Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A): Electrophile, Nucleophile, Nucleophilicity, Leaving group ability & Solvent

A-1. Which of the followings are electrophile ?

(a) CN^- (b) H^+ (c) Br^+ (d) $AlCl_3$

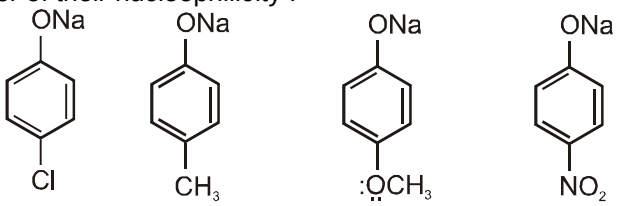
(e) BH_3 (f) $CH_3-\overset{\oplus}{C}=O$ (g) NH_3 (h) $\overset{\oplus}{N}O_2$

A-2. Which of the followings are nucleophile ?

(a) HS^- (b) BF_3 (c) C_2H_5–OH (d) $(CH_3)_3\overset{\oplus}{N}$ (e) $:CH_2$

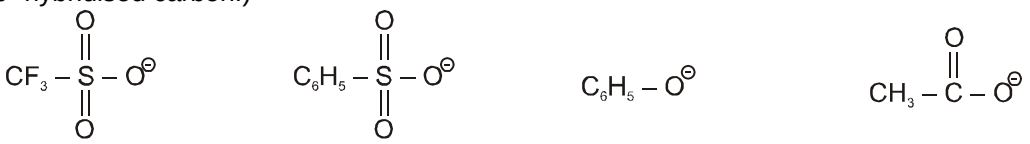
A-3. Arrange the given species in decreasing order of their nucleophilicity :

(a) H_2O $Cl^\ominus$ $Br^\ominus$ $I^\ominus$

(b) 

A-4. Define ambident nucleophile with an example :

A-5. In nucleophilic substitution reactions the leaving ability order for the following species is (when attached to the sp^3 hybridised carbon.)



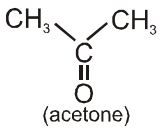
I II III IV

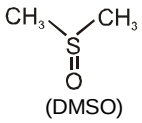
A-6. Label each of the following solvent as Protic or Aprotic

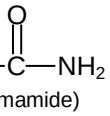
(a)  (Tetrahydrofuran)

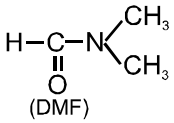
(b) Acetonitrile

(c) Acetic acid

(d)  (acetone)

(e)  (DMSO)

(f)  (Formamide)

(g)  (DMF)

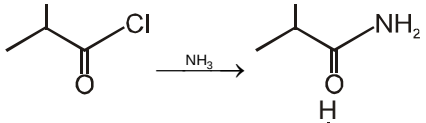
(h) Cyclohexane

(i) Amonia

Section (B) : Types of organic reactions and reactions of acidic hydrogen

B-1. Which of the following reactions are substitution reaction ?

(a) $CH_2=CH_2 \xrightarrow{Ni/H_2} CH_3–CH_3$

(b) 

(c) $CH_3–I + \overset{\ominus}{O}H \longrightarrow CH_3OH + \overset{\ominus}{I}$

(d) $CH_3–CHO \xrightarrow[H^\oplus]{KCN} CH_3-\underset{CN}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH$

B-2. Which of the following reaction are addition reaction ?

(a) $CH_3-CHO \xrightarrow[H^{\oplus}]{KCN} CH_3-\underset{CN}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH$

(b) $CH_3-CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3$

(c) $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3-CH=CH_2-CH_3$

(d) $CH_3-\underset{O}{\overset{\|}{C}}-OH \xrightarrow{CH_3OH} CH_3-\underset{O}{\overset{\|}{C}}-OCH_3$

B-3. Which of the following reaction is an elimination reaction ?

(a) $CH_3-CH_2-CH_2-OH \xrightarrow{PCl_5} CH_3-CH_2-CH_2-Cl$

(b) $\underset{Br}{\underset{|}{CH_2}}-\underset{Br}{\underset{|}{CH_2}} \xrightarrow{Zn} CH_2=CH_2 + ZnBr_2$

(c) $CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3-CH=CH_2$

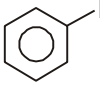
(d) $CH_3-\underset{O}{\overset{\|}{C}}-OH \xrightarrow{CH_3OH} CH_3-\underset{O}{\overset{\|}{C}}-OCH_3$

B-4. An organic compound which have molecular formula $C_4H_4O_3$, gives 3 moles of gas on treatment with methyl magnesium bromide. Give structure of the compound.

B-5. Predict the product of the following reactions

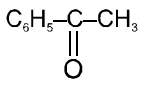
(a) Methylmagnesium iodide + $D_2O \longrightarrow$?

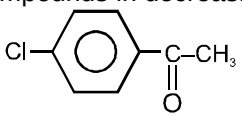
(b) Isobutylmagnesium iodide + Phenylacetylene $\longrightarrow$?

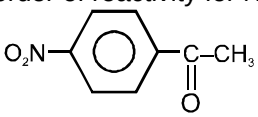
(c)  + $DOCH_3 \longrightarrow$

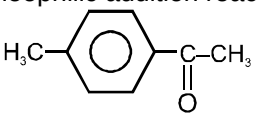
Section (C) : Nucleophilic addition reactions of carbonyl compounds

C-1. Arrange the following compounds in decreasing order of reactivity for Nucleophilic addition reaction:


(I)


(II)


(III)

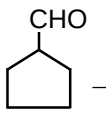

(IV)

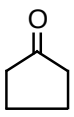
C-2. Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not. Explain why ?

C-3. Complete the following reactions.

(a) $Ph-\underset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[HCl]{NaCN}$

(b) $CH_3-CH_2-CHO \xrightarrow[2.\ H_2O]{1.\ PhMgBr}$

(c)  $\xrightarrow[H_2SO_4]{NaCN}$

(d)  $\xrightarrow[H_2SO_4]{NaCN}$

C-4. Bring about the following conversions

(i) Acetone to 2-Methylpropan-2-ol.

(ii) Ethyl magnesium chloride to propan-1-ol.

C-5. What is the product of each reaction when acetophenone treated with

(a) $LiAlD_4$ followed by H_2O

(b) $LiAlH_4$ followed by D_2O

(c) $NaBD_4$ followed by EtOH

(d) $NaBD_4$ followed by EtOD

Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate (S_N2Th)

D-1. How many reactions given below are proceed through S_N2Th mechanism ?

