

ORGANIC REACTION MECHANISMS-I

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JEE(Advanced) Syllabus

Aldehydes and Ketones : Nucleophilic addition reactions (Grignard addition).

Carboxylic acids: Formation of esters, acid chlorides, amides and ester hydrolysis.

JEE(Main) Syllabus

Aldehydes and Ketones : Nature of carbonyl group, Nucleophilic addition to $>C=O$ group, relative reactivities of aldehydes and ketones, Important reactions such as Nucleophilic addition reactions (addition of HCN and Grignard reagent).

Carboxylic Acids : Chemical properties.



Organic Reaction Mechanisms-I

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

An organic reaction can be represented as



Types of bond dissociation :

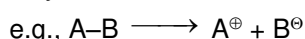
All reactions are initiated with bond dissociation. There are two types of bond dissociation.

- (a) **Homolytic bond dissociation** : A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.



A homolytic bond dissociation generates radicals.

- (b) **Heterolytic bond dissociation** : A bond dissociation in which a bond pair electron is shifted to one atom only.



A heterolytic bond dissociation always generate a cation and an anion.

Types of reagents :

A reagent generates three type of attacking species. Which are :

- (a) Electrophiles (b) Nucleophiles (c) Radicals

- (a) **Electrophiles** : Electrophiles are electron deficient species. Which can accept a pair of electron.

e.g. H^+ , Cl^+ , Br^+ , NO_2^+ , CH_3^+ (positively charged species), PCl_5 , SO_2 , SO_3 , BH_3 (species with vacant orbital at central atom) carbenes etc.

- (b) **Nucleophiles** : Nucleophiles are electron rich species having atleast one unshared pair of electron. It can be neutral or negatively charged. It is always a lewis base.

e.g. CN^- , OH^- , Br^- , I^- , NH_3 , H_2O etc.

- (c) **Radicals** : It is an electron deficient species with odd electron around an atom.

e.g. $\dot{\text{C}}\text{H}_3$, $\text{C}_2\text{H}_5^\bullet$, $\text{C}_2\text{H}_5\text{O}^\bullet$, $\text{CH}_3\text{COO}^\bullet$, X^\bullet etc.

Nucleophilicity :

The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity.

- (i) **Criteria for Nucleophilicity** :

1. The factors which increases e^- density at donor atom increases nucleophilicity.
2. The more polarisable donor atom is the better nucleophile. Therefore size of donor atom increases nucleophilicity also increases.

- (ii) **Periodicity** :

Nucleophilicity decreases from left to right in a period.



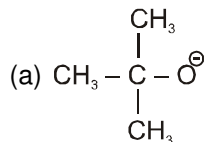
\therefore In a group, nucleophilicity increases from top to bottom because size of donor atom increases but basicity decreases from top to bottom.

Acidic strength : $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

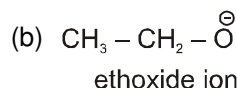
Basic strength : $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

Nucleophilicity : $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

- (iii) **Nucleophilicity of halogenes in polar aprotic solvents** : $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

**(iv) Steric effects on nucleophilicity**

t-butoxide ion

**Note :** Because (a) can not approach to carbon atom easily.

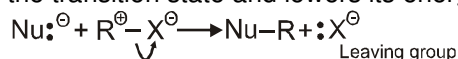
So, nucleophilicity order is : (b) > (a) and basicity order is : (a) > (b)

Ambident nucleophile :

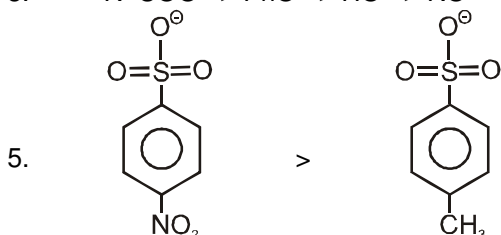
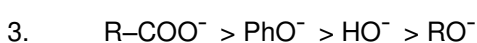
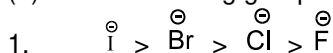
The species which have more than one nucleophilic site for reaction are called ambident nucleophiles.

Example : $\text{CN}^\ominus, \text{NO}_2^\ominus, \text{O}^\ominus - \text{CH} = \text{S}$ **Comparison between Nucleophilicity & Basicity :**

	Nucleophilicity	Basicity	Remarks
1	$\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$	$\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$	If donor atoms belong to same period, then nucleophilicity and basicity order is same
2	$\text{SiH}_3^- > \text{PH}_2^- > \text{SH}^- > \text{Cl}^-$	$\text{SiH}_3^- > \text{PH}_2^- > \text{SH}^- > \text{Cl}^-$	" " "
3	$\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$	$\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$	Down the group nucleophilicity increases while basicity decreases.
4	$\text{OH}^- < \text{SH}^-$	$\text{OH}^- > \text{SH}^-$	" " " "
5	$\text{RO}^- < \text{RS}^-$	$\text{RO}^- > \text{RS}^-$	" " "
6	$\text{RO}^- > \text{HO}^-$	Same	If donor atom is same, then generally nucleophilicity and basicity order is also same.
7	$\text{RCOO}^- < \text{PhO}^- < \text{HO}^- < \text{RO}^-$	Same	" " "
8	$\text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}^\ominus > \text{R}-\overset{\text{O}}{\underset{\text{O}}{\text{S}}}-\text{O}^\ominus$ Tetrahedral (more extensive resonance) [d π -p π bonds]	Same	" " "
9	$\text{HO}^- > \text{H}_2\text{O}$	Same	
10	$\text{NH}_2^- > \text{NH}_3$	Same	
11	$\text{CF}_3\text{SO}_3^- < \text{PhCOO}^- < \text{PhO}^- < \text{RO}^-$	Same	

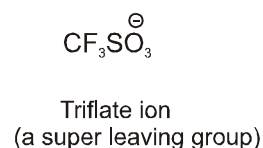
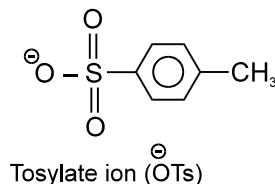
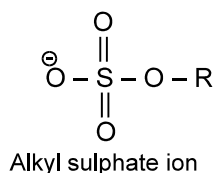
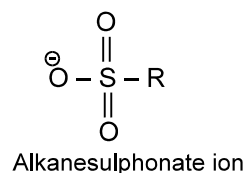
Leaving group ability/Nucleofugality :**Weaker bases are always good leaving groups / nucleofuse.** A good leaving group always stabilize the transition state and lowers its energy of activation hence increases the rate of the reaction.

(a) Order of leaving group ability.

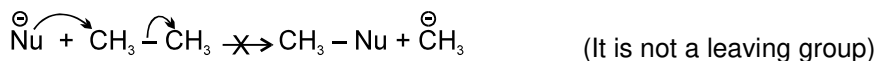




6. Other good leaving groups are



Note : (i) Strong bases rarely act as leaving group \rightarrow



(ii) The leaving group should have lower bond energy with carbon.

(iii) Negative charge should be more stable either by dispersal or delocalization.

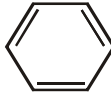

Types of solvents :

(a) Non polar solvents

(b) Polar solvents (i) polar protic (ii) polar aprotic

(i) **Polar protic** : A polar solvent which has acidic hydrogen.

(ii) **Polar aprotic** : A polar solvent which does not have acidic hydrogen.

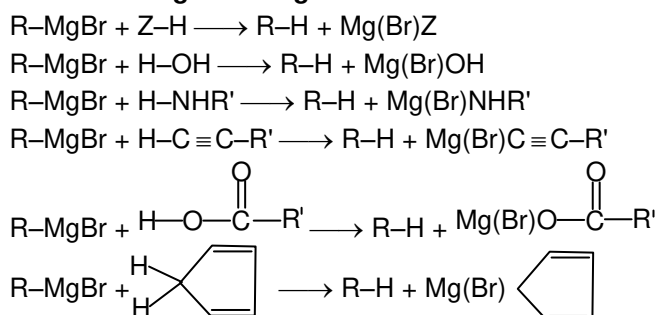
	Solvents	Polar	Protic	Aprotic	Remarks
1.	H ₂ O	✓	✓	—	Polar protic solvent
2.	CH ₃ OH	✓	✓	—	Polar protic solvent
3.	CH ₃ CH ₂ OH	✓	✓	—	Polar protic solvent
4.	H-COOH	✓	✓	—	Polar protic solvent
5.	CH ₃ -COOH	✓	✓	—	Polar protic solvent
6.	NH ₃	✓	✓	—	Polar protic solvent
7.	$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ (acetone)	✓	x	✓	Polar aprotic solvent
8.	$\begin{array}{c} \text{CH}_3-\text{S}-\text{CH}_3 \\ \parallel \\ \text{O} \end{array}$ Dimethyl sulphoxide	✓	x	✓	Polar aprotic solvent
9.	$\begin{array}{c} \text{H}-\text{C}-\text{N}(\text{CH}_3)_2 \\ \parallel \\ \text{O} \end{array}$ Dimethyl formamide	✓	x	✓	Polar aprotic solvent
10.	$\begin{array}{c} \text{CH}_3-\text{C}-\text{N}(\text{CH}_3)_2 \\ \parallel \\ \text{O} \end{array}$ Dimethyl acetamide	✓	x	✓	Polar aprotic solvent
11.		x	x	✓	Non-polar solvent
12.		x	x	✓	Non-polar solvent
13.	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃	x	x	✓	Non-polar solvent



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

Compounds having reactive or acidic hydrogen gives acid base reaction.

- (i) **Reaction with metals :** $\text{CH}_3\text{COOH} + \text{Na} \longrightarrow \text{CH}_3\text{COONa} + \frac{1}{2} \text{H}_2$
 (ii) **Reaction with alkalis :** $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
 (iii) **Reaction with bicarbonates :** $\text{CH}_3\text{COOH} + \text{NaHCO}_3 \longrightarrow \text{CH}_3\text{COONa} + \text{CO}_2 \uparrow + \text{H}_2\text{O}$
 (iv) **Reaction with NaH :** $\text{CH}_3\text{COOH} + \text{NaH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2$
 (v) **Reaction with Grignard reagent :**

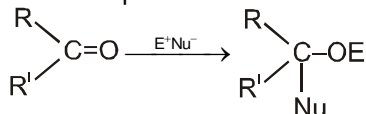


Section (C) : Nucleophilic addition reactions of carbonyl compounds

It is a characteristic reaction of carbonyl compounds (aldehydes and ketones).

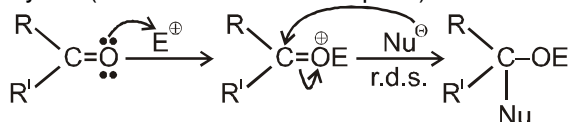
This reaction involves addition of a nucleophile and an electrophile across the (C=O) double bond.

The general nucleophilic addition reaction can be represented as follows :

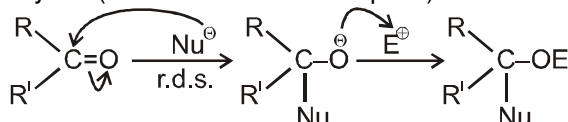


The mechanism can be carried out in following two manners.

- (a) Acid catalysed (first attack is of electrophile)



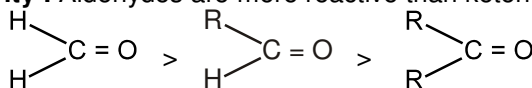
- (b) Base catalysed (first attack is of nucleophile)



Acid catalysed nucleophilic addition is generally faster than base catalysed.

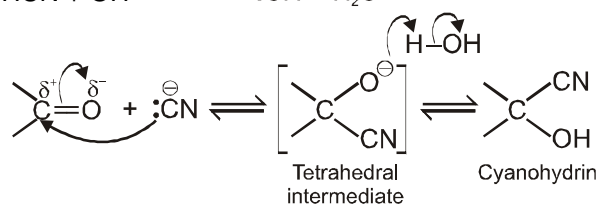
The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, hence it is relatively unhindered and open to attack from either face of the double bond.

Reactivity : Aldehydes are more reactive than ketones in nucleophilic addition reactions.

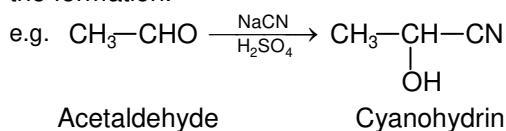
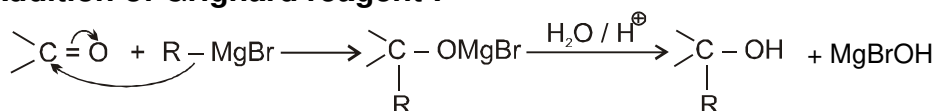


There are two factors which influence the reactivity of ketone and aldehyde.

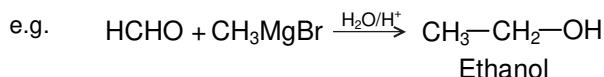
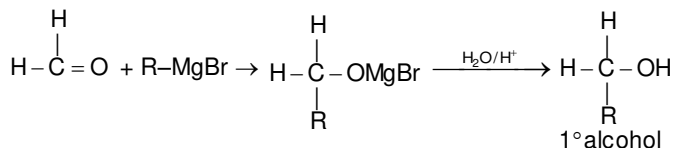
- (i) Inductive effect (ii) steric factor
 (i) + I effect of alkyl group decreases the amount of charge on C^+ (C^+-O^-) in ketones.
 (ii) Steric effect also causes the less reactivity of carbonyl group.

**(i) Addition of hydrogen cyanide (HCN)**

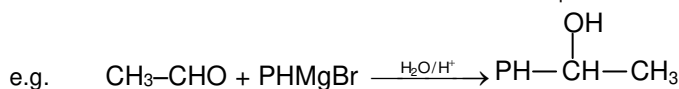
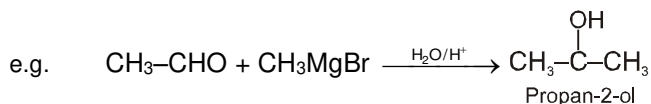
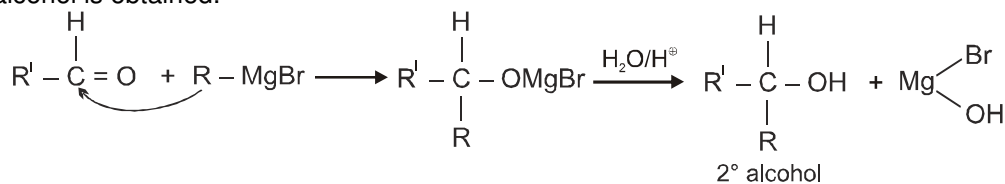
- Note :** (i) Addition of HCN over aldehyde and ketones gives cyanohydrin.
 (ii) Cyanohydrin on acid hydrolysis gives α -hydroxy acid.
 (iii) Cyanohydrin on treating with $\text{NH}_3(l)$ followed by acid hydrolysis gives α -amino acid.
 (iv) In case of ketone cyanohydrin formation is reversible due to bulky groups of ketone which hinder the formation.

