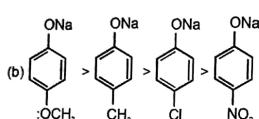
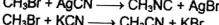
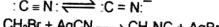
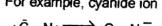
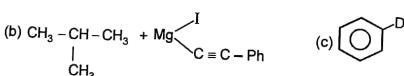
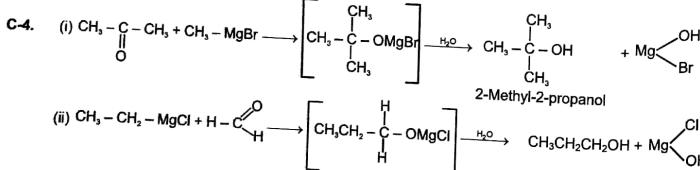
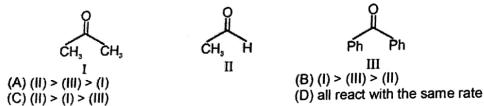


Answers**EXERCISE - 1****PART - I****A-1.** b, c, d, e, f, h**A-2.** a, c, d**A-3.** (a) $I^- > Br^- > Cl^- > H_2O$ **A-4.** Ambident nucleophile : The species which have more than one nucleophilic site for reaction are called ambident nucleophiles. For example, cyanide ion :**A-5.** I > II > III > IV**A-6.** Protic solvent (c, f, i); Aprotic solvent (a, b, d, e, g, h)**B-1.** (b), (c)**B-2.** (a), (b)**B-3.** (b), (c)**B-4.****B-5.** (a) $\text{CH}_3-\text{D} + \text{Mg} \xrightarrow{\text{OD}}$ **C-1.** III > II > I > IV**C-2.** Cyanohydrin is formed by nucleophilic attack on carbonyl group ($\text{C}=\text{O}$), 2, 2, 6-trimethylcyclohexanone has more steric crowding due to three methyl groups.**C-3.** (a) $\text{Ph}-\text{C}(=\text{O})-\text{CH}_3$ **(b) $\text{CH}_3-\text{CH}_2-\text{CH}(\text{Ph})-\text{CH}_2-\text{CH}_3$** **(c) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_3$** **(d) $\text{CH}_3-\text{CH}(\text{CN})-\text{CH}_2-\text{CH}_3$** **C-5.** (a) $\text{Ph}-\text{C}(\text{D})-\text{CH}_3$ **(b) $\text{Ph}-\text{C}(\text{H})-\text{CH}_3$** **(c) $\text{Ph}-\text{C}(\text{D})-\text{CH}_3$** **(d) $\text{Ph}-\text{C}(\text{D})-\text{CH}_3$** **D-1.** 2 (a, d)**D-2.** (a) $\text{CH}_3-\text{C}(=\text{O})-\text{OCH}_3 + \text{HCl}$ **(b) $\text{CH}_3-\text{C}(=\text{O})-\text{OH} + \text{CH}_3\text{CH}_2\text{OH}$** **D-3.** (a) $\text{Ph}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$ **(b) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_{11}$** **(c) $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{OCH}_3$** **D-4.** (A) = PhCOOH , (B) = PhOH **D-5.** (a) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{OH}$ **(b) $\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)(\text{OH})-\text{COOH}$** **PART - II****A-1.** (C)**A-2.** (A)**A-3.** (A)**A-4.** (D)**A-5.** (A)**A-6.** (B)**A-7.** (A)**B-1.** (C)**B-2.** (B)**B-3.** (C)**B-4.** (C)**B-5.** (A)**B-6.** (C)**B-7.** (B)**C-1.** (B)**C-2.** (A)**C-3.** (D)**C-4.** (A)**C-5.** (B)**C-6.** (A)**D-1.** (C)**D-2.** (C)**D-3.** (C)**D-4.** (B)**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)**9.** (D)

Organic Reaction Mechanisms-I

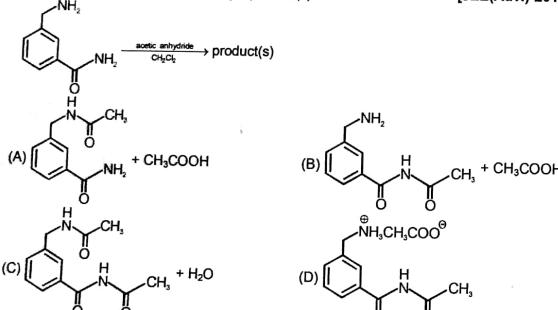
3. The order of reactivity of phenyl magnesium bromide with the following compounds is : [JEE-2004, 3/84]