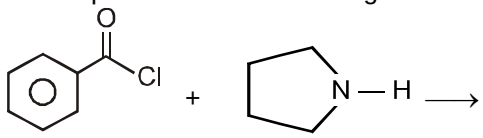
(a) $CH_3-\overset{\overset{O}{\|}}{C}-Cl + NaOH \longrightarrow$ (b) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + NaI \longrightarrow$

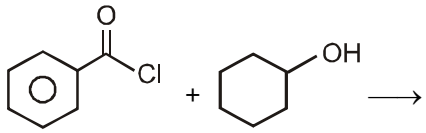
(c) $CH_3-\overset{\overset{O}{\|}}{C}- OH + C_2H_5ONa \longrightarrow$ (d) $CH_3-\overset{\overset{O}{\|}}{C}- OC_2H_5 + NaNH_2 \longrightarrow$

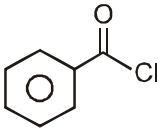
D-2. What will be the major products of the following reactions ?

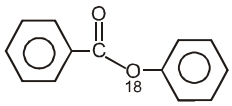
(a) $CH_3-\overset{\overset{O}{\|}}{C}-Cl + CH_3OH \longrightarrow$ (b) $CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O \xrightarrow{H^+}$

D-3. Predict the products of the following reactions :

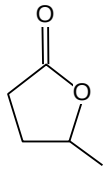
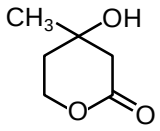
(a)  $\longrightarrow$

(b)  $\longrightarrow$

(c)  $+ CH_3OH \longrightarrow$

D-4.  $\xrightarrow[\Delta]{dil.H_2SO_4}$ A + B, find A and B.

D-5. Write the structure of the hydroxy acid corresponding to each of the following lactones.

(a)  (b) 

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A): Electrophile, Nucleophile, Nucleophilicity, Leaving group ability & Solvent

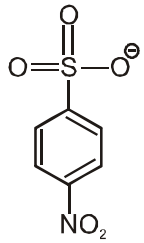
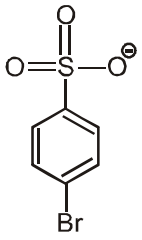
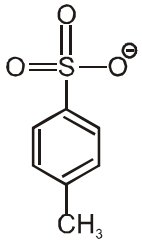
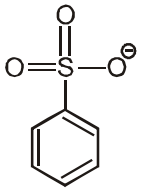
A-1. Which of the following is an electrophilic reagent?
(A) H_2O (B) OH^- (C) NO_2^+ (D) None

A-2. Which of the following is not a nucleophile ?
(A) $AlCl_3$ (B) $(CH_3)_2NH$ (C) C_2H_5OH (D) H_2O

A-3. Which one of the following has maximum nucleophilicity ?
(A) $CH_3S^{\ominus}$ (B) $C_6H_5-\overset{\ominus}{O}$ (C) Et_3N (D) $F^{\ominus}$

A-4. Out of the followings best leaving group is :
(A) F^- (B) Cl^- (C) Br^- (D) I^-

A-5. The best leaving group is :

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

A-6. Which of the following is protic solvent ?

(A) Acetone (B) Ethanol (C) DMF (D) Ether

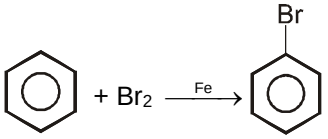
A-7. Which of the following is aprotic solvent ?

(A) DMSO (B) NH_3 (C) H_2O (D) CH_3COOH

Section (B) : Types of organic reactions and reactions of acidic hydrogen

B-1. Which of the following reaction is an example of elimination reaction :

(A) $CH_3–CH=CH_2 \xrightarrow{H_2O} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$ (B) $CH_3–CH_2–Br \xrightarrow{NaOH} CH_3–CH_2–OH$

(C) $CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{Alc. KOH}} CH_3–CH=CH_2$ (D) 

B-2. The following reaction is an example of :

$RCOOH + PCl_5 \longrightarrow RCOCl$

(A) Acid-base reaction (B) Substitution reaction

(C) Addition reaction (D) Elimination reaction

B-3. The following reaction is an example of $CH_3–\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow[H^{\oplus}]{H_2O} CH_3–\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}–CH_3$

(A) Acid-base reaction (B) Substitution reaction

(C) Addition reaction (D) Elimination reaction

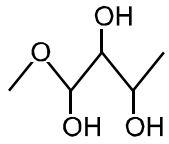
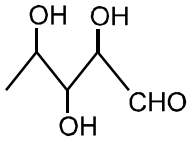
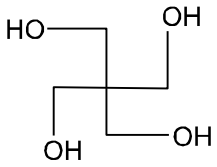
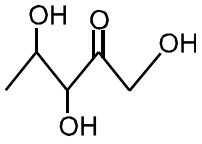
B-4. $C_6H_5COOH + CH_3MgI \longrightarrow$?

(A) $C_6H_5COOMgI$ (B) CH_4 (C) Both A & B (D) none

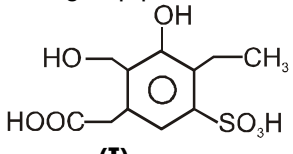
B-5. $(CH_3)_3CMgCl$ on reaction with D_2O produces :

(A) $(CH_3)_3CD$ (B) $(CH_3)_3COD$ (C) $(CD_3)_3CD$ (D) $(CD_3)_3COD$

B-6. A compound X ($C_5H_{12}O_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).

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

B-7. How many functional group produced CH_4 gas by the reaction of compound (I) with CH_3MgBr.



(I)

(A) 3 (B) 4 (C) 5 (D) 6

Section (C) : Nucleophilic addition reactions of carbonyl compounds

C-1. The correct order of reactivity of following compounds with PhMgBr will be.

