hydrolysis

(B) soda lime/ Δ

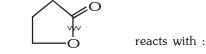
(C) NH₂NH₂/glycol, OH⁻

- (D) P/Br₂
- (E) N_3H
- 3. CH_3COO^- (acetate ion) is more stable than $C_2H_5O^-$ (ethoxide ion). Explain.
- **4.** Which is more reactive in each pair towards \boldsymbol{S}_N reaction ?

5.
$$H_{2}C \xrightarrow{C} C + \bigoplus_{AlG_{3}} A \xrightarrow{Zr(H_{2})} B \xrightarrow{SOG_{2}} C \xrightarrow{AlG_{3}} C$$

$$D \xrightarrow{\text{LiAlH}_4} E \xrightarrow{\text{H}^{\dagger}/\Delta} F \xrightarrow{\text{NBS}} G \xrightarrow{\text{alcoholic KOH}} H$$

Identify A to H.



γ-Butyrolactone (ester)

(A) NH₃

6.

- (B) LiAlH₁
- (C) EtOH, H⁺
- (D) NaBH₄/EtOH

What are the product in each case?

- 7. In case of aldehydes and ketones there is addition of nucleophile but in case of acyl compound there is nucleophilic substitution. Explain.
- 8. $CH_3COOH \xrightarrow{N_3H} A$ $\downarrow NH_3 \qquad A$ $\downarrow NH_3 \qquad A$ $\downarrow Reagent$
 - (i) What are A & B?
 - (ii) Which reagent will convert B into A?
- 9. What happens when?

(i) is reduced by
$${\rm LiAlH_4}.$$

(ii) is reduced by using
$${\rm LiAlH_4}$$
 and by using Lindlar's catalyst.

10. Complete the following sequence of reactions :

BRAIN STORMING SUBJECTIVE EXERCISE

ANSWER KEY

EXERCISE -4(B)

C : CH₃CH=CHCHO (aldol condensation)

- 2. Given compound represents
 - (i) acetal (ii) ester

When it is subjected to acidic hydrolysis, acetal changes to carbonyl group and ester changes to acid.

(X), (Y) and (Z) are thus, other carbon containing product along with $C_5H_6O_3$ which is the main product. $A(C_5H_6O_3)$ has (i) keto group (ii) carboxylic group

$$(A) \longrightarrow (A) \longrightarrow (A)$$

(B) A
$$\xrightarrow{\text{CaO/NaOH}}$$
 O

(C) A
$$\frac{NH_2NH_2}{glycol, OH^0}$$
 (Wolff-Kishner reduction)

(D) A
$$\xrightarrow{P/Br_2}$$
 O (HVZ-reaction)

(E) A
$$\xrightarrow{N_3H}$$
 \longrightarrow NH_2 (Schmidt-reaction)

Electron delocalion, as shown by following resonance structures, causes the negative charge in acetate to be shared equally by both oxygens. This type of resonance effect is not possible in ethoxide ion.

(H)

6. (A)
$$\gamma$$
 ONH₃ OH₂CH₂CH₂CH₂C=OOH NH₂ OH NH₂ alcohol amide

(G)

(D)
$$NaBH_4/EiOH$$
 No reaction (ester is not reduced by NaBH₄).

7. In case of carbonyl compounds H^- or R^- are poor leaving group, therefore addition take place. But in case of acid derivatives, Z^- are good leaving group therefore substitution take palce.