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

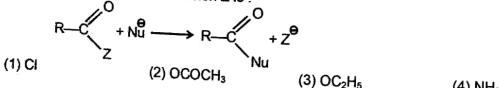
- | Match the compounds/ions in Column I with their properties/reactions in Column II. [JEE 2007, 8/16] | |
|---|--|
| Column-I | Column-II |
| (A) $\text{C}_6\text{H}_5\text{CHO}$ | (p) gives precipitate with 2,4 dinitrophenylhydrazine. |
| (B) $\text{CH}_3\text{C}=\text{CH}$ | (q) gives precipitate with AgNO_3 . |
| (C) CN^- | (r) is a nucleophile. |
| (D) Γ^- | (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)

2. Rate of the reaction is fastest when Z is : (4) Acetyl iodide



Organic Reaction Mechanisms-I

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

- (1) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$ (2) $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$ [AIEEE-2004, 3/225]
 (3) $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$ (4) $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$

4. The decreasing order of the ratio of HCN addition to compounds A to D is [AIEEE-2006, 3/165]
 (A) H₃C (B) CH_3COCH_3 (C) PhCOCH_3 (D) PhCOPh
 (1) d > b > c > a (2) d > c > b > a (3) c > d > b > a (4) a > b > c > d

5. Phenyl magnesium bromide reacts with methanol to give - [AIEEE-2006, 3/165]
 (1) a mixture of anisole and Mg(OH)Br (2) a mixture of benzene and Mg(OMe)Br
 (3) a mixture of toluene and Mg(OMe)Br (4) a mixture of phenol and Mg(OMe)Br

6. The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces [AIEEE-2008, 3/105]
 (1) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (2) $\begin{matrix} \text{H} & \text{H} \\ | & | \\ \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \end{matrix}$ (3) CH_4 (4) $\text{CH}_3-\text{CH}=\text{CH}_2$

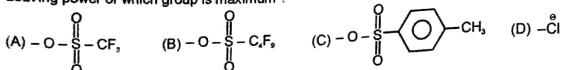
7. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with fruity smell was formed. The liquid was : [AIEEE-2009, 4/144]
 (1) HCHO (2) CH_3COCH_3 (3) CH_3COOH (4) CH_3OH

8. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in the above reaction is : [AIEEE-2011, 4/120]
 (1) Diethyl ether (2) 2-Butanone (3) Ethyl chloride (4) Ethyl ethanoate

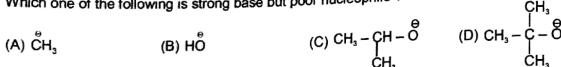
9. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is : [JEE(Main)-2013, 4/12]

Organic Reaction Mechanisms-I

1. Leaving power of which group is maximum?

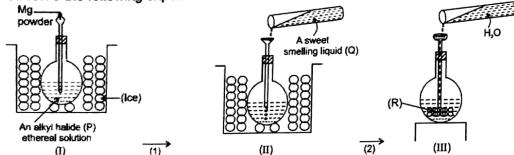


2. Which one of the following is strong base but poor nucleophile?

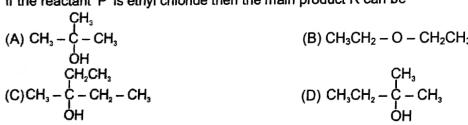


Comprehension # 2

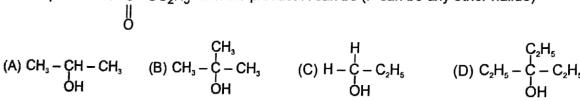
Observe the following experiment



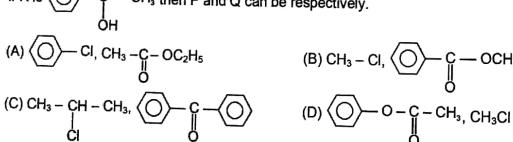
3.a. If the reactant 'P' is ethyl chloride then the main product R can be



4.a. 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.a. If R is



Organic Reaction Mechanisms-I

Comprehension # 3

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

Column-1	Column-2	Column-3
(I) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2-\text{C}(=\text{O})-\text{OH} \xrightarrow{\text{H}^+}$	(i) Acid base reaction	(P) 2,4-DNP test
(II)	(ii) Nucleophilic addition reaction	(Q) Carbylamine test
(III)	(iii) Nucleophilic substitution reaction	(R) Lucas test
(IV) $\text{CH}_3-\text{CH}_2-\text{NH}_2 \xrightarrow{\text{CH}_3\text{MgBr}}$	(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)

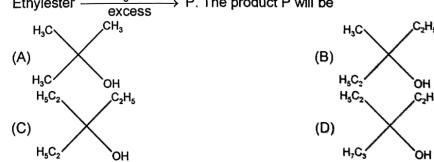
Exercise-3

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

* Marked Questions may have more than one correct option.