$(C_6H_5)_2CO$, $CH_3–CH=O$, $(CH_3)_2C=O$

(1) (2) (3)

(A) 1 > 2 > 3 (B) 2 > 3 > 1 (C) 3 > 2 > 1 (D) 1 > 3 > 2

C-2. $CH_3 – CH_2 – \underset{\underset{O}{\|}}{C} – CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr}$ Product is :

(A) $CH_3 – CH_2 – \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}} – CH_3$ (B) $CH_3 – CH_2 – \underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{CH}} – CH_2$

(C) $CH_3 – CH_2 – \underset{\underset{OH}{|}}{CH} – CH_3$ (D) $CH_3 – CH_2 – \underset{\underset{CH_3}{|}}{CH} – CH_3$

C-3. $P \xrightarrow{PhMgBr} \xrightarrow{H_2O} CH_3–\underset{\underset{OH}{|}}{CH}–Ph$ $(d+\ell)$

P can be :

(A) CH_3COOH (B) $H–COOCH_3$ (C) $CH_3–COCl$ (D) $CH_3–CH=O$

C-4. Butan-2-ol is obtained by using carbonyl compound and Grignard reagent as :

(A) $CH_3–CH=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–CH_2–MgBr}$ (B) $CH_3–(CH_2)_2–CH=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–MgBr}$

(C) $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–MgBr}$ (D) $CH_2=O \xrightarrow[(ii)\ H_2O\ /\ H^{\oplus}]{(i)\ CH_3–\underset{\underset{CH_3}{|}}{CH}–MgBr}$

C-5. HCN reacts with fastest rate with :

(A) Acetone (B) Ethanal (C) Benzophenone (D) Acetophenone

C-6. The product of the reaction $Ph_2C=O \xrightarrow[H_3O^{\oplus}]{LiAlD_4}$ is

(A) $Ph_2CD(OH)$ (B) $Ph_2CH(OD)$ (C) $Ph_2CD(OD)$ (D) None

Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate (S_N2Th)

D-1. The relative reactivity of acyl compounds towards nucleophilic substitution are in the order of :

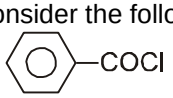
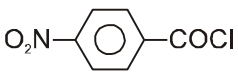
(A) Acid anhydride > Amide > Ester > Acyl chloride

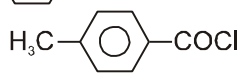
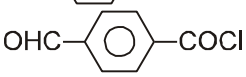
(B) Acyl chloride > Ester > Acid anhydride > Amide

(C) Acyl chloride > Acid anhydride > Ester > Amide

(D) Ester > Acyl chloride > Amide > Acid anhydride

D-2. Consider the following compounds :

(i)  (ii) 

(iii)  (iv) 

The correct order of reactivity towards hydrolysis is :

(A) (i) > (ii) > (iii) > (iv) (B) (iv) > (ii) > (i) > (iii)

(C) (ii) > (iv) > (i) > (iii) (D) (ii) > (iv) > (iii) > (i)

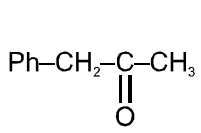
D-3. Which of the following method is not used for the conversion of carboxylic acid into acid halide ?

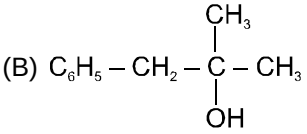
(A) $RCOOH + SOCl_2 \longrightarrow$ (B) $RCOOH + PCl_5 \longrightarrow$

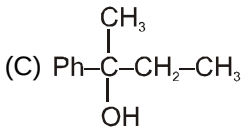
(C) $RCOOH + Cl_2 \longrightarrow$ (D) $RCOOH + PCl_3 \longrightarrow$

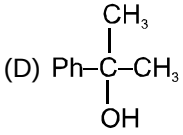
D-4. Predict the major product in the following reaction :

$C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)}$

(A) 

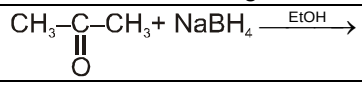
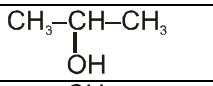
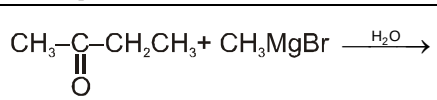
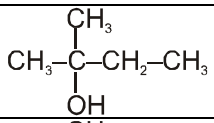
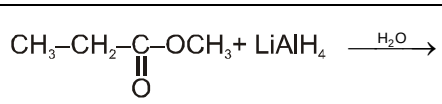
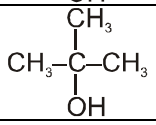
(B) 

(C) 

(D) 

PART - III : MATCH THE COLUMN

1. Match List I (Reaction) with List II (Product) and select the correct answer using the code given below the lists :

	List-I		**List-II**
(P)	$CH_3COCH_3 + CH_3MgBr \xrightarrow{H_2O}$	(1)	$CH_3–CH_2–CH_2–OH$
(Q)		(2)	
(R)		(3)	
(S)		(4)	

Codes :

	P	Q	R	S		P	Q	R	S
(A)	2	4	3	1	(B)	4	2	3	1
(C)	4	2	1	3	(D)	2	4	1	3

2. Match the **List**-I with **List**-II :

	List-I		**List-II**
(A)	$I^{\ominus}$	(p)	Strong nucleophile
(B)	$CF_3SO_3^{\ominus}$	(q)	Strong base
(C)	H_2O	(r)	Good leaving group
(D)	$CH_3CH_2O^{\ominus}$	(s)	Weak base

Exercise-2

Marked questions are recommended for Revision.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Addition reactions involves

(A) Cleavage of a σ-bond and formation of a new σ-bond.

(B) Cleavage of two σ-bonds and formation of a new π-bond.

(C) Cleavage of a π-bond and formation of two new σ-bonds.

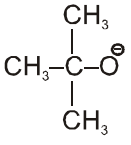
(D) None of these.

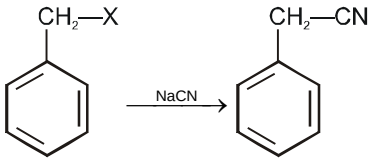
2. Which one of the following has maximum nucleophilicity ?

(A) 

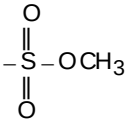
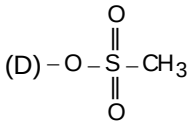
(B) 

(C) 

(D) 

3. 

In the above reaction rate is fastest, when (X) is :

(A) –OH (B)–NH_2 (C)  (D) 

4. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is :

(A) $C_6H_5O^- < CH_3O^- < CH_3COO^- < OH^-$ (B) $CH_3COO^- < C_6H_5O^- < CH_3O^- < OH^-$

(C) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$ (D) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$

5. Which of the following reactions is not feasible ?

(A) $PhSO_3H + NaHCO_3 \longrightarrow$ (B) $Ph–OH + NaNH_2 \longrightarrow$

(C) $CH_3–NH_2 + NaOH \longrightarrow$ (D) $Ph–C\equiv CH + NaH \longrightarrow$

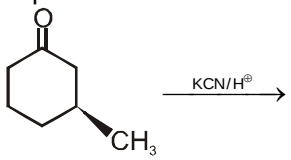
6. Give the decreasing order of nucleophilic addition reaction of the following :

(i) HCHO (ii) PhCHO

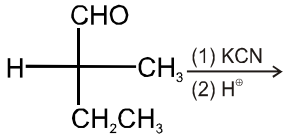
(iii) Chloral ($Cl_3C–CH=O$) (iv) Acetophenone

(A) iii > i > ii > iv (B) iv > ii > i > iii (C) i > iii > ii > iv (D) iii > i > iv > ii

7. Number of products formed in the following reaction(s) is/are



(A) 1 (B) 2 (C) 3 (D) 4

8. 