**(ii) Addition of Grignard reagent :**

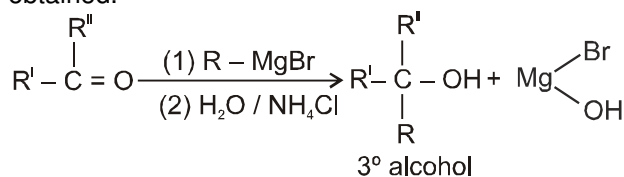
- (a)** When formaldehyde is treated with Grignard reagent followed by acid hydrolysis primary alcohol is obtained.

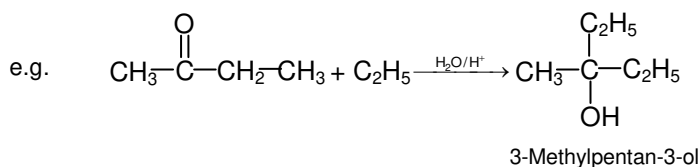


- (b)** When aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis 2° alcohol is obtained.

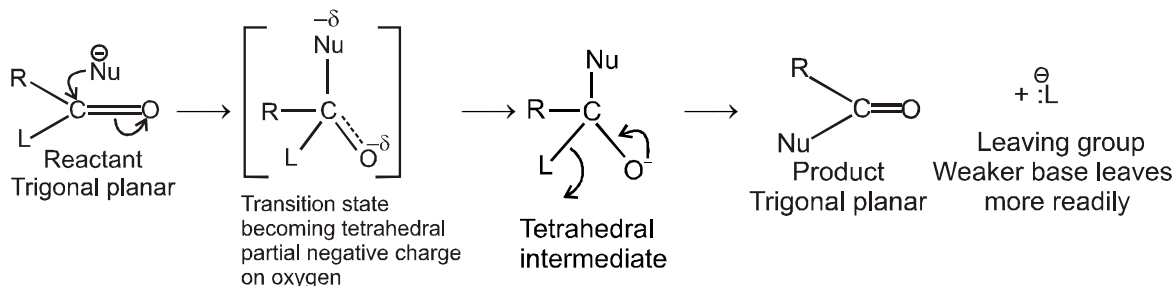


- (c)** When ketone is treated with Grignard reagent followed by acid hydrolysis 3° alcohol is obtained.



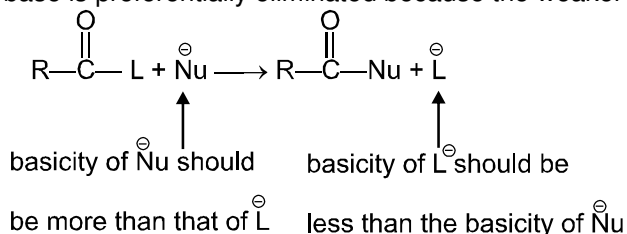
Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate (S_N2Th)

Characteristic reaction of acid and its derivatives (acid halide, anhydride, ester and amide) is S_N2Th . Nucleophilic acyl substitution usually takes place by an **addition-elimination** mechanism. The incoming nucleophile adds to the carbonyl to form a tetrasubstituted intermediate with a tetrahedral carbon.



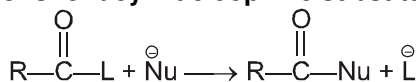
The tetrahedral intermediate formed, when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative, is not stable and can not be isolated.

A pair of nonbonding electrons on the oxygen reforms the π bond, and either L^\ominus or Nu^\ominus is eliminated with its bonding electrons. Whether L^\ominus or Nu^\ominus is eliminated depends on their relative basicities. The weaker base is preferentially eliminated because the weaker base is the better leaving group.

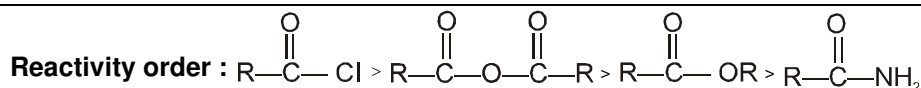


Thus carboxylic acid derivatives will undergo a nucleophilic acyl substitution reaction provided that the incoming nucleophile is a stronger base than the group that is to be replaced. If the incoming nucleophile and the group attached to acyl group in the starting material have similar basicities, the tetrahedral intermediate can expect either group with similar ease. A mixture of starting material and substitution product will result.

Conditions for acyl nucleophilic substitution reactions :



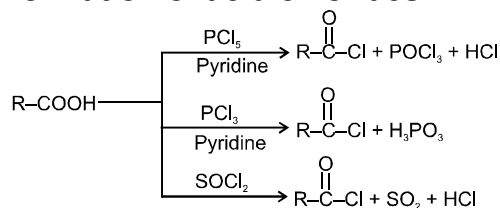
- (i) L^\ominus must be better leaving group than Nu^\ominus , i.e., basicity of Nu^\ominus should be more than that of L^\ominus .
- (ii) Nu^\ominus must be a strong enough nucleophilic to attack $RCOL$.
- (iii) Carbonyl carbon must be enough electrophilic to react with Nu^\ominus .





(a) **S_N2Th Reaction of carboxylic acid :**

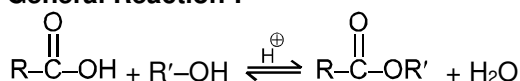
(i) **Formation of acid chlorides :**



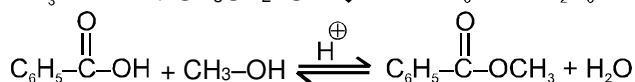
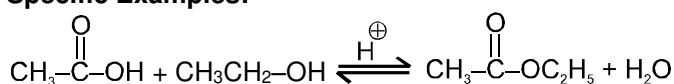
(ii) **Fisher's Esterification :**

Carboxylic acids reacts with alcohol to form esters through a condensation reaction known as esterification.

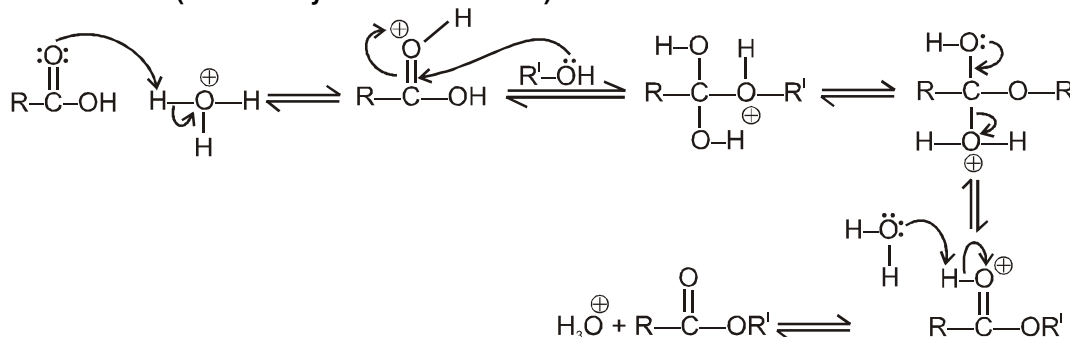
General Reaction :



Specific Examples:

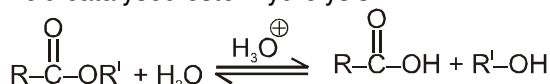


Mechanism : (Acid catalysed esterification)



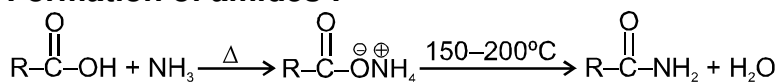
If we follow the forward reactions in this mechanism, we have the mechanism for the acid catalysed esterification of an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester.

Acid catalysed ester hydrolysis.

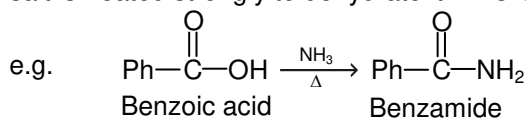


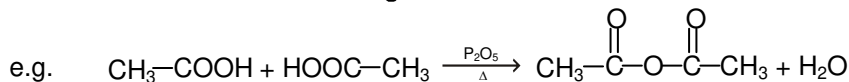
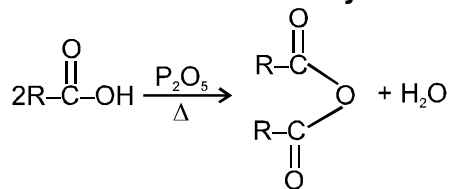
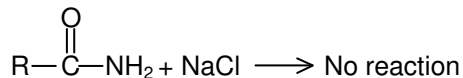
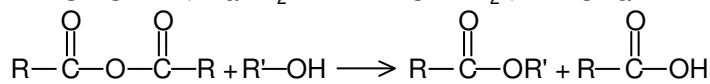
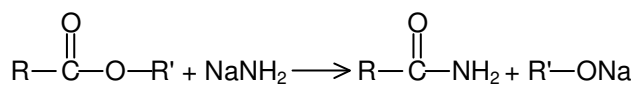
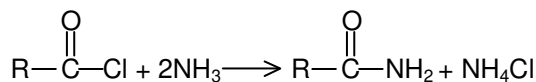
Which result we obtain will depend on the conditions we choose. If we want to esterify an acid, we use an excess of the alcohol and, if possible remove the water as it is formed. If we want to hydrolyse an ester, we use a large excess of water that is we reflux the ester with dilute aqueous HCl or dilute aqueous H₂SO₄.

(iii) **Formation of amides :**

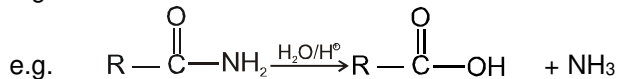
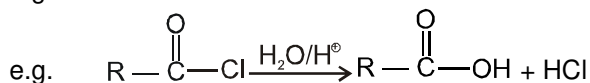
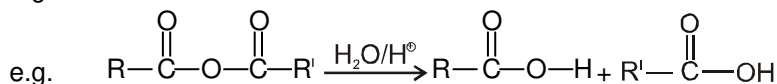
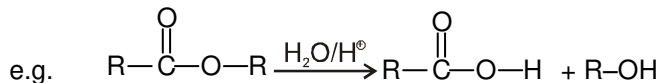
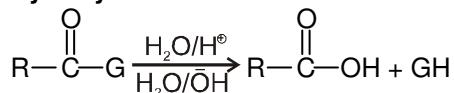


In fact amides can not be prepared from carboxylic acids and amines unless the ammonium salt is heated strongly to dehydrate it. This is not usually a good method of preparing amides.



**(iv) Formation of acid anhydride :****(b) S_N2Th Reaction of acid derivatives :****(i) Conversion of acid derivatives to other acid derivatives.**

Note: An S_N2Th reaction is feasible when nucleophile is more basic than the leaving group.

(ii) Hydrolysis of acid derivatives :

Note: Hydrolysis of amides and esters are not possible in neutral medium.



Exercise-1

Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

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

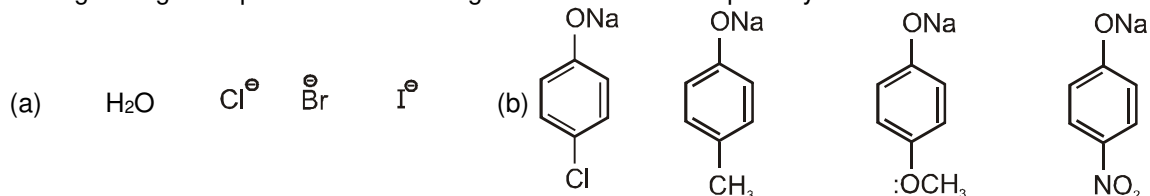
A-1. Which of the followings are electrophile ?

- (a) CN^- (b) H^+ (c) Br^+ (d) AlCl_3
 (e) BH_3 (f) $\text{CH}_3 - \overset{\oplus}{\text{C}} = \text{O}$ (g) NH_3 (h) $\overset{\oplus}{\text{NO}}_2$

A-2. Which of the followings are nucleophile ?

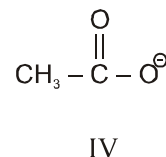
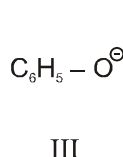
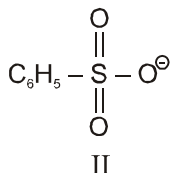
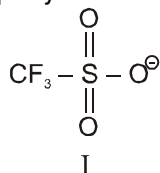
- (a) HS^- (b) BF_3 (c) $\text{C}_2\text{H}_5\text{OH}$ (d) $(\text{CH}_3)_3\ddot{\text{N}}$ (e) $:\text{CH}_2$

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

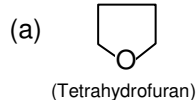


A-4. Define ambident nucleophile with an example :

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

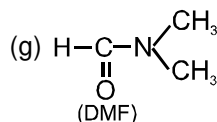
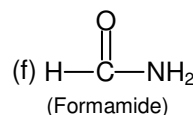
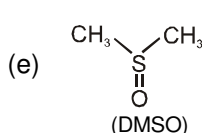
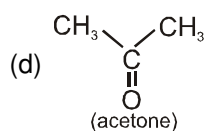


A-6. Label each of the following solvent as Protic or Aprotic



(b) Acetonitrile

(c) Acetic acid

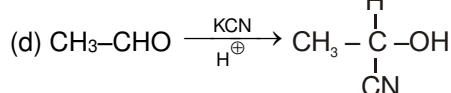
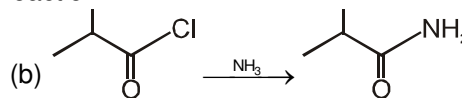
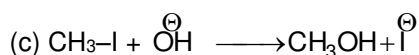
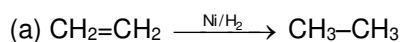


(h) Cyclohexane

(i) Amonia

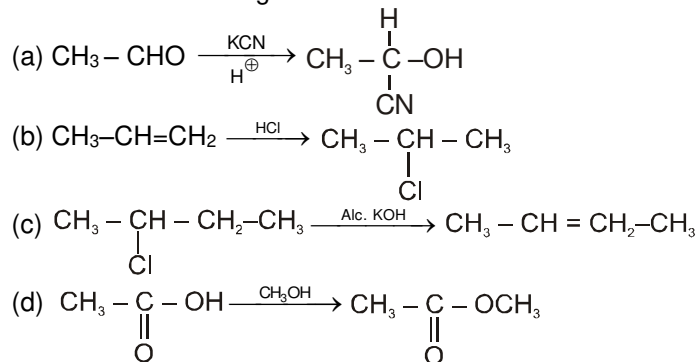
Section (B) : Types of organic reactions and reactions of acidic hydrogen

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

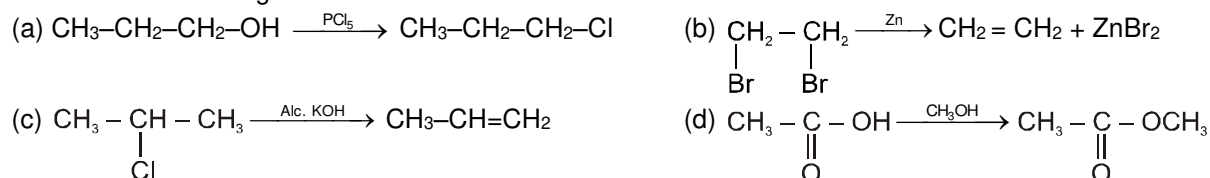




B-2. Which of the following reaction are addition reaction ?