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), $\text{C}_{16}\text{H}_{32}\text{O}$, 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



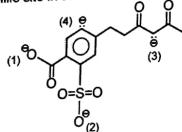
[JEE-2003, 3/84]

Organic Reaction Mechanisms-I

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

- | | | | |
|----------------------|----------------------------|--|----------------------|
| (i) CH_3^+ | (ii) I^- | (iii) NO_2^- | (iv) CH_3^+ |
| (v) NH_3 | (vi) Br^- | (vii) $\overset{\ddagger}{\text{Cl}}$ | (viii) H^+ |
| (ix) AlCl_3 | (x) CH_3OH | (xi) $\text{CH}_3-\overset{\ddagger}{\text{C}}=\text{O}$ | (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^- (C) NaHSO_3 (D) Cl^-

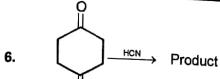
3. The correct order of leaving group ability is/are :

- (A) > (B) $\text{CF}_3\text{SO}_3^- > \text{CCl}_3\text{SO}_3^-$
 (C) $\text{CN}^- > \text{I}^-$ (D) $\text{NH}_2^- > \text{OH}$

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) $\text{PhMgBr} + \text{CH}_3-\text{C}=\text{CH}$

5. Which of the following liberate hydrogen gas with NaH ?
 (A) CH_3COOH (B) $\text{CH}_3-\overset{\ddagger}{\text{C}}-\text{NH}_2$
 (C) $\text{CH}_3-\text{C}=\text{CH}$ (D) $\text{CH}_3-\text{CH}_2-\text{OH}$

Organic Reaction Mechanisms-I



The correct statement about product is

- (A) The product is optical inactive (B) The product is meso compound
 (C) The product is mixture of two enantiomer (D) Products are in two diastereomeric forms

7. $\text{R}-\overset{\ddagger}{\text{C}}-\text{OR}' \xrightarrow[2, \text{H}_2\text{O}^\ddagger]{1, \text{MeMgBr (1 eq)}}$ acetone as the sole organic product.

- which is/are correctly matched with R and R'.
- (A) R is $-\text{H}$ (B) R' is $-\overset{\ddagger}{\text{C}}-\text{CH}_3$
 (C) R' is $-\overset{\ddagger}{\text{CH}}-\text{CH}_2$ (D) R is $-\text{CH}_3$

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

- (A) $\text{PhMgBr} + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{MgBr} \xrightarrow[\text{ether}]{\text{H}^\ddagger} \text{Product}$
 (B) $\text{CH}_3\text{MgBr} + \text{Ph}-\overset{\ddagger}{\text{C}}-\text{C}_2\text{H}_5 \xrightarrow[\text{ether}]{\text{H}^\ddagger} \text{Product}$
 (C) $\text{C}_2\text{H}_5\text{MgBr} + \text{Ph}-\overset{\ddagger}{\text{C}}-\text{CH}_3 \xrightarrow[\text{ether}]{\text{H}^\ddagger} \text{Product}$
 (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr} + \text{PhCHO} \xrightarrow[\text{ether}]{\text{H}^\ddagger} \text{Product}$

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) $(\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{CONH}_2$

10. X (an ethyl ester) $\xrightarrow[\text{(ii)} \text{H}_3\text{O}^\ddagger]{\text{(i) Grignard's reagent (Y) (excess)}}$ product

The product(s) may be :

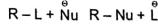
- (A) $\text{Ph}-\overset{\ddagger}{\text{C}}-\text{Ph}$ (B) $\text{CH}_3-\overset{\ddagger}{\text{C}}-\text{C}_2\text{H}_5$ (C) $\text{H}-\overset{\ddagger}{\text{C}}-\text{CHMe}_2$ (D) $\text{Ph}-\overset{\ddagger}{\text{C}}-\text{CH}_2$

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.