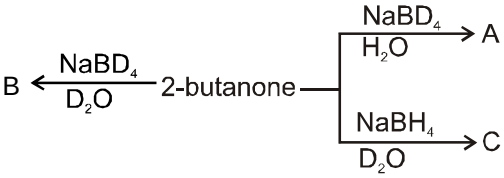
Products

Products obtained in the above reaction is-

(A) Diastereomers (B) Enantiomers

(C) Meso compound (D) Optically pure one product only

9. Consider reduction of 2-butanone.



A, B and C are respectively.

(A) $CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3$ in all cases (B) $CH_3\underset{\underset{D}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CH_3$, $CH_3\underset{\underset{D}{|}}{\overset{\overset{OD}{|}}{C}}CH_2CH_3$, $CH_3\underset{\underset{H}{|}}{\overset{\overset{OD}{|}}{C}}CH_2CH_3$

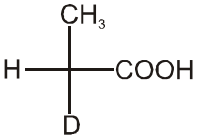
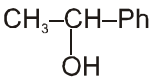
(C) $CH_3\underset{\underset{D}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CH_3$ in all case (D) $CH_3\underset{\underset{D}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CH_3$, $CH_3\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}CH_2CH_3$, $CH_3\underset{\underset{H}{|}}{\overset{\overset{OD}{|}}{C}}CH_2CH_3$

10. Which of the following is correct order of esterification of following acids with CH_3OH :
HCOOH, CH_3COOH , $CH_3–CH_2–COOH$, $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–COOH$

I II III IV

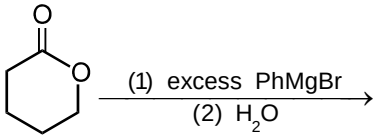
(A) I = II = III = IV (B) I > II > III > IV (C) I < II < III < IV (D) I > IV > III > II

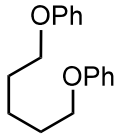
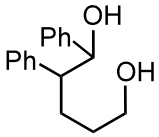
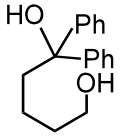
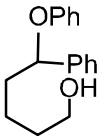
11. Esterification of the acid (P) with the alcohol (Q) will gives.

(P)  ; (Q) : 

(R– configuration) (±)

(A) only one enantiomer (B) a mixture of diastereomer
(C) a mixture of enantiomer (D) only one fraction on fractional distillation

12.  X , X is

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

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

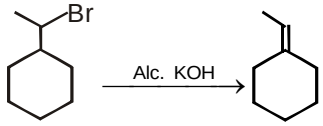
1. How many reactions given below are examples of elimination reactions ?

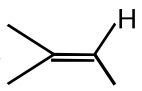
(I) $CH_3–CH=CH_2 \xrightarrow{H_2O} CH_3–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3$

(II) $CH_3–CH_2–Br \xrightarrow{NaOH} CH_3–CH_2–OH$

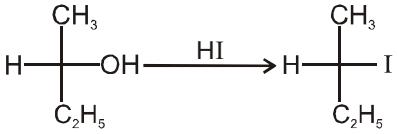
(III) $CH_3–\underset{\displaystyle Br}{\underset{|}{CH}}–CH_3 \xrightarrow{Alc.\ KOH} CH_3–CH=CH_2$

(IV) $CH_3–\underset{\displaystyle CH_3}{\underset{|}{CH}}–\underset{\displaystyle Cl}{\underset{|}{CH}}–CH_3 \xrightarrow{EtOH/\Delta} CH_3–\underset{\displaystyle CH_3}{\underset{|}{C}}=CH–CH_3$

(V) 

(VI) $CH_3–\underset{\displaystyle OH}{\underset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}–CH_2–CH_3 \xrightarrow[\Delta]{Con.\ H_2SO_4}$ 

(VII) $Ph–CH_2–\underset{\displaystyle OH}{\underset{|}{CH}}–CH_3 \xrightarrow{Con.HCl + Anhydrous\ ZnCl_2} Ph–\underset{\displaystyle Cl}{\underset{|}{CH}}–CH_2–CH_3$

(VIII) 

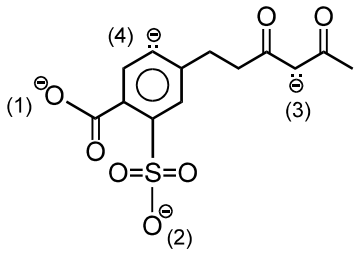
2. Among the following X is the number of electrophiles and Y is the number of nucleophiles. Report your answer as | X | Y |.

(i) $CH_3^{\oplus}$ (ii) $I^{\ominus}$ (iii) $NO_2^{\oplus}$ (iv) $\overset{\ominus}{C}H_3$

(v) NH_3 (vi) $Br^{\oplus}$ (vii) $\overset{\ominus}{Cl}$ (viii) H^+

(ix) $AlCl_3$ (x) CH_3OH (xi) $CH_3 - \overset{\oplus}{C} = O$ (xii) BH_3

3. Which is the strongest nucleophilic site in the following species ?



4. An alcohol (A), 0.22 g of this alcohol librates 56 ml of CH_4 at STP on reaction with CH_3MgBr. Write the molecular weight of alcohol which satisfy these conditions.

5. How many carbonyl compounds will give secondary alcohol with molecular formula $C_5H_{12}O$ after reduction with $LiAlH_4$?

6. How many compounds out of following will give secondary alcohol on treatment with Grignard reagent ?

(a) Ph–CO–CH_3 (b) Ph–CHO (c) HCHO (d) CH_3CH_2CHO

(e) CH_3CHO (f) Ph–CO–Ph (g) HCOCl (h) $CH_3COOC_2H_5$

7. What is the maximum number of moles of CH_3MgCl that can be consumed by one mole of phosgene ?

8. Find the moleculer weight of a sweet smelling compound which react with LAH to gives only ethanol.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Electrophiles are

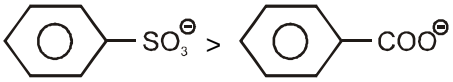
(A) Electron deficent species (B) having atleast one pair of electron

(C) Electron rich species (D) Electron pair acceptor

2. Which of the following is/are ambident nucleophile(s) ?

(A) NO_2^- (B) $CN^{\ominus}$ (C) $NaHSO_3$ (D) $Cl^{\ominus}$

3. The correct order of leaving group ability is/are :

(A)  (B) $CF_3SO_3^{\ominus} > CCl_3SO_3^{\ominus}$

(C) $\overset{\ominus}{C}N > I^{\ominus}$ (D) $\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H$