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

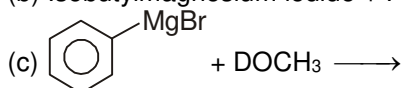


B-4. An organic compound which have molecular formula $\text{C}_4\text{H}_8\text{O}_3$, gives 3 moles of gas on treatment with methyl magnesium bromide. Give structure of the compound.

B-5. Predict the product of the following reactions

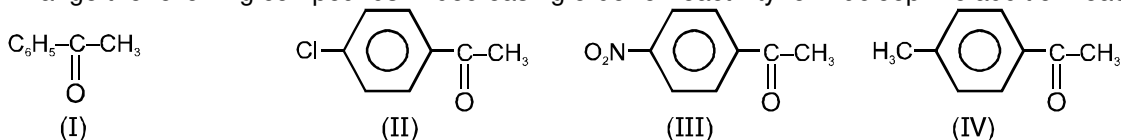
(a) Methylmagnesium iodide + $\text{D}_2\text{O} \longrightarrow ?$

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



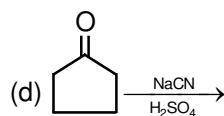
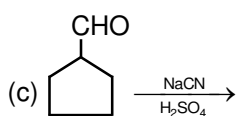
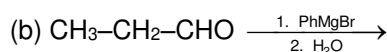
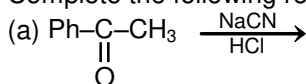
Section (C) : Nucleophilic addition reactions of carbonyl compounds

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



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

C-3. Complete the following reactions.



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

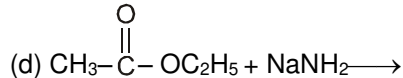
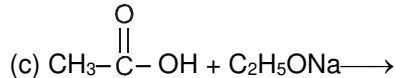
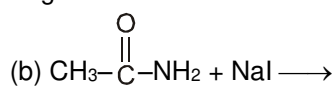
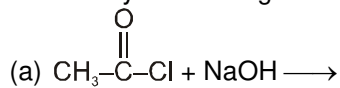
(c) NaBD_4 followed by EtOH

(d) NaBD_4 followed by EtOD

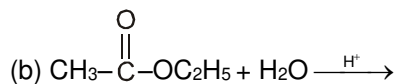
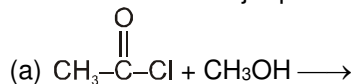


Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate (S_N2Th)

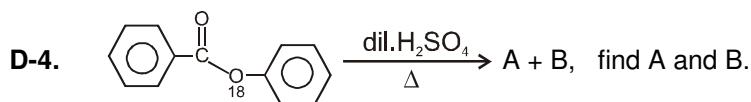
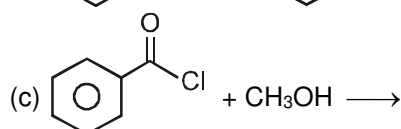
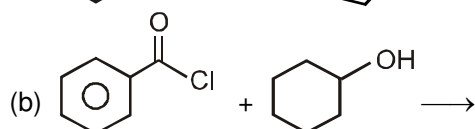
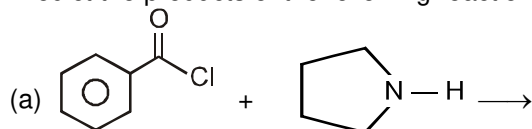
D-1. How many reactions given below are proceed through S_N2Th mechanism ?



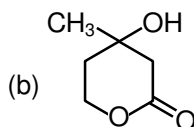
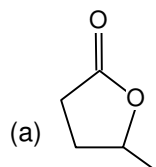
D-2. What will be the major products of the following reactions ?



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



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



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) H₂O (B) OH⁻ (C) NO₂⁺ (D) None

A-2. Which of the following is not a nucleophile ?

- (A) AlCl₃ (B) (CH₃)₂NH (C) C₂H₅OH (D) H₂O

A-3. Which one of the following has maximum nucleophilicity ?

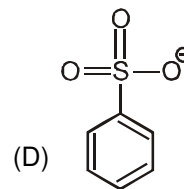
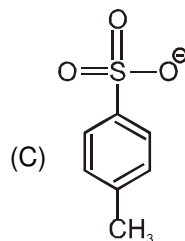
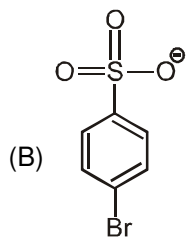
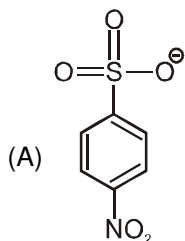
- (A) CH₃S[⊖] (B) C₆H₅O[⊖] (C) Et₃N (D) F[⊖]

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-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

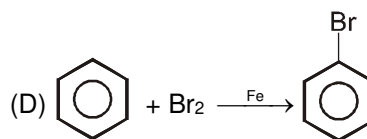
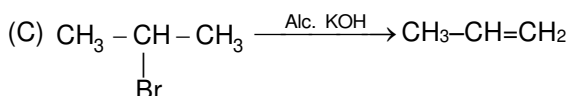
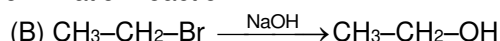
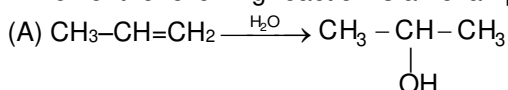
(B) NH₃

(C) H₂O

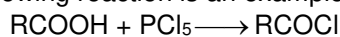
(D) CH₃COOH

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

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



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



(A) Acid-base reaction

(B) Substitution reaction

(C) Addition reaction

(D) Elimination reaction

B-3. The following reaction is an example of $\text{CH}_3\text{--}\underset{\text{CH}_3}{\text{C}}\text{=CH}_2 \xrightarrow[\text{H}^+]{\text{H}_2\text{O}} \text{CH}_3\text{--}\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}\text{--CH}_3$

(A) Acid-base reaction

(B) Substitution reaction

(C) Addition reaction

(D) Elimination reaction

B-4. $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \longrightarrow ?$

(A) $\text{C}_6\text{H}_5\text{COOMgI}$

(B) CH₄

(C) Both A & B

(D) none

B-5. $(\text{CH}_3)_3\text{CMgCl}$ on reaction with D₂O produces :

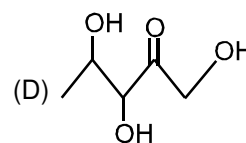
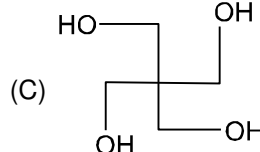
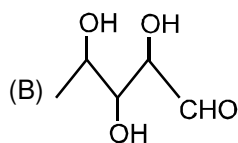
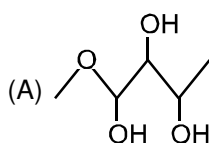
(A) $(\text{CH}_3)_3\text{CD}$

(B) $(\text{CH}_3)_3\text{COD}$

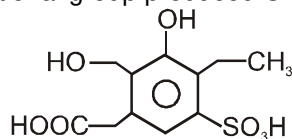
(C) $(\text{CD}_3)_3\text{CD}$

(D) $(\text{CD}_3)_3\text{COD}$

B-6. A compound X (C₅H₁₂O₄) upon treatment with CH₃MgX gives 4 mole of methane. Identify the structure of (X).



B-7. How many functional group produced CH₄ gas by the reaction of compound (I) with CH₃MgBr.



(A) 3

(B) 4

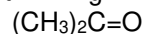
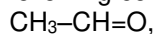
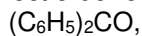
(C) 5

(D) 6



Section (C) : Nucleophilic addition reactions of carbonyl compounds

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



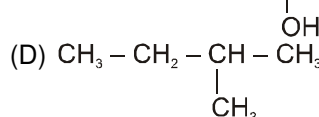
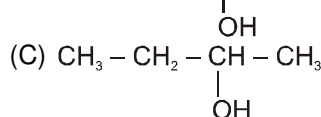
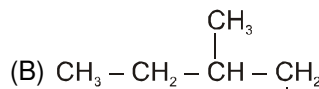
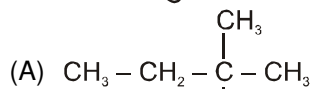
(1)

(2)

(3)

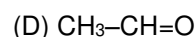
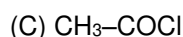
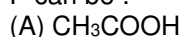
(A) $1 > 2 > 3$ (B) $2 > 3 > 1$ (C) $3 > 2 > 1$ (D) $1 > 3 > 2$

C-2. $\text{CH}_3\text{-CH}_2\text{-C(=O)-CH}_3 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) CH}_3\text{MgBr}}$ Product is :

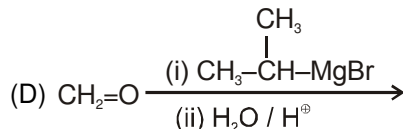
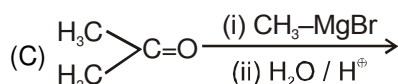
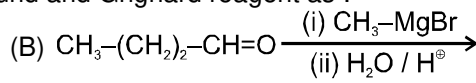
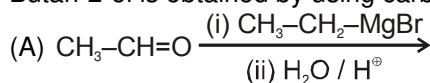


C-3. $\text{P} \xrightarrow{\text{PhMgBr}} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{-CH(OH)-Ph (d+l)}$

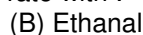
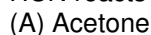
P can be :



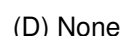
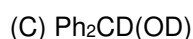
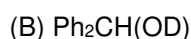
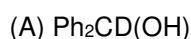
C-4. Butan-2-ol is obtained by using carbonyl compound and Grignard reagent as :



C-5. HCN reacts with fastest rate with :

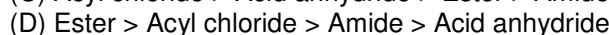
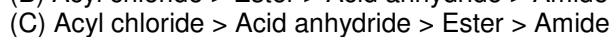
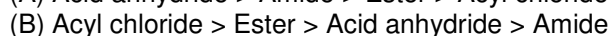
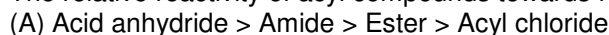


C-6. The product of the reaction $\text{Ph}_2\text{C=O} \xrightarrow[\text{H}_3\text{O}^+]{\text{LiAlD}_4}$ is

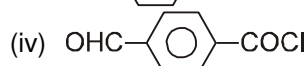
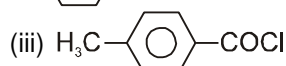
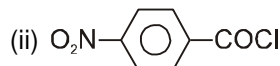
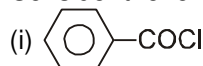


Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate ($\text{S}_{\text{N}}2\text{Th}$)

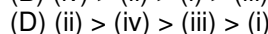
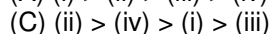
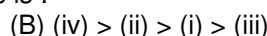
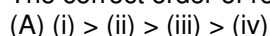
D-1. The relative reactivity of acyl compounds towards nucleophilic substitution are in the order of :



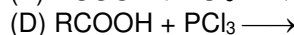
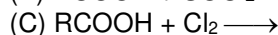
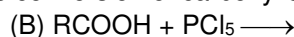
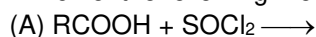
D-2. Consider the following compounds :



The correct order of reactivity towards hydrolysis is :

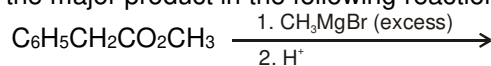


D-3. Which of the following method is not used for the conversion of carboxylic acid into acid halide ?





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



- (A) $\text{Ph}-\text{CH}_2-\text{C}(=\text{O})-\text{CH}_3$ (B) $\text{C}_6\text{H}_5-\text{CH}_2-\text{C}(\text{OH})(\text{CH}_3)_2$ (C) $\text{Ph}-\text{C}(\text{OH})(\text{CH}_3)-\text{CH}_2-\text{CH}_3$ (D) $\text{Ph}-\text{C}(\text{OH})(\text{CH}_3)-\text{CH}_3$

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)	$\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_2\text{O}}$	(1)	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$
(Q)	$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_3 + \text{NaBH}_4 \xrightarrow{\text{EtOH}}$	(2)	$\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_3$
(R)	$\text{CH}_3-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3 + \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_2\text{O}}$	(3)	$\text{CH}_3-\text{C}(\text{OH})(\text{CH}_3)-\text{CH}_2-\text{CH}_3$
(S)	$\text{CH}_3-\text{CH}_2-\text{C}(=\text{O})-\text{OCH}_3 + \text{LiAlH}_4 \xrightarrow{\text{H}_2\text{O}}$	(4)	$\text{CH}_3-\text{C}(\text{OH})(\text{CH}_3)_2$

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)	$\text{CF}_3\text{SO}_3^\ominus$	(q)	Strong base
(C)	H_2O	(r)	Good leaving group
(D)	$\text{CH}_3\text{CH}_2\text{O}^\ominus$	(s)	Weak base

Exercise-2

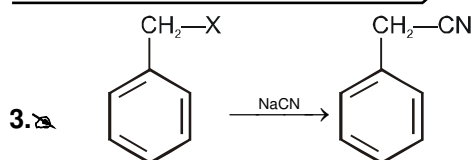
Marked questions are recommended for Revision.

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) CH_3^\ominus (B) NH_2^\ominus (C) $\text{CH}_3\text{O}^\ominus$ (D) $\text{CH}_3-\text{C}(\text{CH}_3)_2-\text{O}^\ominus$



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

- (A) $-\text{OH}$ (B) $-\text{NH}_2$ (C) $-\text{SO}_2\text{OCH}_3$ (D) $-\text{O}-\text{SO}_2\text{CH}_3$

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

- (A) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{CH}_3\text{COO}^- < \text{OH}^-$ (B) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{O}^- < \text{OH}^-$
 (C) $\text{C}_6\text{H}_5\text{O}^- < \text{CH}_3\text{COO}^- < \text{CH}_3\text{O}^- < \text{OH}^-$ (D) $\text{CH}_3\text{COO}^- < \text{C}_6\text{H}_5\text{O}^- < \text{OH}^- < \text{CH}_3\text{O}^-$

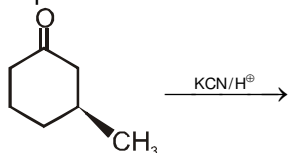
5. Which of the following reactions is not feasible ?