Organic Reaction Mechanisms-I

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

(A) OH (B) NH_2 (C) $\text{S}(\text{O})\text{OCH}_3$ (D) $\text{S}(\text{O})\text{CH}_3$

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

5. Which of the following reactions is not feasible ?

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

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

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

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

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

8. Products obtained in the above reaction is -

(A) Diastereomers (B) Enantiomers
 (C) Meso compound (D) Optically pure one product only

9. Consider reduction of 2-butane.

B $\xleftarrow[\text{D}_2\text{O}]{\text{NaBD}_4}$ 2-butane $\xrightarrow{\text{H}_2\text{O}}$ A
 $\xrightarrow[\text{D}_2\text{O}]{\text{NaBH}_4}$ C

(A) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ in all cases
 (B) $\text{CH}_3\text{CH}(\text{OD})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}(\text{OD})\text{CH}_2\text{CH}_3$
 (C) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ in all case
 (D) $\text{CH}_3\text{CH}(\text{OD})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$

Organic Reaction Mechanisms-I

10. Which of the following is correct order of esterification of following acids with CH_3OH :

HCOOH, CH_3COOH , $\text{CH}_3-\text{CH}_2-\text{COOH}$, $\text{CH}_3-\text{CH}-\text{COOH}$

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

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

(P) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{C}-\text{COOH} \\ | \\ \text{D} \end{array}$; (Q) : $\begin{array}{c} \text{CH}_3-\text{CH}-\text{Ph} \\ | \\ \text{OH} \\ (\pm) \end{array}$

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

12. $\begin{array}{c} \text{O} \\ || \\ \text{Cyclohexene} \end{array} \xrightarrow[\text{(2) H}_2\text{O}]{\text{(1) excess PhMgBr}} \text{X, X is}$

(A) $\text{OPh}-\text{Cyclohexene}$ (B) $\text{Ph}-\text{Cyclohexene}-\text{OH}$
 (C) $\text{HO}-\text{Cyclohexene}-\text{Ph}$ (D) $\text{OPh}-\text{Cyclohexene}-\text{Ph}$

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

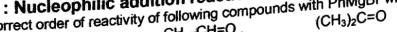
1. How many reactions given below are examples of elimination reactions ?

(I) $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3-\text{CH}-\text{CH}_3$
 (II) $\text{CH}_3-\text{CH}_2-\text{Br} \xrightarrow{\text{NaOH}} \text{CH}_3-\text{CH}_2-\text{OH}$
 (III) $\text{CH}_3-\text{CH}-\text{CH}_3 \xrightarrow{\text{Alc. KOH}} \text{CH}_3-\text{CH}=\text{CH}_2$
 (IV) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{EtOH}/\Delta} \text{CH}_3-\text{C}=\text{CH}-\text{CH}_3$
 (V) $\text{CH}_3-\text{C}(\text{Br})-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{Alc. KOH}} \text{Cyclohexene}$
 (VI) $\text{CH}_3-\text{C}(\text{OH})-\text{CH}_2-\text{CH}_3 \xrightarrow[\Delta]{\text{Con. H}_2\text{SO}_4} \text{Cyclohexene}$
 (VII) $\text{Ph}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3 \xrightarrow{\text{Con. HCl + Anhydrous ZnCl}_2} \text{Ph}-\text{CH}(\text{Cl})-\text{CH}_2-\text{CH}_3$
 (VIII) $\text{H}-\text{C}(\text{C}_2\text{H}_5)-\text{OH} \xrightarrow{\text{HI}} \text{H}-\text{C}(\text{C}_2\text{H}_5)-\text{I}$

Organic Reaction Mechanisms-I

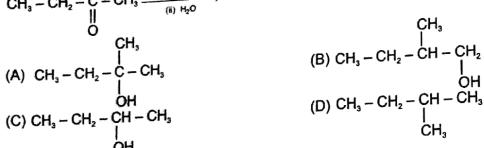
Section (C) : Nucleophilic addition reactions of carbonyl compounds

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



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

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



C-3. $\text{P} \xrightarrow{\text{PhMgBr}} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3-\overset{\text{OH}}{\underset{\text{||}}{\text{C}}}-\text{Ph}$ (d.e.)