4. Which of the following reactions yeild benzene ?

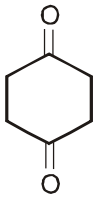
(A) PhMgBr + CH_3–Br (B) PhMgBr + H_2O

(C) PhBr + H_2O (D) PhMgBr + CH_3–C≡CH

5. Which of the following liberate hydrogen gas with NaH.

(A) CH_3–COOH (B) $CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

(C) CH_3–C≡CH (D) CH_3–CH_2–OH

6.  $\xrightarrow{HCN}$ Product

The correct statement about product is

(A) The product is optical inactive (B) The product is meso compound

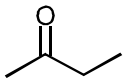
(C) The product is mixture of two enantiomer (D) Products are in two diastereomeric forms

7. $R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[2.\ H_3O^{\oplus}]{1.\ MeMgBr\ (1\ eq.)}$ acetone as the sole organic product.

which is/are correctly matched with R and R′.

(A) R is –H (B) R' is $-\underset{\underset{CH_2}{\|}}{C}-CH_3$ (C) R' is $-\underset{\underset{CH_3}{|}}{CH}-CH_2$ (D) R is $-CH_3$

8. 2-Phenylbutan-2-ol can be prepared by :

(A) PhMgBr +  $\xrightarrow{ether}$ $\xrightarrow{H^{\oplus}}$

(B) $CH_3MgBr + Ph-\underset{\underset{O}{\|}}{C}-C_2H_5 \xrightarrow{ether} \xrightarrow{H^{\oplus}}$

(C) $C_2H_5MgBr + Ph-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{ether} \xrightarrow{H^{\oplus}}$

(D) $CH_3CH_2CH_2MgBr + PhCHO \xrightarrow{ether} \xrightarrow{H^{\oplus}}$

9. The correct decreasing reactivity order of the given compound(s) towards hydrolysis under identical condition is/are :

(A) $CH_3COCl > CH_3CONH_2$ (B) $CH_3COCl > (CH_3CO)_2O$

(C) $CH_3COOCH_3 > CH_3COCl$ (D) $(CH_3CO)_2O > CH_3CONH_2$

10. X (an ethyl ester) $\xrightarrow[(ii)H_3O^{\oplus}]{(i)\ Grignard's\ reagent\ (Y)\ (execess)}$ product

The product(s) may be :

(A) $Ph-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-Ph$ (B) $CH_3-\underset{\underset{OH}{|}}{\overset{\overset{C_2H_5}{|}}{C}}-C_2H_5$ (C) $H-\underset{\underset{OH}{|}}{\overset{\overset{CHMe_2}{|}}{C}}-CHMe_2$ (D) $Ph-\underset{\underset{OH}{|}}{\overset{\overset{CHMe_2}{|}}{C}}-CH_3$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

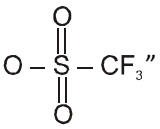
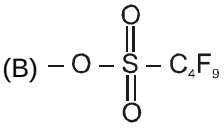
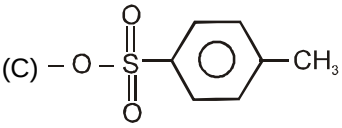
Comprehension # 1

Nucleophilic aliphatic substitution reaction is given by those compounds which have electron rich groups as leaving groups. Less is the basicity of the leaving group, more is its leaving power.

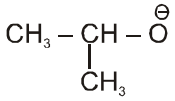
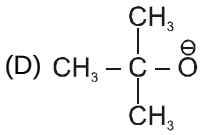
$$R - L + \overset{\ominus}{N}u \rightleftharpoons R - Nu + \overset{\ominus}{L}$$

In the given reaction, L is the leaving group which leaves as nucleophile. $\overset{\ominus}{N}u$ is the incoming group which is always nucleophilic in character. The reaction is nucleophilic substitution reaction which can be unimolecular or bimolecular reaction.

1. Leaving power of which group is maximum ?

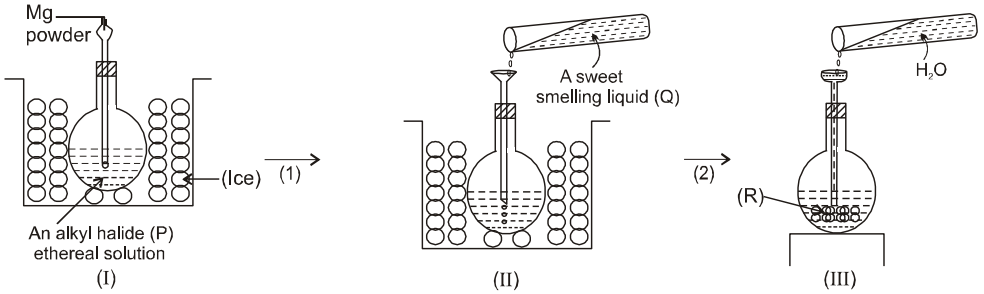
(A)  (B)  (C)  (D) $-\overset{\ominus}{Cl}$

2. Which one of the following is strong base but poor nucleophile ?

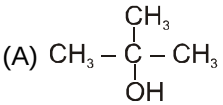
(A) $\overset{\ominus}{CH_3}$ (B) $\overset{\ominus}{HO}$ (C)  (D) 

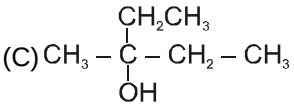
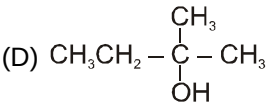
Comprehension # 2

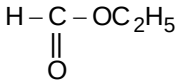
Observe the following experiment

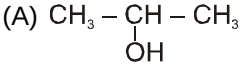
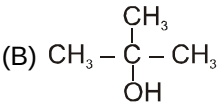


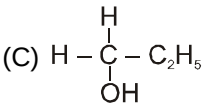
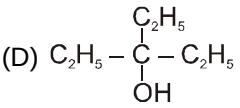
3. If the reactant 'P' is ethyl chloride then the main product R can be

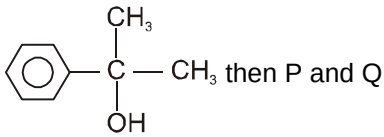
(A)  (B) $CH_3CH_2 - O - CH_2CH_3$

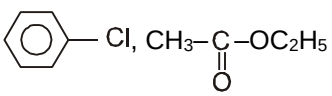
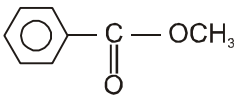
(C)  (D) 

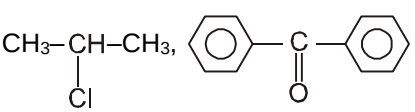
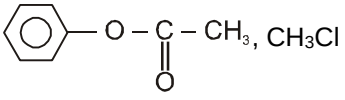
4. If the liquid Q is  then the product R can be (P can be any other halide)

(A)  (B) 

(C)  (D) 

5. If R is  then P and Q can be respectively.

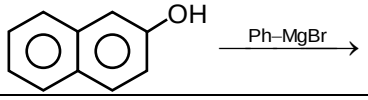
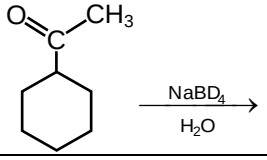
(A)  (B) CH_3–Cl, 

(C)  (D) 

Comprehension # 3

Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Columns 1, 2 and 3 contain reactions, type of reactions and lab test for reactants respectively.