- (A) $\text{PhSO}_3\text{H} + \text{NaHCO}_3 \longrightarrow$ (B) $\text{Ph-OH} + \text{NaNH}_2 \longrightarrow$
 (C) $\text{CH}_3\text{-NH}_2 + \text{NaOH} \longrightarrow$ (D) $\text{Ph-C}\equiv\text{CH} + \text{NaH} \longrightarrow$

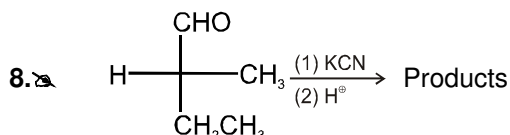
6. Give the decreasing order of nucleophilic addition reaction of the following :

- (i) HCHO (ii) PhCHO
 (iii) Chloral ($\text{Cl}_3\text{C-CH=O}$) (iv) Acetophenone
 (A) $\text{iii} > \text{i} > \text{ii} > \text{iv}$ (B) $\text{iv} > \text{ii} > \text{i} > \text{iii}$ (C) $\text{i} > \text{iii} > \text{ii} > \text{iv}$ (D) $\text{iii} > \text{i} > \text{iv} > \text{ii}$

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



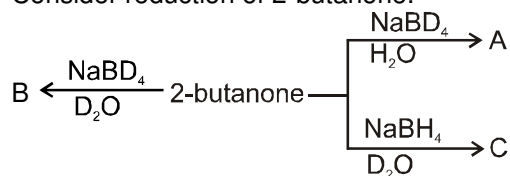
- (A) 1 (B) 2 (C) 3 (D) 4



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.

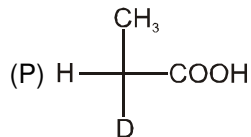
- (A) $\text{CH}_3\text{CHCH}_2\text{CH}_3$ in all cases
 (B)
 (C) $\text{CH}_3\text{CCH}_2\text{CH}_3$ in all case
 (D)



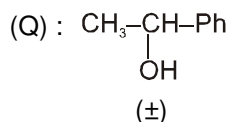
10. Which of the following is correct order of esterification of following acids with CH_3OH :
 HCOOH , CH_3COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$

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

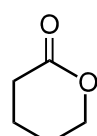
11. Esterification of the acid (P) with the alcohol (Q) will gives.

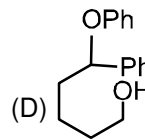
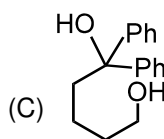
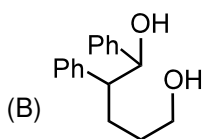
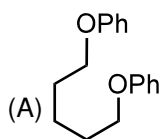


(R- configuration)
 (A) only one enantiomer
 (C) a mixture of enantiomer



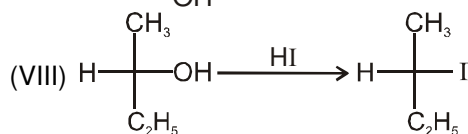
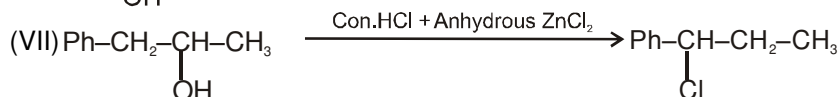
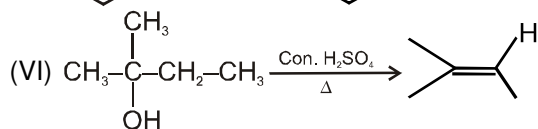
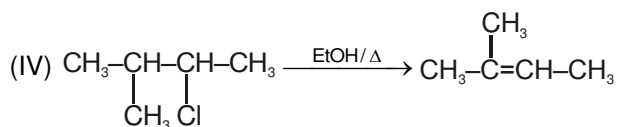
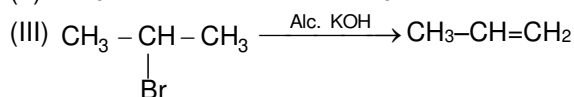
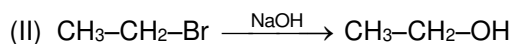
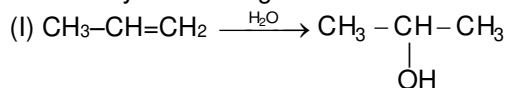
(B) a mixture of diastereomer
 (D) only one fraction on fractional distillation

12.  $\xrightarrow[\text{(2) H}_2\text{O}]{\text{(1) excess PhMgBr}}$ X, X is



PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

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





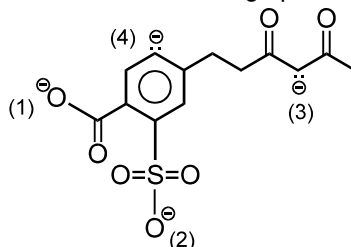
2. Among the following X is the number of electrophiles and Y is the number of nucleophiles. Report your answer as

X	Y
---	---

.

- | | | | |
|---------------------------------|----------------------------|--|----------------------------|
| (i) CH_3^\oplus | (ii) I^\ominus | (iii) NO_2^\oplus | (iv) CH_3^\ominus |
| (v) $\ddot{\text{N}}\text{H}_3$ | (vi) Br^\oplus | (vii) Cl^\ominus | (viii) H^+ |
| (ix) AlCl_3 | (x) CH_3OH | (xi) $\text{CH}_3 - \overset{\oplus}{\text{C}} = \text{O}$ | (xii) BH_3 |

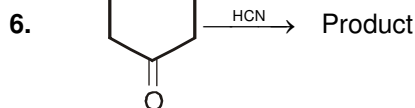
3. Which is the strongest nucleophilic site in the following species ?



4. An alcohol (A), 0.22 g of this alcohol liberates 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 $\text{C}_5\text{H}_{12}\text{O}$ after reduction with LiAlH_4 ?
6. How many compounds out of following will give secondary alcohol on treatment with Grignard reagent ?
 (a) $\text{Ph}-\text{CO}-\text{CH}_3$ (b) $\text{Ph}-\text{CHO}$ (c) HCHO (d) $\text{CH}_3\text{CH}_2\text{CHO}$
 (e) CH_3CHO (f) $\text{Ph}-\text{CO}-\text{Ph}$ (g) HCOCl (h) $\text{CH}_3\text{COOC}_2\text{H}_5$
7. What is the maximum number of moles of CH_3MgCl that can be consumed by one mole of phosgene ?
8. Find the molecular weight of a sweet smelling compound which react with LAH to gives only ethanol.

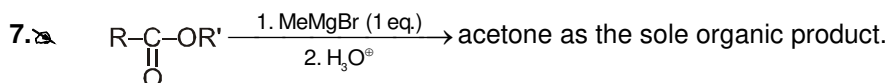
PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Electrophiles are
 (A) Electron deficient 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) $\text{C}_6\text{H}_5\text{SO}_3^\ominus > \text{C}_6\text{H}_5\text{COO}^\ominus$ (B) $\text{CF}_3\text{SO}_3^\ominus > \text{CCl}_3\text{SO}_3^\ominus$
 (C) $\text{CN}^\ominus > \text{I}^\ominus$ (D) $\text{NH}_2^\ominus > \text{OH}^\ominus$
4. Which of the following reactions yield benzene ?
 (A) $\text{PhMgBr} + \text{CH}_3-\text{Br}$ (B) $\text{PhMgBr} + \text{H}_2\text{O}$
 (C) $\text{PhBr} + \text{H}_2\text{O}$ (D) $\text{PhMgBr} + \text{CH}_3-\text{C}\equiv\text{CH}$
5. Which of the following liberate hydrogen gas with NaH .
 (A) CH_3-COOH (B) $\text{CH}_3-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{NH}_2$
 (C) $\text{CH}_3-\text{C}\equiv\text{CH}$ (D) $\text{CH}_3-\text{CH}_2-\text{OH}$



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



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

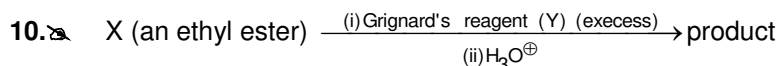
- (A) R is $-\text{H}$ (B) R' is $-\text{C}(\text{CH}_3)_2\text{CH}_2$ (C) R' is $-\text{CH}(\text{CH}_3)\text{CH}_2$ (D) R is $-\text{CH}_3$

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

- (A) $\text{PhMgBr} + \text{CH}_3\text{COCH}_2\text{CH}_3 \xrightarrow{\text{ether}} \xrightarrow{\text{H}^+}$
(B) $\text{CH}_3\text{MgBr} + \text{Ph}-\text{C}(=\text{O})-\text{C}_2\text{H}_5 \xrightarrow{\text{ether}} \xrightarrow{\text{H}^+}$
(C) $\text{C}_2\text{H}_5\text{MgBr} + \text{Ph}-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{\text{ether}} \xrightarrow{\text{H}^+}$
(D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{PhCHO} \xrightarrow{\text{ether}} \xrightarrow{\text{H}^+}$

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

- (A) $\text{CH}_3\text{COCl} > \text{CH}_3\text{CONH}_2$ (B) $\text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O}$
(C) $\text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{COCl}$ (D) $(\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{CONH}_2$



The product(s) may be :

- (A) $\text{Ph}-\text{C}(\text{CH}_3)_2-\text{OH}$ (B) $\text{CH}_3-\text{C}(\text{C}_2\text{H}_5)_2-\text{OH}$ (C) $\text{H}-\text{C}(\text{CHMe}_2)_2-\text{OH}$ (D) $\text{Ph}-\text{C}(\text{CHMe}_2)_2-\text{OH}$

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

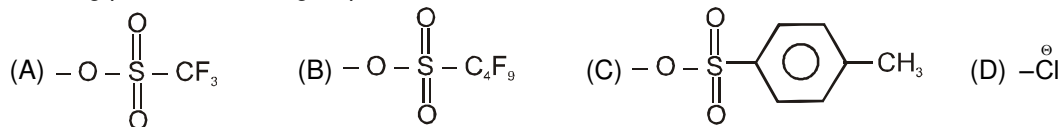
Nucleophilic aliphatic substitution reaction is given by those compounds which have electron rich groups as leaving groups. Less is the basicity of the leaving group, more is its leaving power.



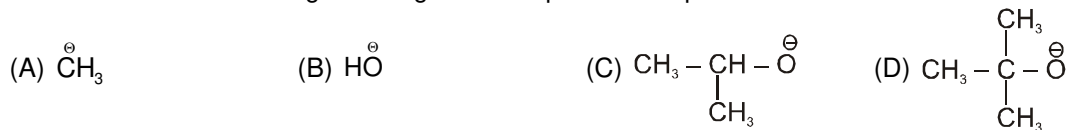
In the given reaction, L is the leaving group which leaves as nucleophile. Nu^- is the incoming group which is always nucleophilic in character. The reaction is nucleophilic substitution reaction which can be unimolecular or bimolecular reaction.



1. Leaving power of which group is maximum ?

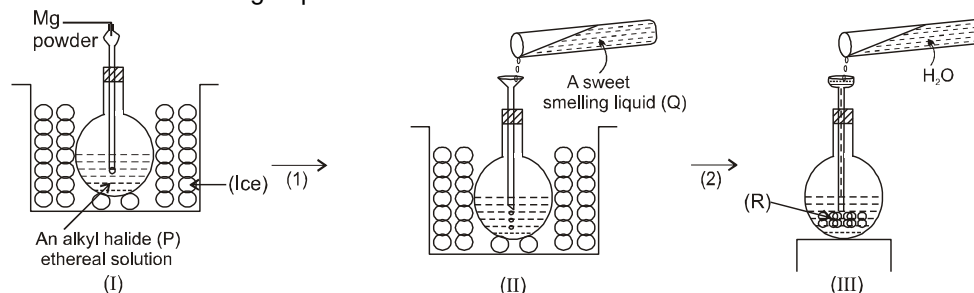


2. Which one of the following is strong base but poor nucleophile ?

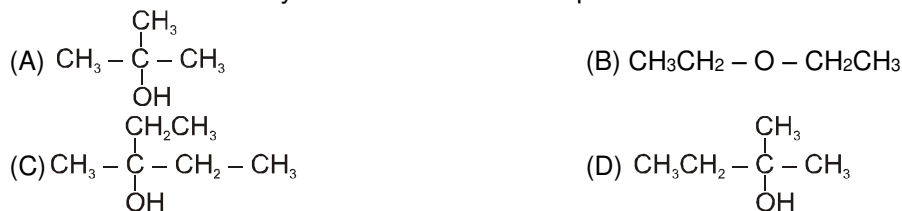


Comprehension # 2

Observe the following experiment



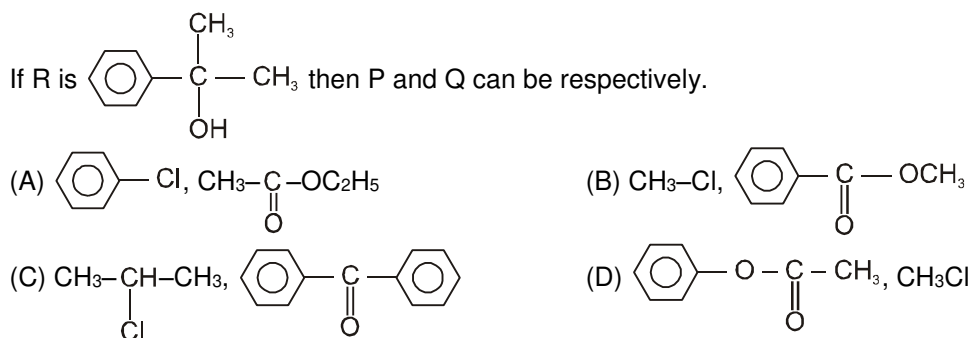
3. If the reactant 'P' is ethyl chloride then the main product R can be



4. If the liquid Q is $\text{H}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$ then the product R can be (P can be any other halide)



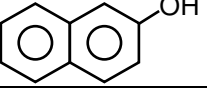
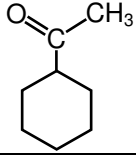
5. If R is $\text{C}_6\text{H}_5-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_3$ then P and Q can be respectively.





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) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\underset{\text{O}}{\text{C}}-\text{OH} \xrightarrow{\text{H}^+}$	(i) Acid base reaction	(P) 2,4-DNP test
(II)  $\xrightarrow{\text{Ph-MgBr}}$	(ii) Nucleophilic addition reaction	(Q) Carbylamine test
(III)  $\xrightarrow[\text{H}_2\text{O}]{\text{NaBD}_4}$	(iii) Nucleophilic substitution reaction	(R) Lucas test
(IV) $\text{CH}_3-\text{CH}_2-\text{NH}_2 \xrightarrow{\text{CH}_3\text{MgBr}}$	(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

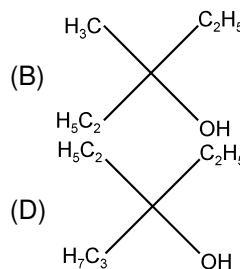
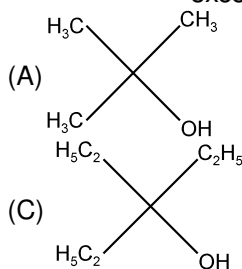
* Marked questions may have more than one correct option.