8. (i) A :
$$CH_3 - NH_2$$
 B : $CH_3 - C - NH_2$

(ii) Reagent =Br₂/Alc. KOH

EXERCISE-05

(C) NaHSO₃

PREVIOUS YEARS QUESTIONS

1. The major product of nitration of Benzoic acid is -[IIT-93] (A) 3-Nitrobenzoic acid (B) 4-Nitrobenzoic acid (C) 2-Nitrobenzoic acid (D) 2,4-dinitrobenzoic acid The organic product formed in the reaction $C_6H_5COOH \xrightarrow{\text{(i) LiAlH}_4}$: 2. [IIT-95] (A) $C_6H_5CH_9OH$ (B) C₆H₅COOH & CH₄ (C) C₆H₅CH₃ & CH₃OH (D) C₆H₅CH₃ & CH₄ 3. Which of the following carboxylic acids undergo decarboxylation easily [IIT-95] (A) C₆H₅CO-CH₂COOH (B) $C_6H_5COCOOH$ (C) C₆H₅CH₂-COOH (D) C₆H₅CH₂-COOH | NH₃ 4. The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to -[IIT-96] (B) Dimerisation of benzoic acid (A) Ionization of benzoic acid (C) Trimerisation of benzoic acid (D) Solvation of benzoic acid $CH_3CH_2COOH \xrightarrow{Br_2} X \xrightarrow{NH_3(alc.)} Y$ 5. Y in the above reaction is -[IIT-96] (A) Lactic acid (B) Ethylamine (C) Propylamine (D) Alanine 6. Among the given compounds, the most susceptible to nucleophilie attack at the carbonyl group is -[IIT-97] (C) MeCOOMe (A) MeCOCl (B) MeCHO (D) MeCOOCOMe 7. Read the following statement and explanation and answer as per the option given below: [IIT-98] **Assertion**: Acetic acid does not undergo haloform reaction. Reason: Acetic acid has no alpha hydrogens. (A) If both assertion and reason are correct, and reason is the correct explanation of the assertion (B) If both assertion and reason are correct, but reason is not correct explanation of the assertion (C) If assertion is correct but reason is incorrect (D) If assertion is incorrect but reason is correct When propionic acid is treated with aqueous NaHCO_3 , CO_2 is liberated. The 'C' of CO_2 comes from -8. (A) Methyl group (B) Carboxylic acid group [IIT-99] (C) Methylene group (D) Bicarbonate 9. Benzoyl chloride is prepared from benzoic acid by -[IIT-2000] (A) Cl₂, hv (B) SO₂Cl₂ (C) SOCl₂ 10. Which of the following acids has the smallest dissociation constant -[IIT-02] (A) CH₂CHFCOOH (B) FCH₂CH₂COOH (C) BrCH₂CH₂COOH (D) CH₃CHBrCOOH CH₃ Acidic Product 11. HC formed by P & Q can be differentiated by : [IIT-03] (A) 2, 4- DNP (B) Lucas reagent (ZnCl₂ & conc. HCl)

(D) Fehlings solution

12. MeO—CHO + X
$$\xrightarrow{\text{CH}_3\text{COONa}}$$
 MeO—CH-CH-CH-COOH [IIT-05] What is X?

(A) CH_2COOH (B) BrCH_2-COOH (C) COOH(CH_3CO)_2O (D) (CH_3CO)_2O

CHO

- Compound (A) $C_5H_8O_2$ liberated CO_2 on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yielded compound (B). $C_5H_{10}O_2$ on hydrogenation. Compound (B) can be separated into enantiomorphs. Write structures of (A) and (B). [IIT-87]
- An organic compound (A) on treatment with acetic acid in presence of sulphuric acid produces an ester (B).

 (A) on mild oxidation gives (C). (C) with 50% KOH followed by acidification with dilute HCl generates (A) and (D). (D) with PCl₅ followed by reaction with ammonia gives (E). (E) on dehydration produces hydrocyanic acid. Identify (A) to (E)