Column-1	Column-2	Column-3
(I) $CH_3–\underset{\underset{OH}{|}}{CH}–CH_2–CH_2–\underset{\underset{O}{||}}{C}–OH \xrightarrow{H^+}$	(i) Acid base reaction	(P) 2,4-DNP test
(II) 	(ii) Nucleophilic addition reaction	(Q) Carbylamine test
(III) 	(iii) Nucleophilic substitution reaction	(R) Lucas test
(IV) $CH_3–CH_2–NH_2 \xrightarrow{CH_3MgBr}$	(iv) Fischer esterification	(S) Neutral $FeCl_3$ test

6. For the synthesis of hydrocarbon, the only correct combination is :
(A) (II) (i) (R) (B) (III) (ii) (P) (C) (IV) (i) (Q) (D) (I) (iii) (S)

7. The only correct combination that gives two different stereoisomeric products is :
(A) (II) (i) (S) (B) (III) (iii) (P) (C) (IV) (iii) (Q) (D) (I) (iv) (R)

8. The only correct combination in which the reaction product gives iodoform test.
(A) (I) (iii) (R) (B) (III) (ii) (P) (C) (II) (i) (S) (D) (IV) (i) (Q)

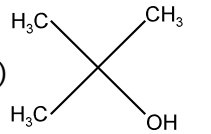
Exercise-3

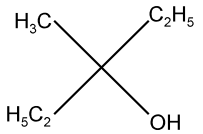
*** Marked questions may have more than one correct option.**

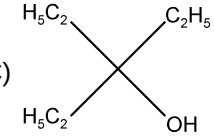
PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

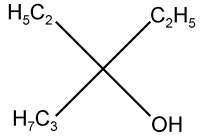
1. A biologically active compound, Bombykol ($C_{16}H_{30}O$) is obtained from a natural source. The structure of the compound is determined by the following reactions.
(i) On hydrogenation, Bombykol gives a compound (A), $C_{16}H_{34}O$, which reacts with acetic anhydride to give an ester.
(ii) Bombykol also reacts with acetic anhydride to give another ester (B), which on oxidative ozonolysis (O_3 /H_2O_2) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.
Determine the number of double bonds in bombykol. Write the structures of compound A and B. How many geometrical isomers are possible for Bombykol ? **[IIT-JEE-2002(Main), 5/150]**

2. Ethylester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be **[JEE-2003, 3/84]**

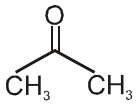
(A) 

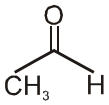
(B) 

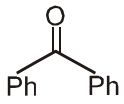
(C) 

(D) 

3. The order or reactivity of phenyl magnesium bromide with the following compounds is : **[JEE-2004, 3/84]**


I

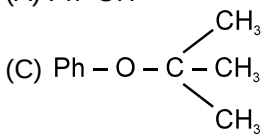

II

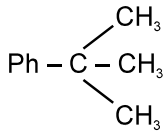

III

(A) (II) > (III) > (I)
(B) (I) > (III) > (II)
(C) (II) > (I) > (III)
(D) all react with the same rate

4. Phenyl magnesium bromide reacting with t-Butyl alcohol gives **[JEE-2005, 3/60]**

(A) Ph–OH
(B) Ph–H

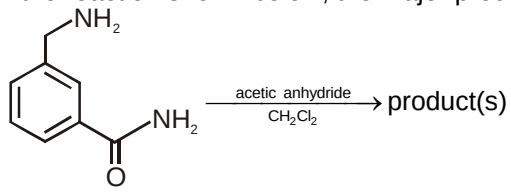
(C) 

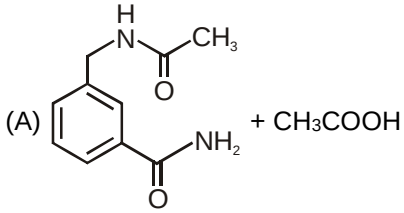
(D) 

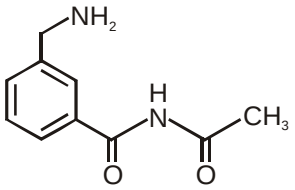
5. Match the compounds/ions in Column I with their properties/reactions in Column II. **[JEE 2007, 8/162]**

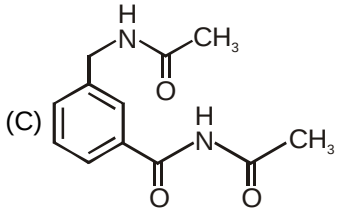
	Column-I		**Column-II**
(A)	C_6H_5CHO	(p)	gives precipitate with 2,4 dinitrophenylhydrazine.
(B)	$CH_3C{\equiv}CH$	(q)	gives precipitate with $AgNO_3$.
(C)	CN^-	(r)	is a nucleophile.
(D)	I^-	(s)	is involved in cyanohydrin formation.