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

1. A biologically active compound, Bombykol ($\text{C}_{16}\text{H}_{30}\text{O}$) 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), $\text{C}_{16}\text{H}_{34}\text{O}$, 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 ($\text{O}_3/\text{H}_2\text{O}_2$) 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 $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P will be

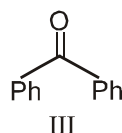
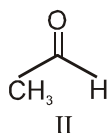
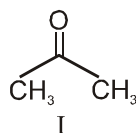
[JEE-2003, 3/84]





3. The order of reactivity of phenyl magnesium bromide with the following compounds is :

[JEE-2004, 3/84]



- (A) (II) > (III) > (I)
(C) (II) > (I) > (III)

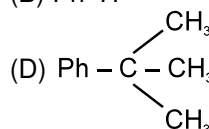
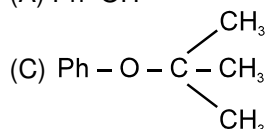
- (B) (I) > (III) > (II)
(D) all react with the same rate

4. Phenyl magnesium bromide reacting with t-Butyl alcohol gives

[JEE-2005, 3/60]

(A) Ph-OH

(B) Ph-H

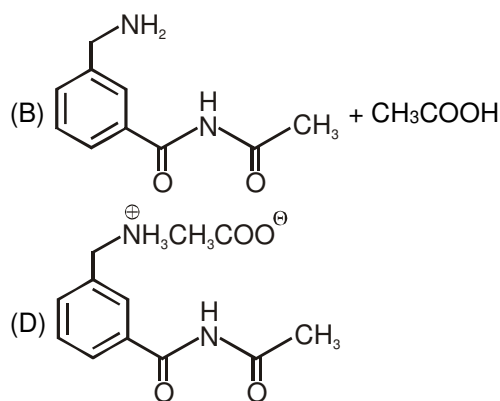
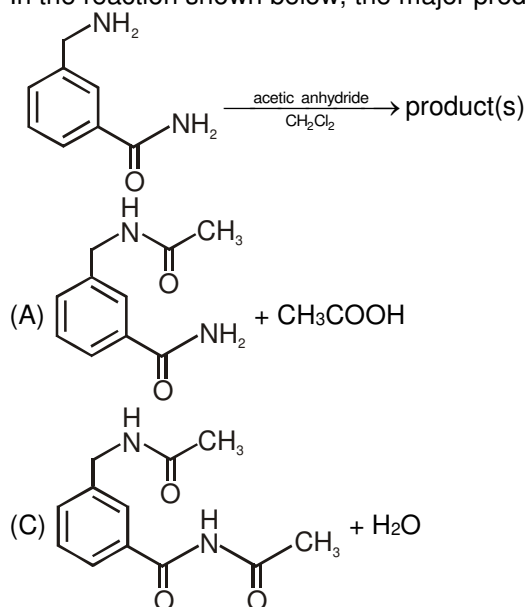


5. Match the compounds/ions in Column I with their properties/reactions in Column II. [JEE 2007, 8/162]

	Column-I		Column-II
(A)	$\text{C}_6\text{H}_5\text{CHO}$	(p)	gives precipitate with 2,4 dinitrophenylhydrazine.
(B)	$\text{CH}_3\text{C}\equiv\text{CH}$	(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]



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

JEE(MAIN) OFFLINE PROBLEMS

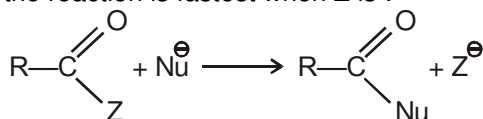
1. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives
- (1) Acetone (2) Acetamide
(3) 2-Methyl-2-propanol (4) Acetyl iodide

[AIEEE-2004, 3/225]



2. Rate of the reaction is fastest when Z is :

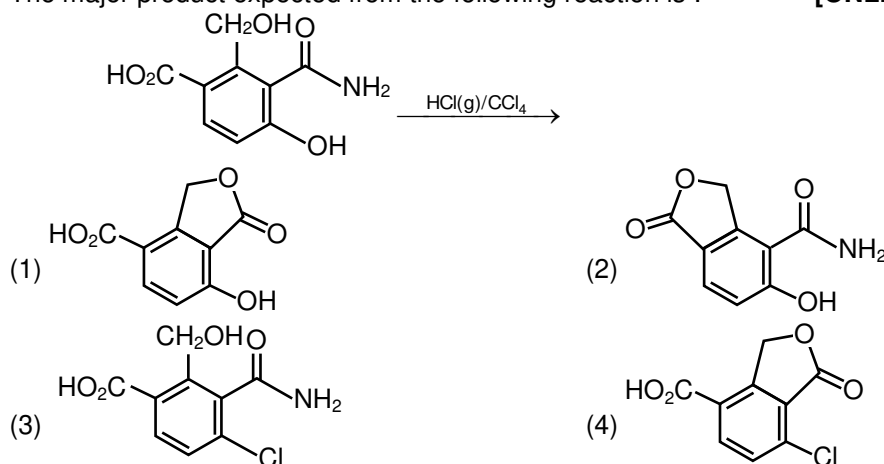
[AIEEE-2004, 3/225]



- (1) Cl (2) OCOCH₃ (3) OC₂H₅ (4) NH₂
3. On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is :
[AIEEE-2004, 3/225]
(1) CH₃COOC₂H₅ + NaCl (2) CH₃Cl + C₂H₅COONa
(3) CH₃COCl + C₂H₅OH + NaOH (4) CH₃COONa + C₂H₅OH
4. The decreasing order of the ratio of HCN addition to compounds A to D is [AIEEE-2006, 3/165]
(a) HCHO (b) CH₃COCH₃ (c) PhCOCH₃ (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 CH₃MgX with CH₃C≡C-H produces [AIEEE-2008, 3/105]
(1) CH₃C≡C-CH₃ (2) $\text{CH}_3-\overset{\text{H}}{\underset{|}{\text{C}}}=\overset{\text{H}}{\underset{|}{\text{C}}}-\text{CH}_3$ (3) CH₄ (4) CH₃-CH=CH₂
7. A liquid was mixed with ethanol and a drop of concentrated H₂SO₄ was added. A compound with a fruity smell was formed. The liquid was : [AIEEE-2009, 4/144]
(1) HCHO (2) CH₃COCH₃ (3) CH₃COOH (4) CH₃OH
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 CH₃COCl 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

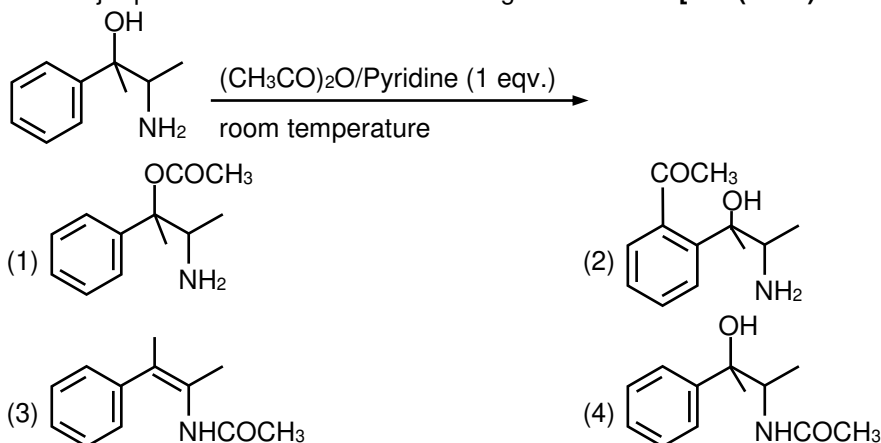
JEE(MAIN) ONLINE PROBLEMS

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

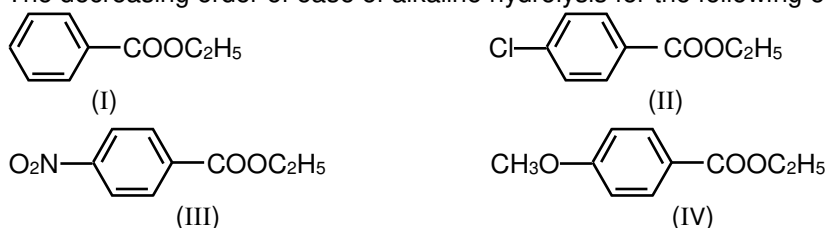




2. The major product obtained in the following reaction is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**



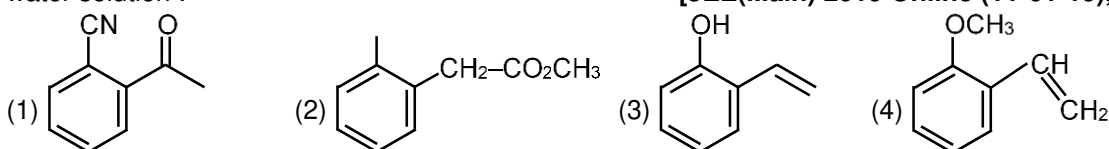
3. The decreasing order of ease of alkaline hydrolysis for the following esters is



[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]**



5. $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{Ph})\text{CH}_3$ cannot be prepared by :

[JEE(Main) 2019 Online (12-01-19), 4/120]

- (1) $\text{HCHO} + \text{PhCH}(\text{CH}_3)\text{CH}_2\text{Mg}$ (2) $\text{PhCOCH}_2\text{CH}_3 + \text{CH}_3\text{MgX}$
 (3) $\text{PhCOCH}_3 + \text{CH}_3\text{CH}_2\text{MgX}$ (4) $\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{PhMgX}$

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

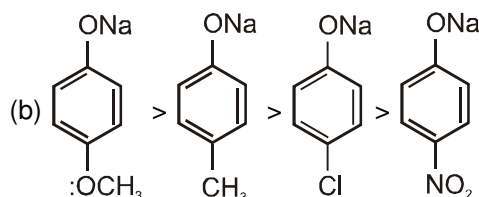
EXERCISE – 1

PART – I

A-1. b, c, d, e, f, h

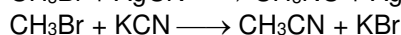
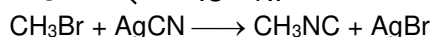
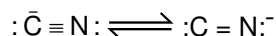
A-2. a, c, d

A-3. (a) $I^- > Br^- > Cl^- > H_2O$



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

For example, cyanide ion :



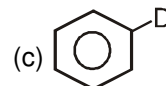
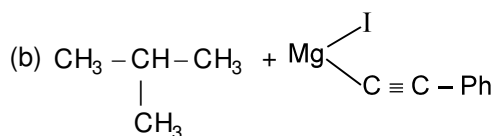
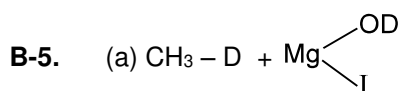
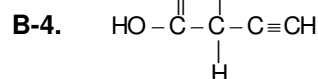
A-5. I > II > IV > III

A-6. Protic solvent (c, f, i) ; Aprotic solvent (a, b, d, e, g, h)

B-1. (b), (c)

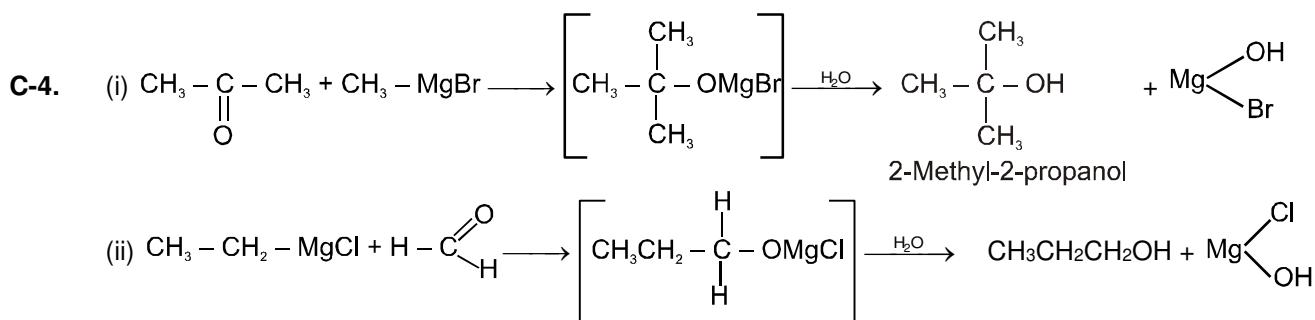
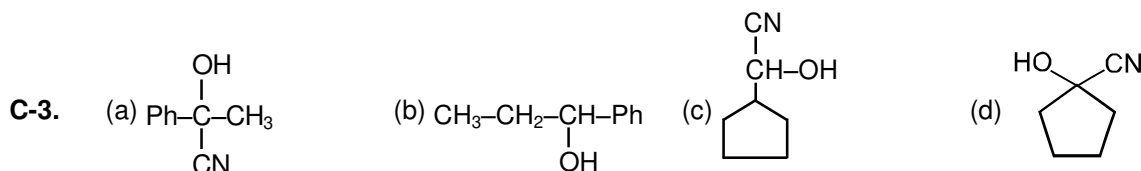
B-2. (a), (b)

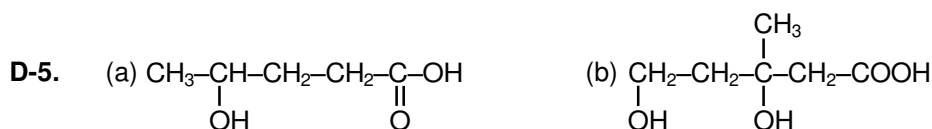
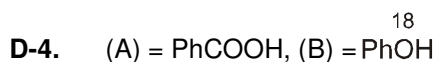
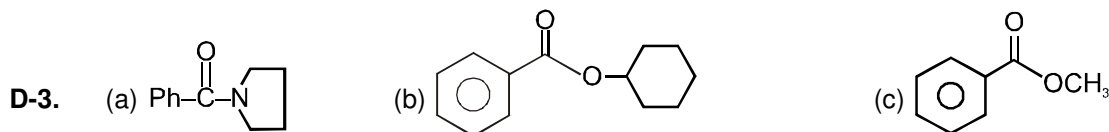
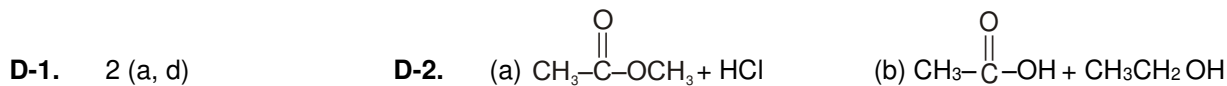
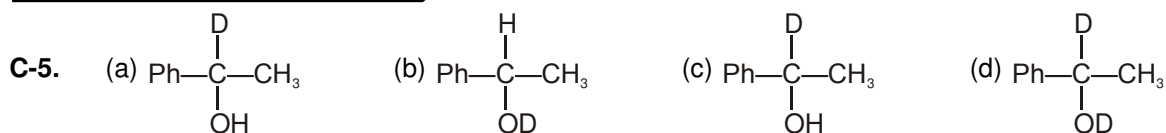
B-3. (b), (c)



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.