- P can be :
 (A) CH_3COOH (B) $\text{H}-\text{COOCH}_3$ (C) CH_3COCl (D) $\text{CH}_3\text{CH=O}$

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

- (A) $\text{CH}_3\text{CH=O} \xrightarrow{\text{(i) CH}_3\text{CH}_2\text{-MgBr}}$
 (ii) $\text{H}_2\text{O} / \text{H}^\circ$



C-5. HCN reacts with fastest rate with :

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

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

- (A) $\text{Ph}_2\text{CD(OH)}$ (B) $\text{Ph}_2\text{CH(OD)}$ (C) $\text{Ph}_2\text{CD(OD)}$ (D) None

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 :

- (A) Acid anhydride > Amide > Ester > Acyl chloride
 (B) Acyl chloride > Ester > Acid anhydride > Amide
 (C) Acyl chloride > Acid anhydride > Ester > Amide
 (D) Ester > Acyl chloride > Amide > Acid anhydride

D-2. Consider the following compounds :



The correct order of reactivity towards hydrolysis is :

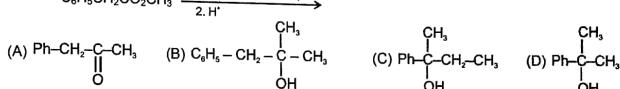
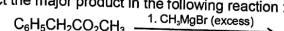
- (A) (i) > (ii) > (iii) > (iv)
 (B) (iv) > (ii) > (i) > (iii)
 (C) (ii) > (iv) > (i) > (iii)
 (D) (ii) > (iv) > (iii) > (i)

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

- (A) $\text{RCOOH} + \text{SOCl}_2 \longrightarrow$
 (B) $\text{RCOOH} + \text{PCl}_5 \longrightarrow$
 (C) $\text{RCOOH} + \text{Cl}_2 \longrightarrow$
 (D) $\text{RCOOH} + \text{PCl}_3 \longrightarrow$

Organic Reaction Mechanisms-I

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



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

Codes :
 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

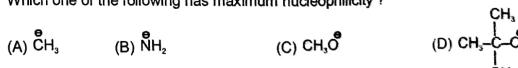
Marked Questions may have for Revision Questions.

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 ?



Organic Reaction Mechanisms-I

Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate (S_N2 Th)

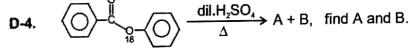
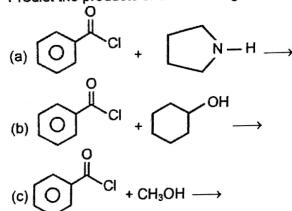
D-1. How many reactions given below are proceed through S_N2 Th mechanism?

- (a) $\text{CH}_3\text{C}(=\text{O})\text{Cl} + \text{NaOH} \longrightarrow$ (b) $\text{CH}_3\text{C}(=\text{O})\text{NH}_2 + \text{NaI} \longrightarrow$
 (c) $\text{CH}_3\text{C}(=\text{O})\text{OH} + \text{C}_2\text{H}_5\text{ONa} \longrightarrow$ (d) $\text{CH}_3\text{C}(=\text{O})\text{OC}_2\text{H}_5 + \text{NaNH}_2 \longrightarrow$

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

- (a) $\text{CH}_3\text{C}(=\text{O})\text{Cl} + \text{CH}_3\text{OH} \longrightarrow$ (b) $\text{CH}_3\text{C}(=\text{O})\text{OC}_2\text{H}_5 + \text{H}_2\text{O} \xrightarrow{-\text{H}^+} \longrightarrow$

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.



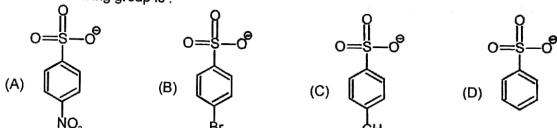
PART - II : ONLY ONE OPTION CORRECT TYPE

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

- A-1. Which of the following is an electrophilic reagent?
 (A) H_2O (B) OH^- (C) NO_2^+ (D) None
 A-2. Which of the following is not a nucleophile?
 (A) AlCl_3 (B) $(\text{CH}_3)_2\text{NH}$ (C) $\text{C}_2\text{H}_5\text{OH}$ (D) H_2O
 A-3. Which one of the following has maximum nucleophilicity?
 (A) $\text{CH}_3\text{S}^\ominus$ (B) $\text{C}_6\text{H}_5\text{O}^\ominus$ (C) $\text{Et}_3\text{N}^\ominus$ (D) F^\ominus
 A-4. Out of the following best leaving group is:
 (A) F^- (B) Cl^- (C) Br^- (D) I^-

Organic Reaction Mechanisms-I

A-5. The best leaving group is :



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

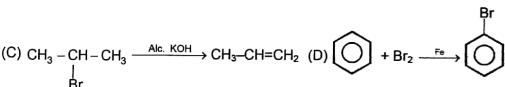
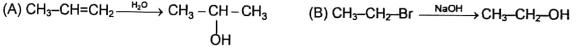
- (A) Acetone (B) Ethanol (C) DMF (D) Ether