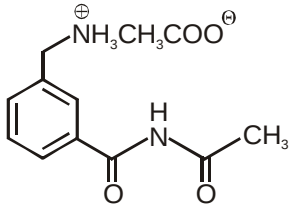
6. In the reaction shown below, the major product(s) formed is/are **[JEE(Adv.)-2014, 3/120]**



(A)  + CH_3COOH

(B)  + CH_3COOH

(C)  + H_2O

(D) 

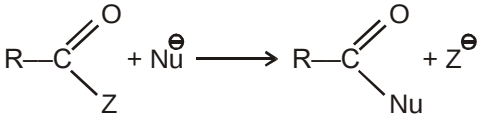
PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives **[AIEEE-2004, 3/225]**

(1) Acetone
(2) Acetamide
(3) 2-Methyl-2-propanol
(4) Acetyl iodide

2. Rate of the reaction is fastest when Z is : **[AIEEE-2004, 3/225]**



(1) Cl (2) $OCOCH_3$ (3) OC_2H_5 (4) NH_2

3. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is : **[AIEEE-2004, 3/225]**

(1) $CH_3COOC_2H_5 + NaCl$ (2) $CH_3Cl + C_2H_5COONa$
(3) $CH_3COCl + C_2H_5OH + NaOH$ (4) $CH_3COONa + C_2H_5OH$

4. The decreasing order of the ratio of HCN addition to compounds A to D is **[AIEEE-2006, 3/165]**

(a) HCHO (b) CH_3COCH_3 (c) $PhCOCH_3$ (d) PhCOPh
(1) d > b > c > a (2) d > c > b > a (3) c > d > b > a (4) a > b > c > d

5. Phenyl magnesium bromide reacts with methanol to give - **[AIEEE-2006, 3/165]**

(1) a mixture of anisole and Mg(OH)Br (2) a mixture of benzene and Mg(OMe)Br
(3) a mixture of toluene and Mg(OMe)Br (4) a mixture of phenol and Mg(Me)Br

6. The treatment of CH_3MgX with $CH_3C{\equiv}C{-}H$ produces **[AIEEE-2008, 3/105]**

(1) $CH_3C{\equiv}C{-}CH_3$ (2) $CH_3{-}\overset{H}{\underset{|}{C}}{=}\overset{H}{\underset{|}{C}}{-}CH_3$ (3) CH_4 (4) $CH_3{-}CH{=}CH_2$

7. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was : **[AIEEE-2009, 4/144]**

(1) HCHO (2) CH_3COCH_3 (3) CH_3COOH (4) CH_3OH

8. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is : **[AIEEE-2011, 4/120]**

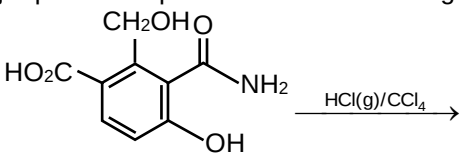
(1) Diethyl ether (2) 2-Butanone (3) Ethyl chloride (4) Ethyl ethanoate

9. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : **[JEE(Main)-2013, 4/120]**

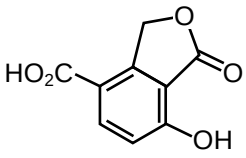
(1) 2 (2) 5 (3) 4 (4) 6

JEE(MAIN) ONLINE PROBLEMS

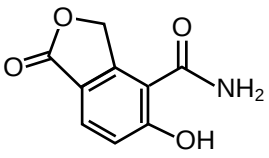
1. The major product expected from the following reaction is : **[ONLINE - JEE(Main) 08-04-2017]**



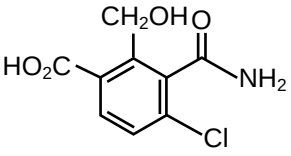
(1)



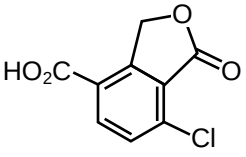
(2)



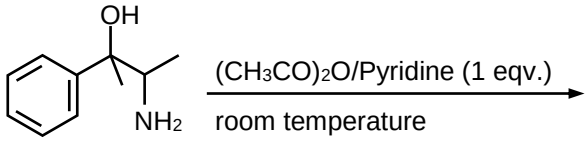
(3)

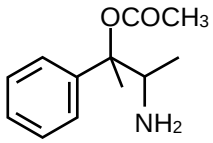


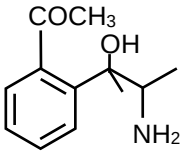
(4)

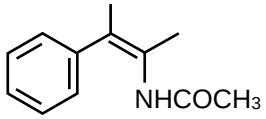


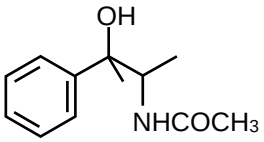
2. The major product obtained in the following reaction is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**



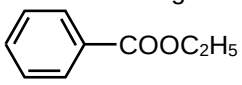
(1) 

(2) 

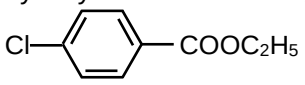
(3) 

(4) 

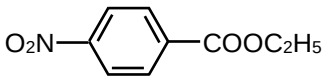
3. The decreasing order of ease of alkaline hydrolysis for the following esters is



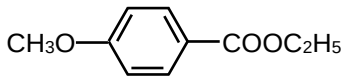
(I)



(II)



(III)

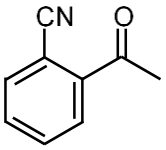


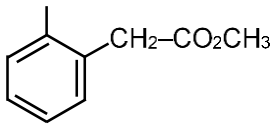
(IV)

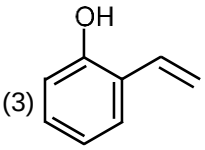
[JEE(Main) 2019 Online (10-01-19), 4/120]

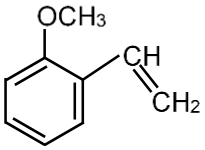
(1) III > II > IV > I (2) II > III > I > IV (3) IV > II > III > I (4) III > II > I > IV

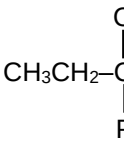
4. Which of the following compounds reacts with ethyl magnesium bromide and also decolourizes bromine water solution : **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) 

(2) 

(3) 

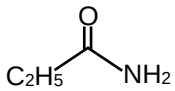
(4) 

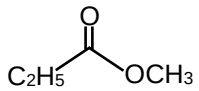
5. 