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 $\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH=CH--CH=CH(CH}_2)_8\text{CH}_2\text{OH}$
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) | | | |



Additional Problems for Self Practice (APSP)

✎ Marked questions are recommended for Revision.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.

Max. Marks : 120

Important Instructions

- The test is of **1 hour** duration.
- The Test Booklet consists of **30** questions. The maximum marks are **120**.
- Each question is allotted **4 (four)** marks for correct response.
- Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
 $\frac{1}{4}$ (**one fourth**) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
- There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

- Which solvent is non-polar solvent ?
 (1) $\text{CH}_3\text{--CO--CH}_3$ (2) $\text{CH}_3\text{--SO--CH}_3$ (3) CH_3COOH (4) Cyclohexane
- Which one of the following has minimum nucleophilicity ?
 (1) $(\text{CH}_3)_3\text{CLi}$ (2) NaNH_2 (3) CH_3ONa (4) NaOH
- Which of the following compound gives fastest nucleophilic addition reaction :

(1)

(2)

(3)

(4)
- ✎ Benzoyl chloride on treatment with ammonia gives
 (1) Benzamide (2) Acetamide (3) Benzylamine (4) Benzoic acid
- ✎ Which of the following is a nucleophile ?
 (1) $\cdot\dot{\text{C}}\text{H}_3$ (2) $\text{CH}_2\cdot$ (3) $\text{CH}_3\text{--}\ddot{\text{N}}\cdot$ (4) $\text{CH}_3\text{--}\ddot{\text{N}}\text{H}_2$
- Which of the following reactants will give only one organic product when reacted with $\text{NaCN} / \text{H}_2\text{SO}_4$ (small amounts) (No other isomer is obtained)

(1) CH_3CHO

(2) HCHO

(3) PhCHO

(4)
- ✎ Which of the following compound give methane on treatment with CH_3MgI .

(1)

(2)

(3)

(4)
- The correct order of leaving ability is :

(1) $\text{OH}^- > \text{H}_2\text{O}$


(2) $\text{OH}^- > \text{SH}^-$

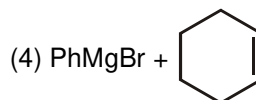
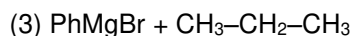
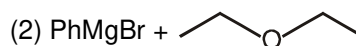
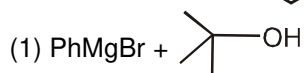
(3)

(4) $\text{Cl}^- > \text{I}^-$

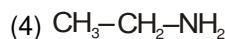
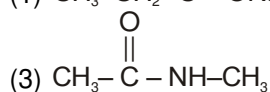
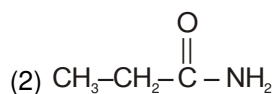
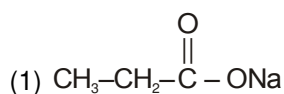
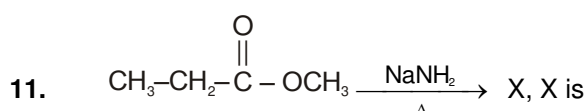
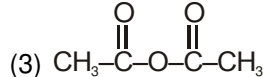
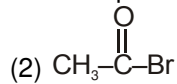
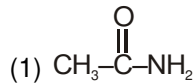




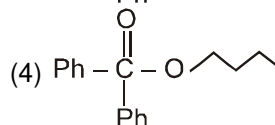
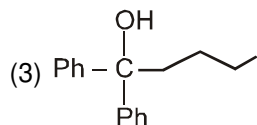
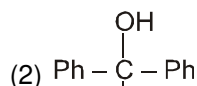
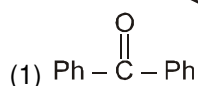
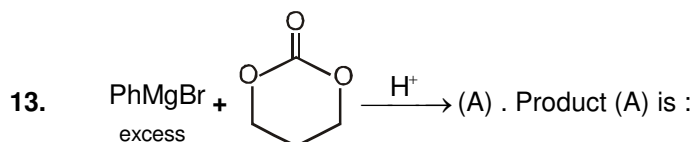
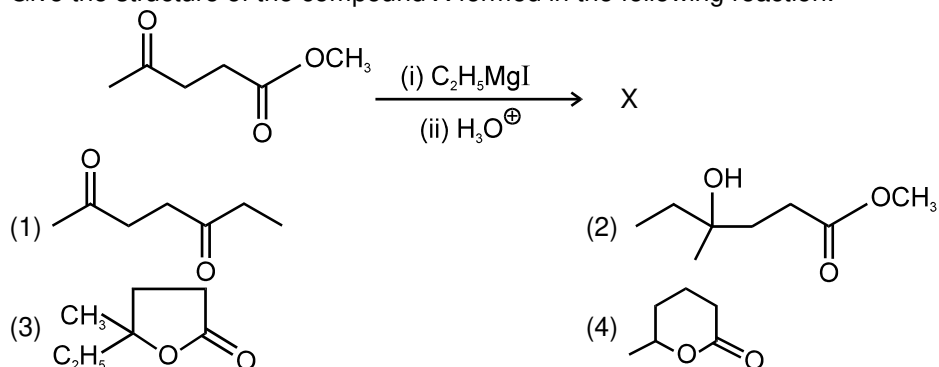
9. In which of reaction  will be obtained as a product ?

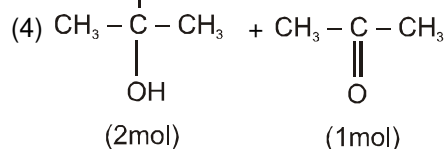
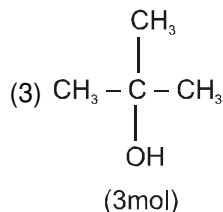
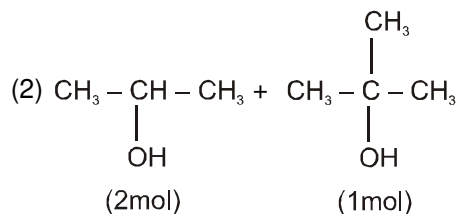
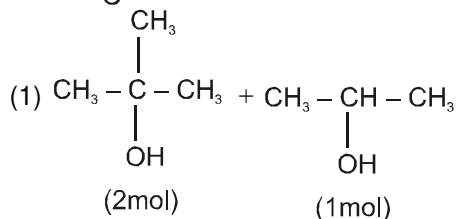
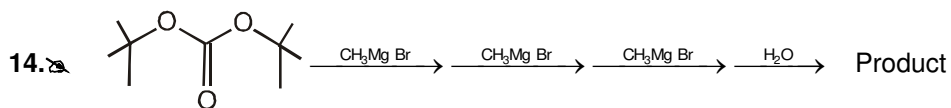


10. Which of the following is the most reactive towards nucleophilic acyl substitution ?

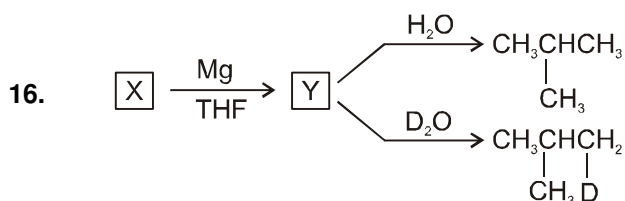
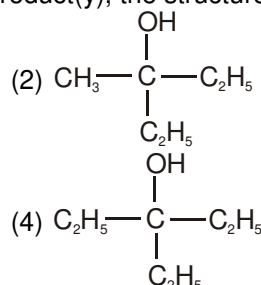
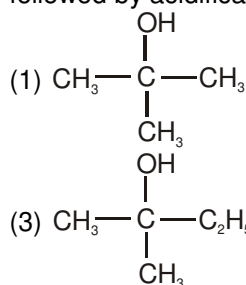


12. Give the structure of the compound X formed in the following reaction.

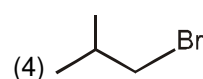
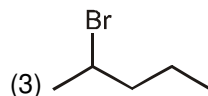
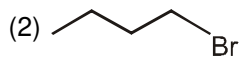
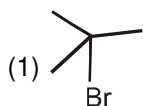




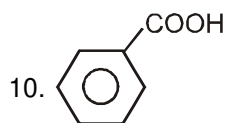
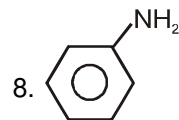
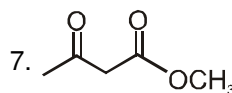
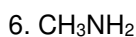
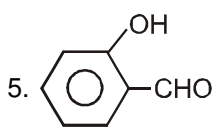
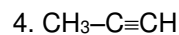
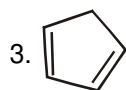
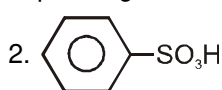
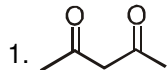
15. A sweet smelling compound(x) with molecular formula $\text{C}_8\text{H}_{16}\text{O}_2$ on reaction with excess of CH_3MgBr followed by acidification gives a single organic product(y), the structure of (y) can be :



Give the structure of X.



17. Which of the following compound give benzene on reaction with PhMgBr .



(1) 2,3,4,5

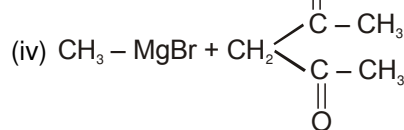
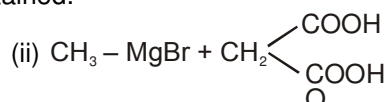
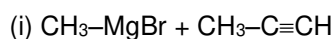
(2) 7,8,9

(3) 2,4,5,7,10

(4) All



18. In which of the following reaction CH_4 will be obtained.



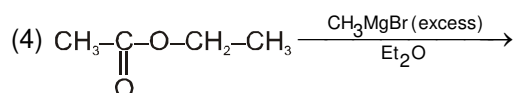
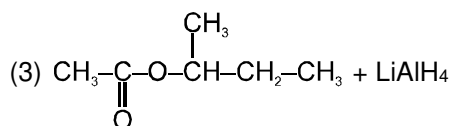
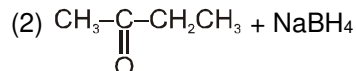
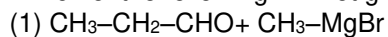
(1) (i), (ii) & (iii)

(2) (i), (ii), (iii) & (iv)

(3) (iii) & (iv)

(4) (iii), (i) & (iv)

19. Which of the following will not give 2° alcohol ?



20. Which of these statements is incorrect about nucleophiles ?

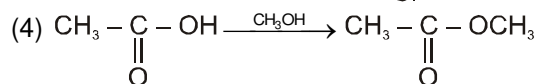
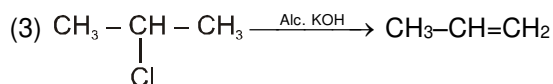
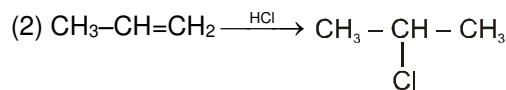
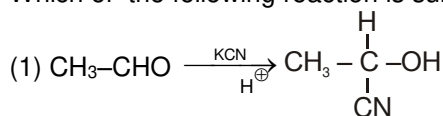
(1) Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species.

(2) The nucleophilicity of an element (as electron donor) generally increases on going down a group in the periodic table.

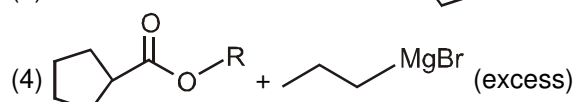
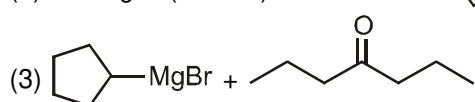
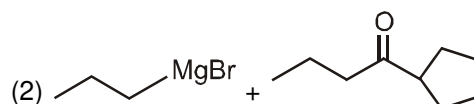
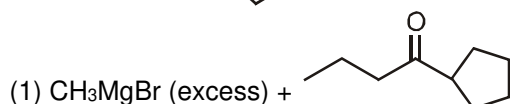
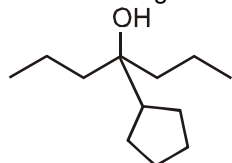
(3) A nucleophile is electron-deficient species

(4) All good nucleophiles are good bases when we deal across the period.

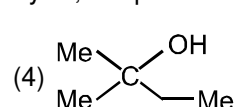
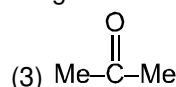
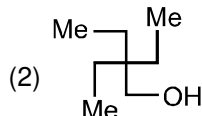
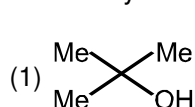
21. Which of the following reaction is substitution reaction ?



22. Which of the following combination of reactants can not be used to prepare the following compound ?



23. When ethyl ethanoate is treated with excess of MeMgBr followed by hydrolysis, the product is :



24. What product is formed when acetic acid heated with P_2O_5 .

(1) Acetyl chloride

(2) Acetate ester

(3) Acetic anhydride

(4) Acetaldehyde





25. Which species will not be considered as an electrophile ?
 (1) $\text{CH}_3 - \text{CH}_2^\oplus$ (2) AlCl_3 (3) NH_3 (4) SO_3
26. When grignard reagent is treated with isopropyl formate followed by acid hydrolysis we get :
 (1) Aldehyde (2) 2° alcohol (3) 3° alcohol (4) 1° alcohol
27. Compound $\text{CH}_3 - \text{CH}_2 - \underset{\text{Ph-CH-OH}}{\text{CH}} - \text{CH}_3$ can be prepared by :
 (1) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CHO} \xrightarrow[\text{(ii) H}_3\text{O}^\oplus]{\text{(i) PhMgBr}}$
 (2) $\text{CH}_3 - \underset{\text{MgBr}}{\text{CH}} - \text{CH}_3 \xrightarrow[\text{(ii) H}_3\text{O}^\oplus]{\text{(i) PhCH}_2\text{CHO}}$
 (3) $\text{Ph} - \text{COCH}_3 \xrightarrow[\text{(ii) H}_3\text{O}^\oplus]{\text{(i) CH}_3\text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{MgBr}}$
 (4) $\text{PhCHO} \xrightarrow[\text{(ii) H}_3\text{O}^\oplus]{\text{(i) CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{MgBr}}$
28. Identify the correct set of aprotic solvent .
 (1) Water, DMSO (2) DMSO, Acetone
 (3) Ethanol, Acetone (4) Diethylether, Methyl amine
29. Acid hydrolysis of which of the following compounds yields two different organic compounds?
 (1) CH_3COOH (2) CH_3CONH_2 (3) $\text{CH}_3\text{COOC}_2\text{H}_5$ (4) $(\text{CH}_3\text{CO})_2\text{O}$
30. Leaving group ability order amongst the following
 (I) $\text{C}_6\text{H}_5\text{O}^-$ (II) $p\text{-(CH}_3\text{)} \text{C}_6\text{H}_4\text{O}^-$ (III) $p\text{-(OCH}_3\text{)} \text{C}_6\text{H}_4\text{O}^-$ (IV) $p\text{-(NO}_2\text{)} \text{C}_6\text{H}_4\text{O}^-$
 (1) $\text{I} > \text{II} > \text{III} > \text{IV}$ (2) $\text{III} > \text{II} > \text{I} > \text{IV}$
 (3) $\text{IV} > \text{I} > \text{II} > \text{III}$ (4) $\text{IV} > \text{III} > \text{II} > \text{I}$