 [IIT-87]
- Compound (A) $(C_6H_{12}O_2)$ on reduction with LiAlH₄ yielded two compounds (B) and (C). The compound (B) on oxidation gave (D). 2 moles of (D) on treatment with alkali (aqueous) and subsequent heating furnished (E). The later on catalytic hydrogenation gave (C). The compound (D) was oxidized further to give (F) which was found to be monobasic acid (m.wt. 60.0). Deduce structures of (A) to (F). [IIT-90]
- The sodium salt of a carboxylic acid, (A) was produced by passing a gas (B) into aqueous solution of caustic alkali at an elevated temperature and pressure (A) on heating in presence of sodium hydroxide followed by treatment with sulphuric acid gave a dibasic acid (C). A sample of 0.4g of (C) on combustion gave 0.08g of H_2O and 0.39g of CO_2 . The silver salt of the acid, weighing 1.0g, on ignition yielded 0.71 g of Ag as residue. Identify (A), (B) and (C).
- 17. Two mole of an ester (A) are condensed in presence of sodium ethoxide to give a β -keto ester (B) and ethanol. On heating in an acidic solution (B) gives ethanol and β keto acid (C). On decarboxylation (C) gives 3-pentanone. Identify (A), (B) and (C) with proper reasoning and give reactions. [IIT-92]
- An organic compound $A(C_4H_6O_3)$ on treatment with ethyl alcohol gives a carboxylic acid B and compound C. Hydrolysis of C under acidic conditions gives B and D. Oxidation of D with $KMnO_4$ also gives B. B on heating with $Ca(OH)_2$ gives E (Molecular formula C_3H_6O) E does not gives Tollen's test and does not reduce Fehling solution but forms 2,4-dinitrophenylhydrazone. Identify A to E. [IIT-92]
- An acidic compound (A), C_4H_8O loses its optical activity on strong heating yielding (B). $C_4H_6O_2$ which reacts readily with $KMnO_4$. (B) forms a derivative (C) with $SOCl_2$, which on reaction with CH_3NH_2 gives (D). The compound (A) on oxidation with dilute chromic acid gives an unstable compound (E) which decarboxylate readily to give (F), C_3H_6O . The compound (F) gives a hydrocarbon (G) on treatment with amalgamated Zn and HCl. Give structures of (A) to (G) with proper reasoning. [IIT-95]
- 20. An liquid (X) having molecular formula $C_6H_{12}O_2$ is hydrolysed with water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). Oxidation of (Z) with chromic acid gives (Y). What are (X), (Y) and (Z).
- 21. Acetophenone on reaction with hydroxylamine-hydrochloride can produce two isomeric oximes. Write structures of the oximes. [IIT-97]
- 22. An organic acid (A), $C_5H_{10}O_2$ reacts with Br_2 in the presence of phosphorus to give (B). Compound (B) contains an asymmetric carbon atom and yields (C) on dehydrobromination. Compound (C) does not show geometric isomerism and on decarboxylation gives an alkene (D) which on ozonolysis gives (E) and (F). compound (E) gives a positive schiff's test but (F) does not. Give structures of (A) to (F) with reasons.

[IIT-97]

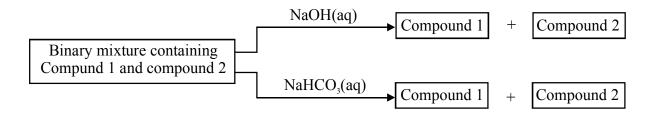
- 23. The correct IUPAC name of C_6H_5COCl is
 - (A) Benzoyl chloride

(B) Benzene chloro ketone

(C) Benzene carbonyl chloride

- (D) Chloro phenyl ketone
- [IIT 2006]
- Which of the following reactants on reaction with conc. NaOH followed by acidification gives the following lactone as the only product? [IIT 2006]

25. Identify the binary mixtures (s) that cna be separated into the individual compounds, by differential extraction, as shown in the given scheme - [IIT 2012]