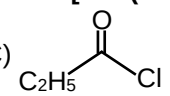
cannot be prepared by : **[JEE(Main) 2019 Online (12-01-19), 4/120]**

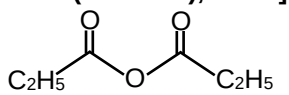
(1) HCHO + $PhCH(CH_3)CH_2Mg$ (2) $PhCOCH_2CH_3 + CH_3MgX$
(3) $PhCOCH_3 + CH_3CH_3MgX$ (4) $CH_3CH_2COCH_3 + PhMgX$

6. The increasing order of the reactivity of the following with $LiAlH_4$ is:
[JEE(Main) 2019 Online (12-01-19), 4/120]

(A) 

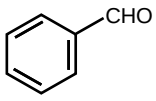
(B) 

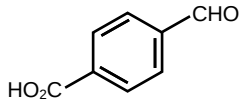
(C) 

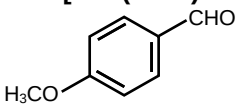
(D) 

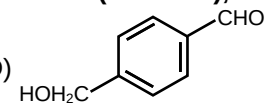
(1) (A) < (B) < (C) < (D) (2) (A) < (B) < (D) < (C)
(3) (B) < (A) < (D) < (C) (4) (B) < (A) < (C) < (D)

7. The aldehydes which will not form Grignard product with the equivalent Grignard reagents are:
[JEE(Main) 2019 Online (12-01-19), 4/120]

(A) 

(B) 

(C) 

(D) 

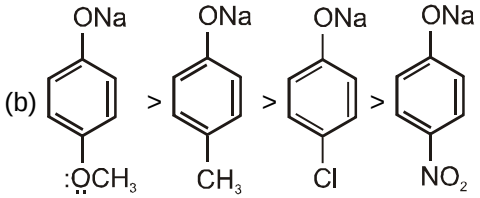
(1) (B), (D) (2) (B), (C) (3) (C), (D) (4) (B), (C), (D)

Answers

EXERCISE – 1

PART – I

A-1. b, c, d, e, f, h **A-2.** a, c, d

A-3. (a) $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > H_2O$ (b) 

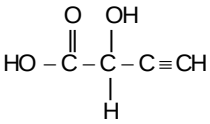
A-4. **Ambident nucleophile:** The species which have more than one nucleophilic site for reaction are called ambident nucleophiles.
For example, cyanide ion :

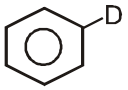
$: \bar{C} \equiv N : \rightleftharpoons :C = N:^{-}$

$CH_3Br + AgCN \longrightarrow CH_3NC + AgBr$

$CH_3Br + KCN \longrightarrow CH_3CN + KBr$

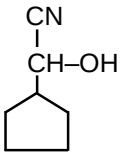
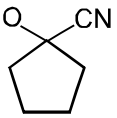
A-5. I > II > IV > III **A-6.** Protic solvent (c, f, i) ; Aprotic solvent (a, b, d, e, g, h)

B-1. (b), (c) **B-2.** (a), (b) **B-3.** (b), (c) **B-4.** 

B-5. (a) $CH_3 - D + Mg(OD)(I)$ (b) $CH_3 - CH(CH_3) - CH_3 + Mg(I)(C \equiv C - Ph)$ (c) 

C-1. III > II > I > IV

C-2. Cyanohydrin is formed by nucleophilic attack on carbonyl group (C=O), 2,2,6-trimethylcyclohexanone has more steric crowding due to three methyl groups.

C-3. (a) $Ph-C(OH)(CN)-CH_3$ (b) $CH_3-CH_2-CH(OH)-Ph$ (c)  (d) 

C-4. (i) $CH_3 - C(=O) - CH_3 + CH_3 - MgBr \longrightarrow [CH_3 - C(CH_3)(CH_3) - OMgBr] \xrightarrow{H_2O} CH_3 - C(CH_3)(CH_3) - OH + Mg(OH)(Br)$

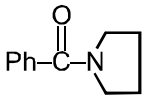
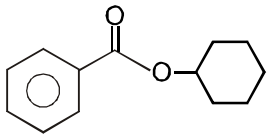
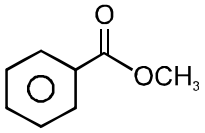
2-Methyl-2-propanol

(ii) $CH_3 - CH_2 - MgCl + H - C(=O) - H \longrightarrow [CH_3CH_2 - C(H)(H) - OMgCl] \xrightarrow{H_2O} CH_3CH_2CH_2OH + Mg(Cl)(OH)$

C-5. (a) $Ph-C(D)(OH)-CH_3$ (b) $Ph-C(H)(OD)-CH_3$ (c) $Ph-C(D)(OH)-CH_3$ (d) $Ph-C(D)(OD)-CH_3$

D-1. 2 (a, d)

D-2. (a) $CH_3-\overset{O}{\overset{\|}{C}}-OCH_3 + HCl$ (b) $CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3CH_2OH$

D-3. (a)  (b)  (c) 

D-4. (A) = PhCOOH, (B) = $Ph^{18}OH$

D-5. (a) $CH_3-\underset{OH}{CH}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH$ (b) $CH_2(OH)-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_2-COOH$

PART - II

A-1.	(C)	**A-2.**	(A)	**A-3.**	(A)	**A-4.**	(D)	**A-5.**	(A)
A-6.	(B)	**A-7.**	(A)	**B-1.**	(C)	**B-2.**	(B)	**B-3.**	(C)
B-4.	(C)	**B-5.**	(A)	**B-6.**	(C)	**B-7.**	(B)	**C-1.**	(B)
C-2.	(A)	**C-3.**	(D)	**C-4.**	(A)	**C-5.**	(B)	**C-6.**	(A)
D-1.	(C)	**D-2.**	(C)	**D-3.**	(C)	**D-4.**	(B)		

PART - III

1. (B) **2.** (A) - p, r, s ; (B) - r, s ; (C) - r, s ; (D) - p, q

EXERCISE - 2

PART - I

1.	(C)	**2.**	(A)	**3.**	(D)	**4.**	(D)	**5.**	(C)
6.	(C)	**7.**	(B)	**8.**	(A)	**9.**	(B)	**10.**	(B)
11.	(B)	**12.**	(C)						

PART - II

1.	4 (III, IV, V, VI)	**2.**	75	**3.**	4	**4.**	88 gm.	**5.**	3
6.	4 (b, d, e, g)	**7.**	3	**8.**	88				

PART - III

1.	(AD)	**2.**	(ABC)	**3.**	(AB)	**4.**	(BD)	**5.**	(ABCD)
6.	(AD)	**7.**	(BD)	**8.**	(ABC)	**9.**	(ABD)	**10.**	(ABC)

PART - IV

1.	(B)	**2.**	(D)	**3.**	(C)	**4.**	(A)	**5.**	(B)
6.	(C)	**7.**	(D)	**8.**	(B)				

EXERCISE - 3

PART - I

1. Structure of Bombykol is $CH_3–CH_2–CH_2–CH=CH–CH=CH(CH_2)_8CH_2OH$

2. (A) **3.** (C) **4.** (B)

5. (A) – (p, q, s) ; (B) – (q) ; (C) – (q, r, s) ; (D) – (q, r) **6.** (A)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1. (3) **2.** (1) **3.** (1) **4.** (4) **5.** (2)

6. (3) **7.** (3) **8.** (4) **9.** (2)

JEE(MAIN) ONLINE PROBLEMS

1. (2) **2.** (4) **3.** (4) **4.** (3) **5.** (1)

6. (2) **7.** (1)