Practice Test-1 (IIT-JEE (Main Pattern))

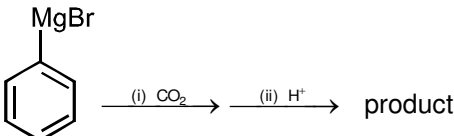
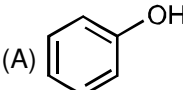
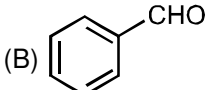
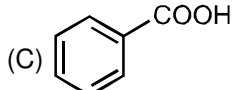
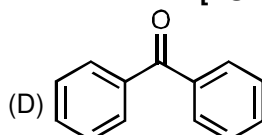
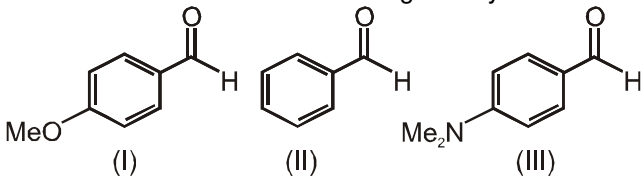
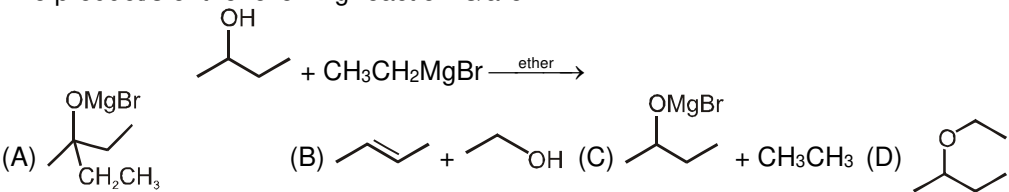
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

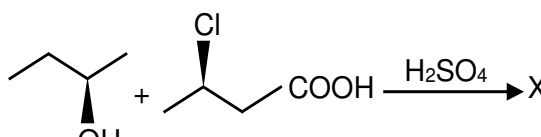
PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. Which of the following is NOT a nucleophile ? [NSEC-2001]
 (A) H_2 (B) CH_3OH (C) H_2O (D) NH_3
2. Which of the following compounds would react with PhMgBr subsequently yield Ph_3COH ? [NSEC-2002]
 (A) a ketone (B) an ester other than formic
 (C) diethyl carbonate (D) all of these.
3. Absolutely pure hydrogen cyanide fails to react with aldehydes because [NSEC-2002]
 (A) hydrogen cyanide is not a strong nucleophile
 (B) hydrogen cyanide is undissociated when pure
 (C) hydrogen cyanide cannot add to the carbonyl group on its own
 (D) all the above are correct.



4. The group which contains a Lewis acid, a nucleophile and a radical is [NSEC-2003]
 (A) C_2H_6 , Br^+ , Cl atom (B) NH_3 , $AlCl_3$, H atom (C) H^+ , BF_3 , H_2O^+ (D) C_6H_6 , CH_3^+ , Cl_2 .
5. The non-nucleophilic base is [NSEC-2004]
 (A) CN^- (B) $-OC(Me)_3$ (C) HO^- (D) MeO^-
- 6.* The reagent with which both hexanol and 2-pentanone reacts is [NSEC-2004]
 (A) Fehling's solution (B) Grignard reagent (C) Schiff's reagent (D) Tollen's reagent.
7. The relative reactivity of carbonyl compounds towards nucleophilic addition is [NSEC-2005]
 (A) $CH_3CHO > CH_3COCH_3 > CH_3COOCH_3 > CH_3CONH_2$
 (B) $CH_3COOCH_3 > CH_3CONH_2 > CH_3CHO > CH_3COCH_3$
 (C) $CH_3CONH_2 > CH_3CHO > CH_3COCH_3 > CH_3COOCH_3$
 (D) $CH_3CHO > CH_3COOCH_3 > CH_3CONH_2 > CH_3COCH_3$.
8. In the reactions $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{H-OH} CH_3CH(OH)COOH$, the acid obtained [NSEC-2006]
 (A) D-isomer (B) L-isomer
 (C) 80% D + 20% L mixture (D) 50% D + 50% L mixture.
9.  The product in this reaction will be [NSEC-2006]
 (A)  (B)  (C)  (D) 
10. The K_{eq} values in HCN addition to following aldehydes are in the order : [NSEC-2007]

 (A) $I > II > III$ (B) $II > III > I$ (C) $III > I > II$ (D) $II > I > III$
11. Identify the ester which upon addition of excess Grignard's reagent will provide a secondary alcohol : [NSEC-2007]
 (A) CH_3CO_2Et (B) $(CH_3)_2CHCO_2Et$ (C) HCO_2Et (D) $C_6H_5CO_2Et$
12. Which of the following series contains only nucleophiles ? [NSEC-2008]
 (A) NH_3 , H_2O , CN^- , I^- (B) $AlCl_3$, NH_3 , H_2O , I^-
 (C) $AlCl_3$, BF_3 , H_2O , NH_3 (D) $AlCl_3$, BF_3 , NO_2^+ , NH_3
13. The product/s of the following reaction is/are [NSEC-2010]

14. The best nucleophile among the following is : [NSEC-2011]
 (A) H_2O (B) CH_3SH (C) Cl^- (D) NH_3
15. A catalyst accelerates a reaction primarily by stabilizing the [NSEC-2012]
 (A) substrate (B) product (C) intermediate (D) transition state



16. Which of the following information is not provided by a reaction mechanism? [NSEC-2012]
 (A) Which bonds are formed and which bonds are broken
 (B) Which intermediates and transition states are formed.
 (C) Energy content of the reacting species
 (D) Which is the slowest step
17. When a nucleophile attacks a carbonyl group to form an intermediate, the hybridisation of the carbon atom changes from [NSEC-2014]
 (A) sp^3 to sp^2 (B) sp^2 to sp (C) sp to sp^2 (D) sp^2 to sp^3
18. The product X formed in the following reaction is [NSEC-2014]
 $C_6H_5MgBr + CH_3OH \rightarrow X$
 (A) benzene (B) methoxybenzene (C) phenol (D) toluene
19. A group which departs from the substrate in a nucleophilic substitution reaction is called a leaving group. The ease of departure is determined by the acidity of the conjugate acid of the leaving group; higher the acidity better is the leaving group. The correct order of the reactivity of the following compounds in a given nucleophilic reaction is : [NSEC-2016]
 (A) $R-Cl > R-OCOCH_3 > R-OSO_2CH_3 > RI$ (B) $R-OSO_2CH_3 > R-Cl > R-OCOCH_3 > ROH$
 (C) $R-I > RNH_2 > R-OCOCH_3 > R-OSO_2CH_3$ (D) $R-Br > R-OSO_2CH_3 > R-OCOCH_3 > ROCH_3$
20. The correct order of the ability of the leaving group is [NSEC-2017]
 (A) $OCOC_2H_5 > OC_2H_5 > OSO_2Et > OSO_2CF_3$ (B) $OC_2H_5 > OCOC_2H_5 > OSO_2CF_3 > OSO_2Me$
 (C) $OSO_2CF_3 > OSO_2Me > OCOC_2H_5 > OC_2H_5$ (D) $OCOC_2H_5 > OSO_3CF_3 > OC_2H_5 > OSO_2Me$
21. The best reaction sequence for the synthesis of 2-pentanone would be - [NSEC-2017]
 (A) $CH_3CH_2CH_2CHO \xrightarrow{CH_3MgI/ether} X \xrightarrow{H^+, H_2O}$
 (B) $CH_3CH_2CH_2CN \xrightarrow{CH_3MgI/ether} X \xrightarrow{H^+, H_2O}$
 (C) $CH_3CH_2CH_2CHO \xrightarrow{CH_3MgI/ether} X \xrightarrow{H^+, H_2O}$
 (D) $CH_3CH_2CH_2MgI + CH_2O \xrightarrow{ether} X \xrightarrow{H^+, H_2O}$
22. The product 'X' in the following reaction is [NSEC-2018]

 (A) a racemic mixture of ester (B) an optically inactive ester
 (C) an optically active ester (D) a meso ester

PART - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

Important Instructions

A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

- Each part consists of five sections.
- Section 1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section 2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section 3 contains 4 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).



7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme :

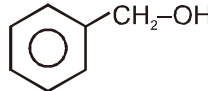
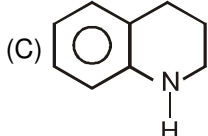
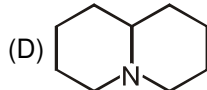
9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (-1) mark will be awarded.
10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

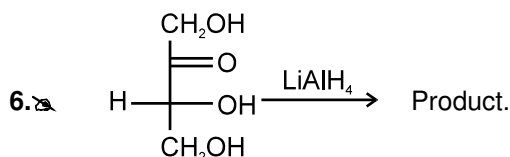
SECTION-1 : (Only One Option Correct Type)

This section contains 8 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1. 0.34 g of hydrocarbon when treated with excess of CH_3MgI liberates 112 mL of CH_4 at STP the structure of hydrocarbon is
- (A) $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{C} \equiv \text{C} - \text{H}$ (B) $\text{CH}_3 - \text{C} \equiv \text{C} - \text{H}$
- (C) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{C} - \text{H}$ (D) $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{C} \equiv \text{C} - \text{H}$
2. An ester on treatment with excess of Grignard reagent followed by acidification gives Butane-2-ol and 3-methylpentan-3-ol. Predict the reactant from the following :
- (A) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3 + \text{C}_2\text{H}_5\text{MgBr}$ (B) $\text{C}_2\text{H}_5 - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{CH}_2 - \text{CH}_3 + \text{CH}_3\text{MgBr}$
- (C) $\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \underset{\text{CH}_3}{\text{CH}} - \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{MgBr}$ (D) $\text{H} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{C}_2\text{H}_5 + \text{BrMg} - \underset{\text{C}_2\text{H}_5}{\overset{\text{C}_2\text{H}_5}{\text{C}}} - \text{CH}_3$
3. Decreasing order of relative nucleophilicity of the following nucleophiles in protic solvent is :
- (A) $\text{SH}^- > \text{OH}^- > \text{H}_2\text{O} > \text{AcO}^- > \text{PhO}^-$ (B) $\text{SH}^- > \text{OH}^- > \text{PhO}^- > \text{AcO}^- > \text{H}_2\text{O}$
- (C) $\text{SH}^- > \text{PhO}^- > \text{OH}^- > \text{H}_2\text{O} > \text{AcO}^-$ (D) $\text{OH}^- > \text{SH}^- > \text{PhO}^- > \text{AcO}^- > \text{H}_2\text{O}$
4. Which of the following is not nucleophile ?
- (A) OH^- (B) CN^- (C) BF_3 (D) NH_3

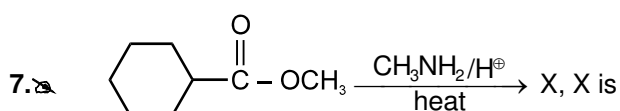


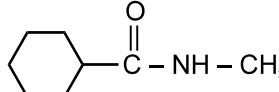
5. Which of the following will not react with acetyl chloride CH_3COCl ?
- (A) H_2O (B)  (C)  (D) 



In the given reaction the product is.

- (A) An optically inactive mixture of two compounds
 (B) An optically active mixture of two compounds
 (C) An optically inactive mixture of three compounds
 (D) An optically active mixture of three compounds

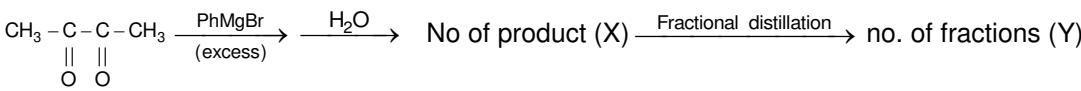


- (A)  (B) 
 (C)  (D) 

8. Which of the following is not correct order for Nucleophilicity as well as basicity.
 (A) $\text{HO}^\ominus \gg \text{H}_2\text{O}$ (B) $\text{NH}_2^\ominus \gg \text{NH}_3$ (C) $\text{I}^\ominus > \text{Br}^\ominus > \text{Cl}^\ominus > \text{F}^\ominus$ (D) $\text{MeO}^\ominus > \text{HO}^\ominus > \text{MeCOO}^\ominus$

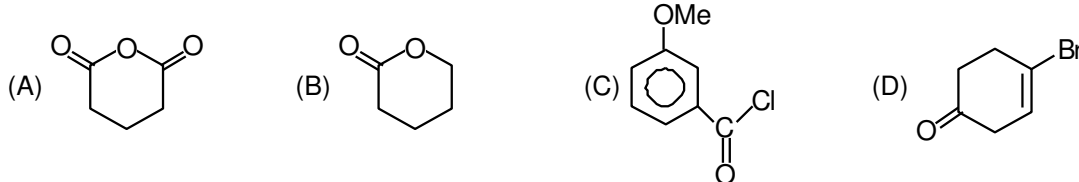
Section-2 : (One or More than one options correct Type)

This section contains 6 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

9. The correct nucleophilicity order(s) is/are:
 (A) $\text{CH}_3\text{O}^\ominus > \text{CH}_3^\ominus$ (B) $\text{CH}_3\text{S}^\ominus > \text{CH}_3\text{SH}$
 (C) $\text{NH}_3 > \text{H}_2\text{O}$ (D) $(\text{CH}_3\text{CH}_2)_3\text{N} > (\text{CH}_3\text{CH}_2)_3\text{P}$
10.  No of product (X) $\xrightarrow{\text{Fractional distillation}}$ no. of fractions (Y)
 X and Y are :
 (A) 3 (B) 2 (C) 4 (D) 5
11. Which of the followings give product by $\text{S}_{\text{N}}2$ mechanism ?
 (A) $\text{CH}_3\text{COCl} \xrightarrow{\text{NaOH}} \text{CH}_3\text{COOH}$ (B) $\text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{NaOH}} \text{CH}_3\text{CH}_2\text{OH}$
 (C) $\text{CH}_3\text{COOH} \xrightarrow{\text{PCl}_5} \text{CH}_3\text{COCl}$ (D) $\text{CH}_3\text{CH}(\text{CH}_3)\text{OH} \xrightarrow{\text{PCl}_5} \text{CH}_3\text{CH}(\text{CH}_3)\text{Cl}$
12. Choose the correct order of nucleophilicity.
 (A) $\text{F}^\ominus_{(\text{DMSO})} > \text{Cl}^\ominus_{(\text{DMSO})} > \text{Br}^\ominus_{(\text{DMSO})} > \text{I}^\ominus_{(\text{DMSO})}$ (B) $\text{F}^\ominus_{(\text{aq})} > \text{Cl}^\ominus_{(\text{aq})} > \text{Br}^\ominus_{(\text{aq})} > \text{I}^\ominus_{(\text{aq})}$
 (C) $\text{I}^\ominus_{(\text{aq})} > \text{Br}^\ominus_{(\text{aq})} > \text{Cl}^\ominus_{(\text{aq})} > \text{F}^\ominus_{(\text{aq})}$ (D) $\text{I}^\ominus_{(\text{DMSO})} > \text{Br}^\ominus_{(\text{DMSO})} > \text{Cl}^\ominus_{(\text{DMSO})} > \text{F}^\ominus_{(\text{DMSO})}$



13. NaSH will produce a substitution product in significant quantity with :

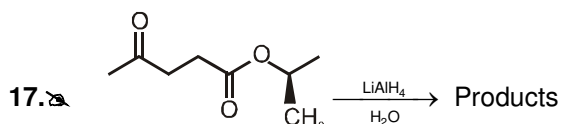
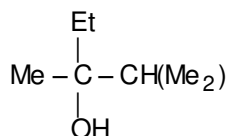


14. Which statement is/are correct for halogen
- (A) Bond dissociation energy for $H-X$ follow $H-F > H-Cl > H-Br > H-I$
- (B) Basicity order follows $F^- > Cl^- > Br^- > I^-$
- (C) Nucleophilicity order follows $I^- > Br^- > Cl^- > F^-$
- (D) Electronegativity order follows $F > Cl > Br > I$

Section-3 : (Single/ Double Integer Value Correct Type.)