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

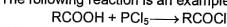
- (A) DMSO (B) NH_3 (C) H_2O (D) CH_3COOH

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

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



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 $\text{CH}_3-\text{C}(=\text{O})\text{CH}_2 \xrightarrow[\text{H}^+]{} \text{CH}_3-\text{C}(=\text{O})\text{CH}_3$

- (A) Acid-base reaction (B) Substitution reaction
 (C) Addition reaction (D) Elimination reaction

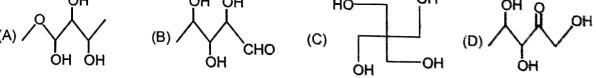
B-4. $\text{C}_6\text{H}_5\text{COOH} + \text{CH}_3\text{MgI} \longrightarrow ?$

- (A) $\text{C}_6\text{H}_5\text{COOMgI}$ (B) CH_4 (C) Both A & B (D) none

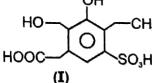
B-5. $(\text{CH}_3)_2\text{CMgCl}$ on reaction with D_2O produces:

- (A) $(\text{CH}_3)_2\text{CD}$ (B) $(\text{CH}_3)_2\text{COD}$ (C) $(\text{CD}_3)_2\text{CD}$ (D) $(\text{CD}_3)_2\text{COD}$

B-6. A compound X ($\text{C}_5\text{H}_{10}\text{O}_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).



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



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

Exercise-1

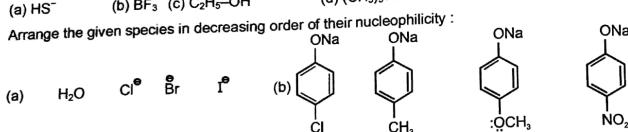
Marked Questions may have for Revision Questions.

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) NO_2

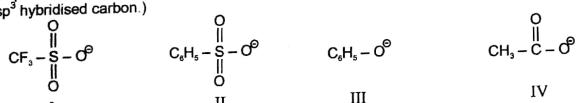
- A-2.** Which of the followings are nucleophile ?
 (a) HS^- (b) BF_3 (c) $\text{C}_2\text{H}_5\text{-OH}$ (d) $(\text{CH}_3)_3\ddot{\text{N}}$ (e) $:\text{CH}_2$

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

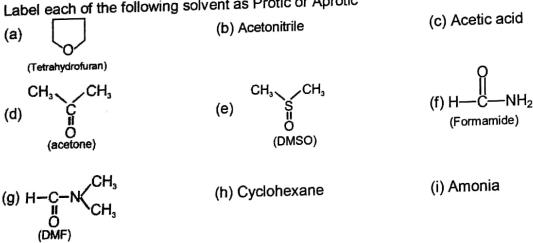


- A-4.** Define ambident nucleophile with an example :

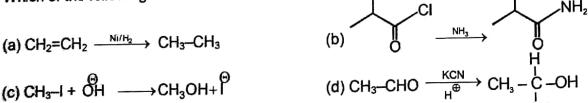
- A-5.** In nucleophilic substitution reactions the leaving ability order for the following species is (when attached to the sp^2 hybridised carbon.)



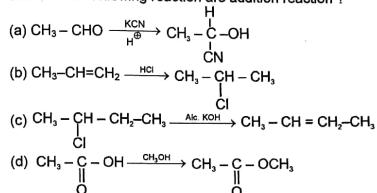
- A-6.** Label each of the following solvent as Protic or Aprotic

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

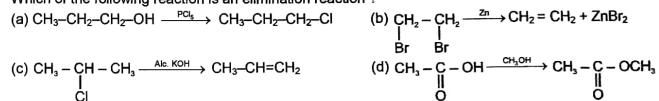
- B-1.** Which of the following reactions are substitution reaction ?



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

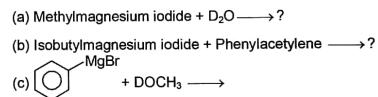


- B-3.** Which of the following reaction is an elimination reaction ?

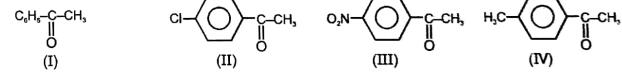


- B-4.** An organic compound which have molecular formula $\text{C}_4\text{H}_4\text{O}_3$, gives 3 moles of gas on treatment with methyl magnesium bromide. Give structure of the compound.