(A) C_6H_5OH and C_6H_5COOH

(B) C₆H₅COOH and C₆H₅CH₂OH

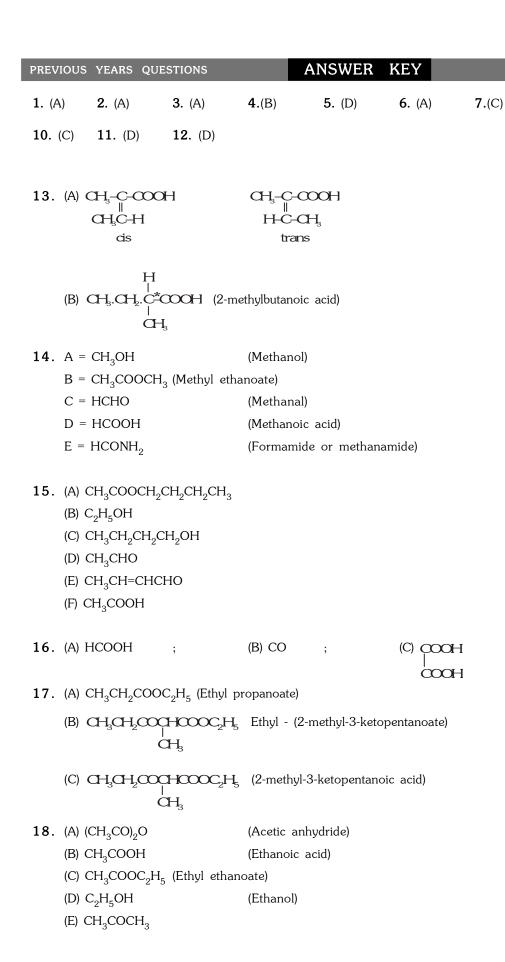
(C) C₆H₅CH₉OH and C₆H₅OH

- (D) C₆H₅CH₂OH and C₆H₅CH₂COOH
- 26. The total number of carboxylic acid groups in the product P is

[JEE 2013]

$$\begin{array}{c}
O \\
O \\
O
\end{array}$$

$$\begin{array}{c}
O \\
\hline
\begin{array}{c}
1. \text{ H}_3\text{O}^+, \Delta \\
\hline
2. \text{ O}_3 \\
3. \text{ H}_2\text{O}_2
\end{array}
} P$$



EXERCISE -5

. (C)

. (D)

. B, D

. (2)

E = HCHO

. C

. C

EXERCISE # JEE MAIN ALL QUESTIONS BASED ON

HALOGEN & OXYGEN CONTAINING ORGANIC COMPOUND

1. Following reaction :

 $(CH_3)_3C-Br + H_2O \longrightarrow (CH_3)_3C-OH + HBr$

is an example of-

[AIEEE-2002]

- (A) Elimination reaction
- (C) Nucleophilic substitution

(B) Free radical substitution(D) Electrophilic substitution

2. SN¹ reaction is easible in-

[AIEEE-2002]

$$(A) \rightarrow CI + KOH \rightarrow$$

(B)
$$\bigwedge^{Cl}$$
 + KOH \longrightarrow

(C)
$$\langle - C \rangle$$
 -CI + KOH \longrightarrow

(D)
$$\langle -aH_2aH_2-a+kaH \longrightarrow \rangle$$

- Bottles containing C_6H_5I and $C_6H_5-CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment. [AIEEE-2003]
 - (A) A was C₆H₅I

(B) A was C₆H₅CH₂I

(C) B was C_eH_eI

- (D) Addition of HNO3 was unnecessary
- 4. The reaction of chloroform with alcoholic KOH and p-toluidine form-

[AIEEE-2003]

(A)
$$H_3C$$
—CN

(B)
$$H_3C$$
 \longrightarrow N_2C

(C)
$$H_3C \longrightarrow NHCHC_2$$

(D)
$$H_3C$$

- 5. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is-
 - (A) Gammaxe

(B) DDT

(C) Freon

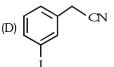
- (D) Hexa chloro ethane
- 6. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is-

[AIEEE-2006]

(A) CH₃CH₂CH(OH)CH₂CH₃

- (D) PhCHOHCH₃
- 7. The structure of the major product formed in the following reaction is :

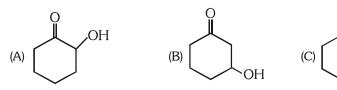
[AIEEE-2006]