This section contains 4 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

15. A sample of 3 mg of an unknown alcohol (ROH) is added to methyl magnesium iodide then 1.12 ml gas is evolved. What will be the molecular weight of alcohol is
16. How many types of Grignard reagent (RMgCl) can be used to prepare the following alcohol, by using different Ketones.



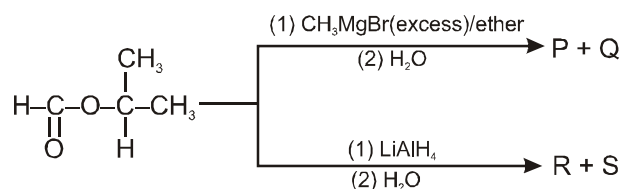
Total number of products in the above reaction :

18. On conversion into the Grignard reagent followed by treatment with water how many structural alkyl bromides would yield isopentane ?

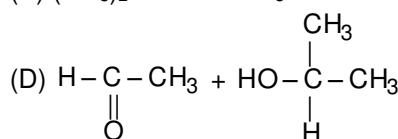
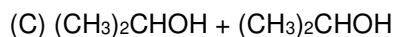
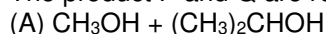
SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 3 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Questions 19 to 21



19. The product P and Q are respectively :





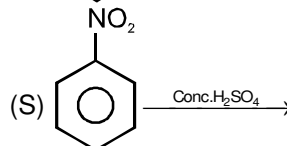
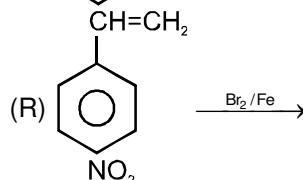
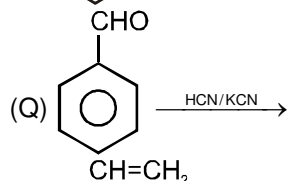
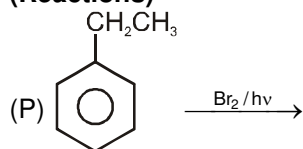
20. The product R and S are :
 (A) Both 2° alcohols. (B) Both 1° alcohols.
 (C) One is 1°-OH, other is 2°-OH. (D) One of these is CH₃-CH₂-OH.
21. One of the product of following reaction is :
 (P or Q or R or S) + CH₃MgBr →
 (A) 3° alcohol (B) An ether (C) Methane (D) Propane

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

22. Match List I (Reaction) with List II (Type of reaction) and select the correct answer using the code given below the lists :

List I (Reactions)



List II (Type of mechanism)

(1) Electrophilic addition

(2) Electrophilic substitution

(3) Nucleophilic addition

(4) Free radical substitution

Codes :

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

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22								
Ans.										



APSP Answers

PART - I

1.	(4)	2.	(4)	3.	(3)	4.	(1)	5.	(4)
6.	(2)	7.	(2)	8.	(3)	9.	(1)	10.	(2)
11.	(2)	12.	(3)	13.	(2)	14.	(3)	15.	(3)
16.	(4)	17.	(4)	18.	(2)	19.	(4)	20.	(3)
21.	(4)	22.	(1)	23.	(1)	24.	(3)	25.	(3)
26.	(2)	27.	(4)	28.	(2)	29.	(3)	30.	(3)

PART - II

1.	(A)	2.	(D)	3.	(D)	4.	(B)	5.	(B)
6.	(B)	7.	(A)	8.	(D)	9.	(C)	10.	(D)
11.	(C)	12.	(A)	13.	(C)	14.	(C)	15.	(D)
16.	(C)	17.	(D)	18.	(A)	19.	(B)	20.	(C)
21.	(B)	21.	(C)						

PART - III

1.	(A)	2.	(C)	3.	(B)	4.	(C)	5.	(D)
6.	(B)	7.	(C)	8.	(C)	9.	(BC)	10.	(AB)
11.	(AC)	12.	(AC)	13.	(AC)	14.	(ABCD)	15.	60
16.	3	17.	3	18.	4	19.	(C)	20.	(C)
21.	(C)	22.	(B)						

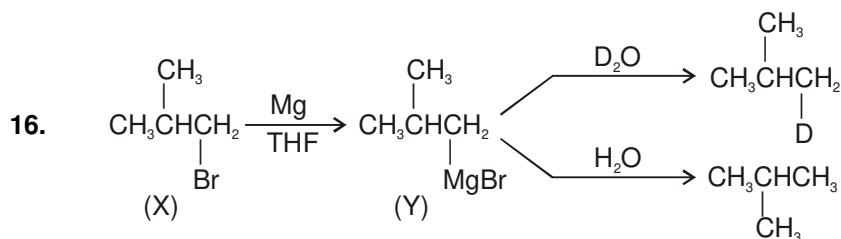
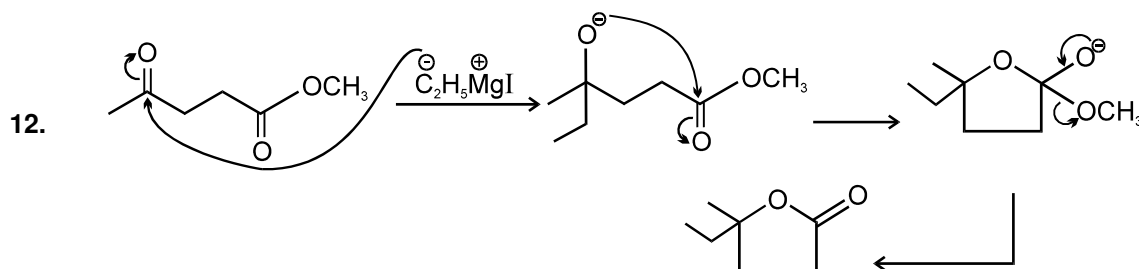
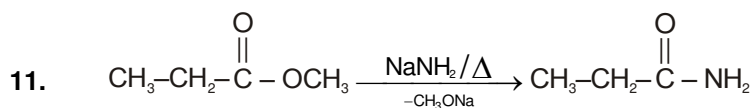
APSP Solutions

PART - I

- The nucleophilicity order is $R^{\ominus} > \overset{\ominus}{N}H_2 > CH_3O^{\ominus} > OH^{\ominus}$
- $Ph-COCl \xrightarrow{NH_3} Ph-CONH_2 + HCl$
- The species with incomplete octet can not be a nucleophile.
- Except HCHO all given carbonyl compound will give racemic mixture (\pm).

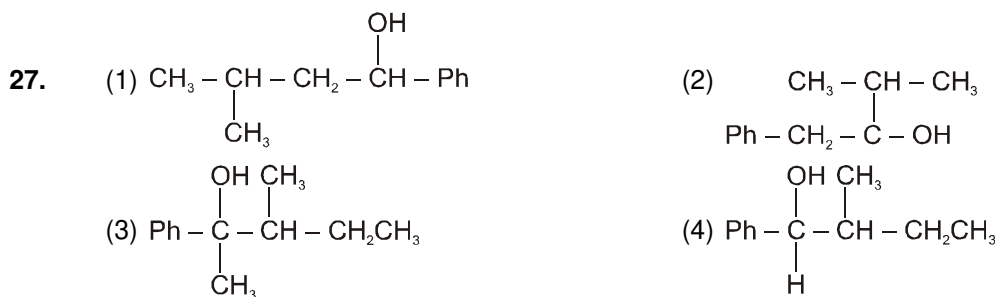
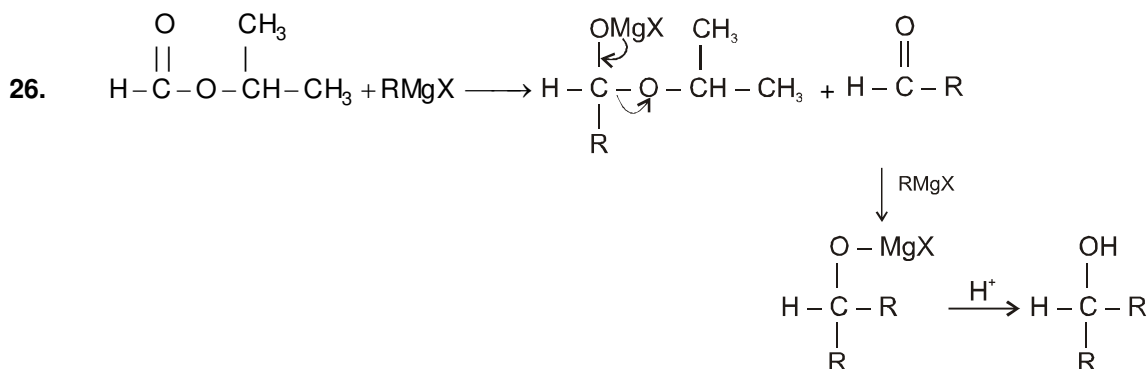


8. Weaker bases are better leaving group.



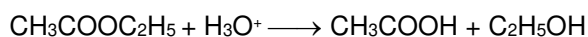
18. All of these reaction give CH_4 .

20. Nucleophiles are electron rich species.

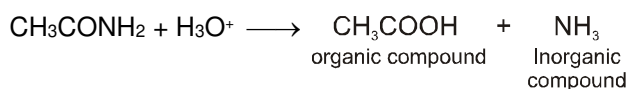




29. Acid hydrolysis of an ester gives two different organic compounds.



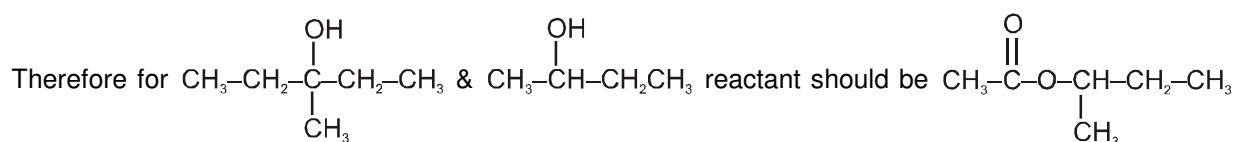
While the acid hydrolysis of an amide gives one organic and one inorganic product as



30. Conjugated base of strong acid is weak base and behave as better leaving group.

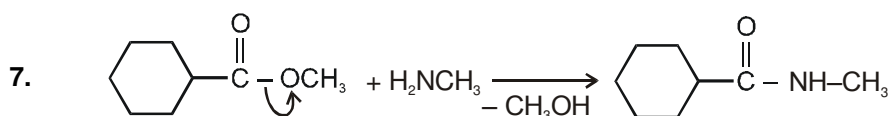
PART - III

2. Alcohols obtained from reaction of ester with Grignard reagent will have two identical alkyl group which comes from Grignard reagent.

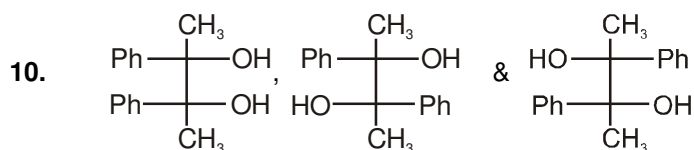


and $\text{CH}_3\text{CH}_2\text{MgBr}$.

3. Nucleophilicity \propto Size (in group)



9. Anionic nucleophiles are better nucleophile than their neutral species.



Methane gas is released on reacting CH_3MgI with a compound containing reactive hydrogen atom. The reaction is used for estimation of reactive hydrogen atoms present in a molecule. This method is called zerewitinaff method of estimation of reactive hydrogen atom.

12. In aprotic solvent Nu^\ominus increases, as compare to polar protic solvent.

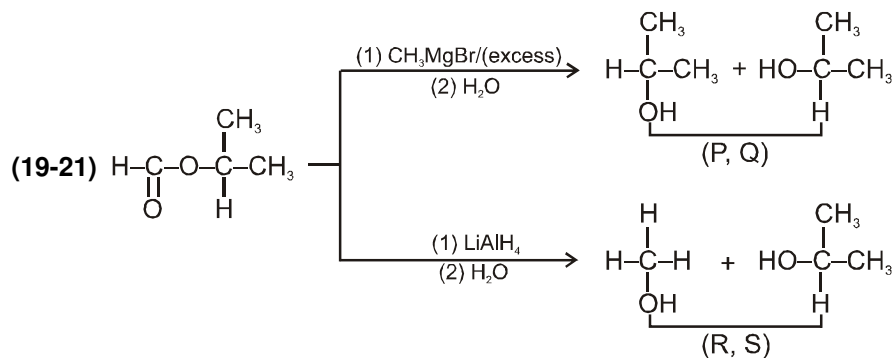
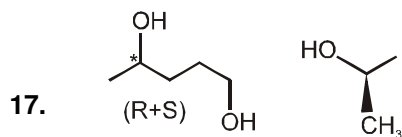
13. HS^- is better base than Cl^- or $\text{---}\overset{\text{O}}{\parallel}{\text{C}}\text{---O}^-$. Hence, it can substitute (A) & (C), but not (B) or (D), (D) contain single halide which fails to undergo substitution.

14. Self understood



15. Number of millimoles of alcohol = $\frac{1.12 \text{ ml}}{22.4 \text{ ml/mole}}$

molecular weight of alcohol = $\frac{\text{Wt of alcohol (mg)}}{\text{No. of milli moles of alcohol}} = \frac{3}{1.12/22.4} = 60.$



[P, Q, R, S = R-OH] + CH₃MgBr → (CH₄) as common product.