- B-5.** Predict the product of the following reactions

**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

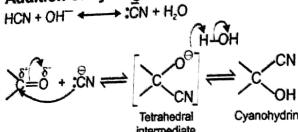


- C-5.** What is the product of each reaction when acetophenone treated with



Organic Reaction Mechanisms-I

(i) Addition of hydrogen cyanide (HCN)

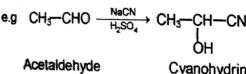


Note : (i) Addition of HCN over aldehyde and ketones gives cyanohydrin.

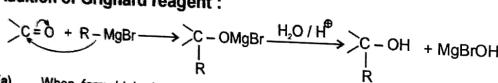
(ii) Cyanohydrin on acid hydrolysis gives α -hydroxy acid.

(iii) Cyanohydrin on treating with $\text{NH}_3(\text{l})$ followed by acid hydrolysis gives α -amino acid.

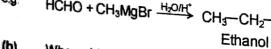
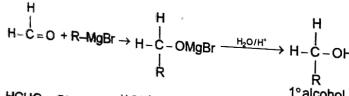
(iv) In case of ketone cyanohydrin formation is reversible due to bulky groups of ketone which hinder the formation.



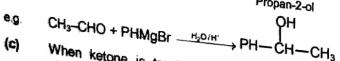
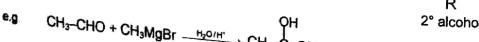
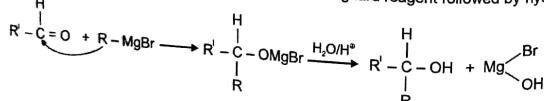
(ii) Addition of Grignard reagent :



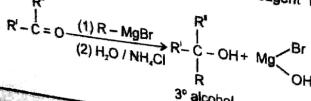
(a) When formaldehyde is treated with Grignard reagent followed by acid hydrolysis primary alcohol is obtained.



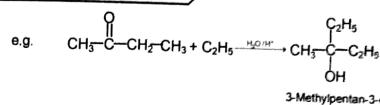
(b) When aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis 2° alcohol is obtained.



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

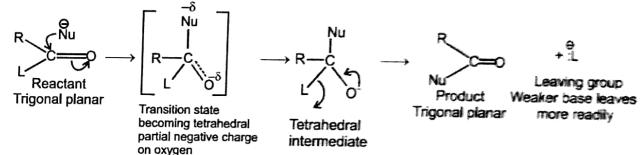


Organic Reaction Mechanisms-I



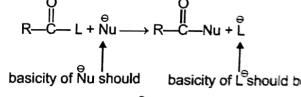
Section (D) : Bimolecular nucleophilic substitution reaction with tetrahedral intermediate ($\text{S}_{\text{N}}\text{2Th}$)

Characteristic reaction of acid and its derivatives (acid halide, anhydride, ester and amide) is $\text{S}_{\text{N}}\text{2Th}$. 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.



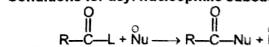
The tetrahedral intermediate formed, when a nucleophile attacks the carbonyl carbon of a carboxylic acid derivative, is not stable and can not be isolated.

A pair of nonbonding electrons on the oxygen reforms the π bond, and either L^- or Nu^- is eliminated with its bonding electrons. Whether L^- or Nu^- 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.

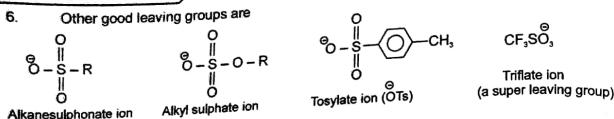
Conditions for acyl nucleophilic substitution reactions :



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

Reactivity order : $\text{R}-\text{C}(=\text{O})-\text{Cl} > \text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R} > \text{R}-\text{C}(=\text{O})-\text{OR} > \text{R}-\text{C}(=\text{O})-\text{NH}_2$

Organic Reaction Mechanisms-I



Note :

- (i) Strong bases rarely act as leaving group \rightarrow
 $\text{Br} + \text{R}-\text{OH} \rightleftharpoons \text{R}-\text{Br} + \text{OH}^-$ (Strong base / poor leaving group)
 $\text{Nu} + \text{CH}_3-\text{CH}_2 \rightleftharpoons \text{CH}_3-\text{Nu} + \text{CH}_2^-$ (It is not a leaving group)

(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.