8. Which of the following on heating with aqueous KOH, produces acetaldehyde?

[AIEEE-2009]

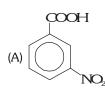
- (A) CH₂ClCH₂Cl
- (B) CH₃CHCl₂
- (C) CH₃COCl
- (D) CH₃CH₂Cl

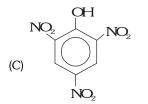


$$\begin{array}{c} O \\ O \\ O \\ O \\ O \\ \end{array} \qquad \begin{array}{c} CH_2 \\ O \\ O \\ \end{array}$$

10. Picric acid is -

[AIEEE-2002]





11. An ether is more volatile than an alcohol having the same molecular formula. This is due to -

[AIEEE-2003]

- (A) Inter molecular hydrogen bonding in ethers
- (B) Inter molecular hydrogen bonding in alcohols

(C) Dipolar character of ethers

- (D) Alcohols having resonance structures
- 12. When $CH_2 = CH-COOH$ is reduced with LiAlH₄, the compound obtained will be [AIEEE-2003]
 - (A) $CH_3 CH_2 CH_2OH$
- (B) CH₃-CH₂-CHO
- (C) CH₃-CH₂-COOH
- (D) CH₂=CH-CH₂OH

13. The general formula $C_nH_{2n}O_2$ represents

[AIEEE-2003]

(A) Diols

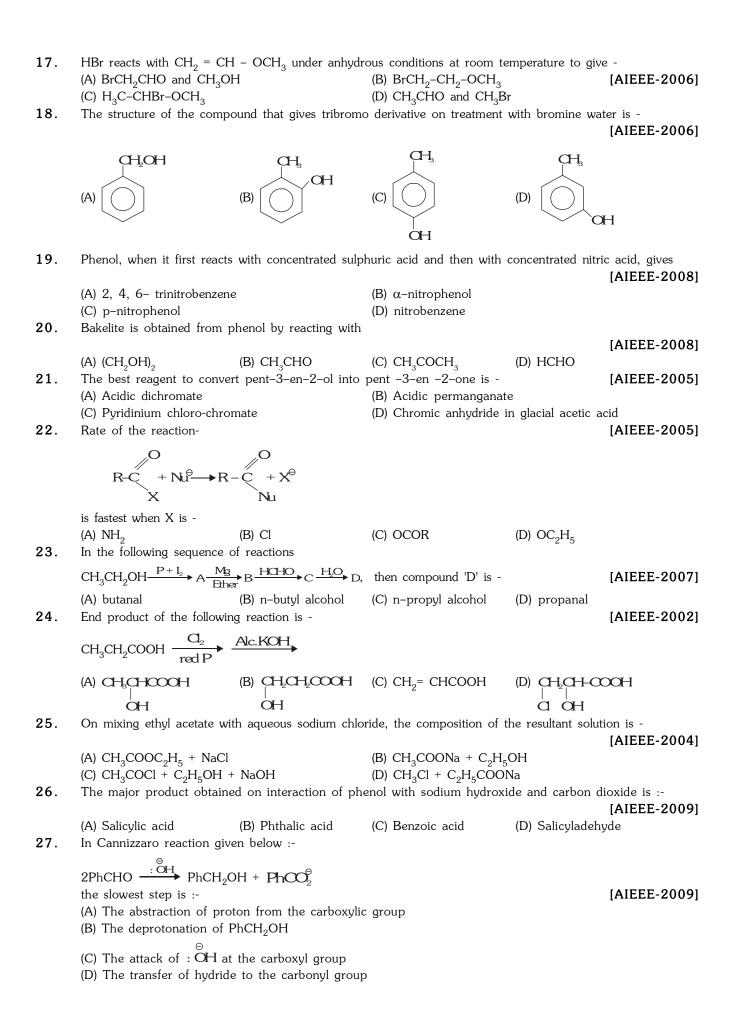
- (B) Dialdehydes
- (C) Diketones
- (D) Carboxylic acids
- 14. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid?