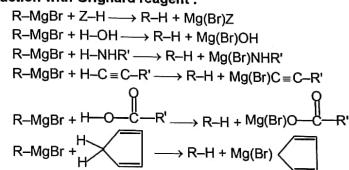
Solvents	Polar	Protic	Aprotic	Remarks
1. H_2O	✓	✓	—	Polar protic solvent
2. CH_3OH	✓	✓	—	Polar protic solvent
3. $\text{CH}_3\text{CH}_2\text{OH}$	✓	✓	—	Polar protic solvent
4. $\text{H}-\text{COOH}$	✓	✓	—	Polar protic solvent
5. CH_3-COOH	✓	✓	—	Polar protic solvent
6. NH_3	✓	✓	—	Polar protic solvent
7. $\begin{array}{c} \text{CH}_3-\text{C}=\text{O} \\ \\ \text{CH}_3 \end{array}$ (acetone)	✓	x	✓	Polar aprotic solvent
8. $\begin{array}{c} \text{CH}_3-\text{S}-\text{CH}_3 \\ \\ \text{O} \end{array}$ Dimethyl sulphoxide	✓	x	✓	Polar aprotic solvent
9. $\begin{array}{c} \text{H}-\text{C}=\text{N}-\text{CH}_3 \\ \\ \text{O} \\ \text{H}-\text{C}-\text{N}-\text{CH}_3 \end{array}$ Dimethyl formamide	✓	x	✓	Polar aprotic solvent
10. $\begin{array}{c} \text{CH}_3-\text{C}-\text{N}-\text{CH}_3 \\ \\ \text{O} \\ \text{H}-\text{C}-\text{N}-\text{CH}_3 \end{array}$ Dimethyl acetamide	✓	x	✓	Polar aprotic solvent
11.	x	x	✓	Non-polar solvent
12.	x	x	✓	Non-polar solvent
13. $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	x	x	✓	Non-polar solvent

Organic Reaction Mechanisms-I

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 alkalies : $\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$
 - (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 :

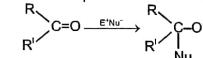


Section (C) : Nucleophilic addition reactions of carbonyl compounds

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

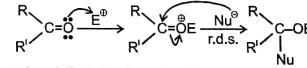
This reaction involves addition of a nucleophile and an electrophile across the ($\text{C}=\text{O}$) double bond.

The general nucleophilic addition reaction can be represented as follows :

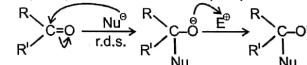


The mechanism can be carried out in following two manners.

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



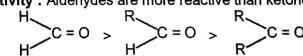
(b) Base catalysed (first attack is of nucleophile)



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.



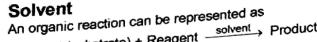
There are two factors which influence the reactivity of ketone and aldehyde.

- (i) Inductive effect
- (ii) steric factor
- (i) + I effect of alkyl group decrease the amount of charge on C^{\oplus} ($\text{C}^{\oplus}-\text{O}^{\ominus}$) in ketones.
- (ii) Steric effect also causes the less reactivity of carbonyl group.

Organic Reaction Mechanisms-I

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

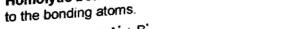
An organic reaction can be represented as



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.



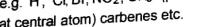
A heterolytic bond dissociation always generate a cation and an anion.

Types of reagents :

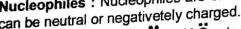
A reagent generates three type of attacking species. Which are :

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

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



(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.



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



Nucleophilicity :

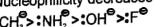
The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity.

(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.



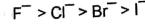
\therefore In a group, nucleophilicity increases from top to bottom because size of donor atom increases but basicity decreases from top to bottom.

Acidic strength : HI > HBr > HCl > HF

Basic strength : F $^-$ > Cl $^-$ > Br $^-$ > I $^-$

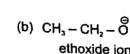
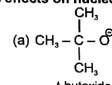
Nucleophilicity : F $^-$ < Cl $^-$ < Br $^-$ < I $^-$

(iii) Nucleophilicity of halogenes in polar aprotic solvents :



Organic Reaction Mechanisms-I

(iv) Steric effects on nucleophilicity

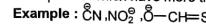


Note : Because (a) can not approach to carbon atom easily.

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.

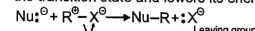


Comparison between Nucleophilicity & Basicity :

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 $\begin{array}{c} \text{R}-\text{C}-\text{O}^+ > \text{R}-\text{S}-\text{O}^+ \\ \qquad \qquad \\ \text{O} \qquad \qquad \text{O} \end{array}$ 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.