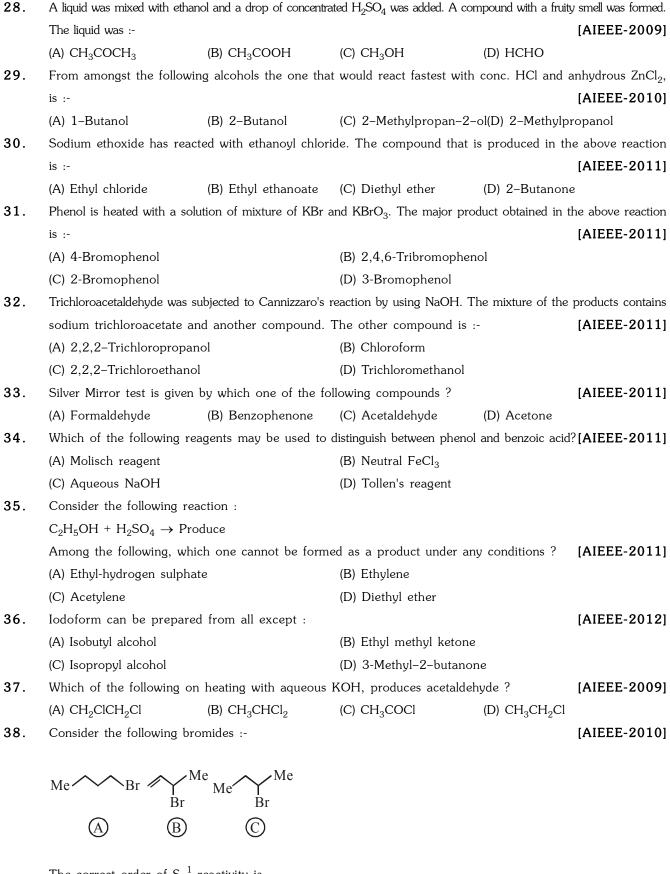
 [AIEEE-2004]
 - (A) Phenol
- (B) Benzaldehyde
- (C) Butanal
- (D) Benzoic acid
- 15. Among the following compounds which can be dehydrated very easily is -

[AIEEE-2004]



p-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form, the compound B. The later on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is [AIEEE-2005]





The correct order of S_N^{-1} reactivity is

(A) A > B > C

(B) B > C > A (C) B > A > C (D) C > B > A

- 39. A solution of (-) -1-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl₅, due to the formation of :- [JEE-MAIN 2013]
 - (A) carbanion
- (B) Carbene
- (C) carbocation
- (D) free radical
- 40. Arrange the following compounds in order of decreasing acidity :

$$\begin{array}{cccc}
OH & OH & OH & OH \\
\hline
CI & CH_3 & NO_2 & OCH_2 \\
(I) & (II) & (III) & (IV)
\end{array}$$

- (A) II > IV > I > III
- (B) I > II > III > IV
- (C) III > I > II > IV (D) IV > III > I > II
- **41.** Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A):

- 42. An organic compound A upon reacting with NH_3 gives B. On heating, B gives C. C in presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. A is :-
 - (A) CH₃COOH

(B) CH₃CH₂CH₂COOH

(C) CH₃-CH-COOH CH₃

- (D) CH₃CH₂COOH
- **43.** An unknown alcohol is treated with the "Lucas reagent' to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism:
 - (A) secondary alcohol by SN1

(B) tertiary alcohol by SN1

(C) secondary alcohol by SN2

(D) tertiary alcohol by SN2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13
Ans	В	С	В	D	D	В	С	Α	В	С	В	D	D
Que.	14	15	16	17	18	19	20	21	22	23	24	25	26
Ans	В	С	Α	D	D	Bonus	D	D	В	С	С	В	Α
Que.	27	28	29	30	31	32	33	34	35	36	37	38	39
Ans	D	В	С	В	В	С	A,C	В	С	Α			
Que.	40	41	42	43									
Ans	С	D	D	В									