Exercise-1

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

Section (A) : Reagents (Electrophiles, Nucleophiles, Carbene), Solvents, leaving group

A-5. Sol. CN^- is a nucleophile due to presence of negative charge.

A-7. Sol. On going left to right in period nucleophilicity decreases.

A-8. Sol. CN^- is an ambident nucleophile because it has two lone pair donar atom (C and N).

A-11. Sol. SO_3 is electron deficient specie thus it is a lewis acid.

A-12. Sol. $\overset{\oplus}{N}H_4$ do not have lone pair of electron.

A-13. Sol. Sulphur belongs to IIIrd period so it has maximum nucleophilicity.

A-14. Sol. On going top to bottom in group nucleophilicity increases.

A-15. Sol. As delocalisation of negative charge increases nucleophilicity decreases.

A-16. Sol. Leaving group ability ∝ stability of anion.

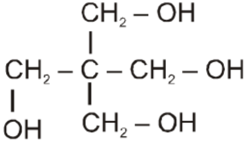
Section (B) : Reaction of acidic Hydrogen

B-2. Sol. (A) $C_6H_5COOH + CH_3MgI \longrightarrow CH_4 + C_6H_5COOMgI$

B-3. Sol. $(CH_3)_3CMgCl + D_2O \longrightarrow (CH_3)_3CD + Mg(OD)Cl$

B-4. Sol. $C_5H_{12}O_4 \xrightarrow{CH_3MgBr} 4CH_4\uparrow$.

It means compound (X) contains 4 acidic hydrogen.

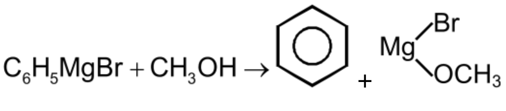


$$\begin{array}{ccl} & CH_2-OH & \\ & | & \\ CH_2- & C & -CH_2-OH \\ | & | & \\ OH & CH_2-OH & \end{array}$$

B-5. Sol. Active hydrogen containing functional group release CH_4 gas with CH_3MgBr. (i.e. OH, COOH, SO_3H)

B-7. Sol. All of these reaction give CH_4.

B-8. Sol.



Section (C) : Nucleophilic addition reaction of Aldehydes and Ketones

C-1. Sol. Basic Information.

C-2. Sol. Nucleophilic attack can be faster at carbon containing more partial (+) charge (more electrophilic centre) and less steric crowding.

Rate of Nucleophilic addition reaction ∝ δ^+ at C=O group.

$$\propto \frac{1}{\text{steric hinderance at } C=O \text{ group}}$$

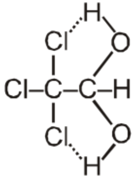
C-3. **Sol.** Nucleophilic attack can be faster at carbon containing more partial (+) charge (more electrophilic centre) and less steric crowding.

Rate of Nucleophilic addition reaction $\propto \delta^+$ at C=O group.

$$\propto \frac{1}{\text{steric hinderance at } C=O \text{ group}}$$

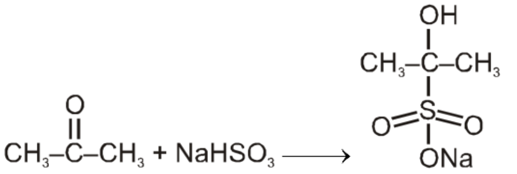
C-5. **Sol** As steric hinderance increases around carbonyl group, the rate of nucleophilic addition reaction decreases.

C-6. **Sol.** Those hydrates are stable which can be stabilised by any factor (e.g. Intramolecular H-bonding)



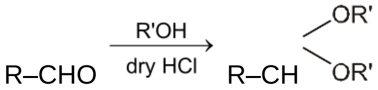
(Chloral hydrate is a stable compound)

C-7. **Sol.**



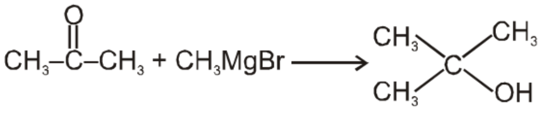
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + NaHSO_3 \longrightarrow CH_3-\overset{OH}{\overset{|}{C}}(SO_2ONa)-CH_3$$

C-8. **Sol.**



$$R-CHO \xrightarrow[\text{dry HCl}]{R'OH} R-CH(OR')_2$$

(Acetal)

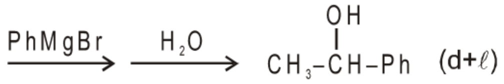


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \longrightarrow (CH_3)_3C-OH$$

(3°alcohol)

C-10. **Sol.**

C-11. **C-12.** P

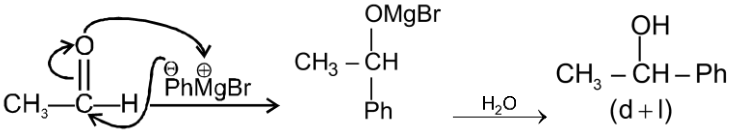


$$P \xrightarrow{PhMgBr} \xrightarrow{H_2O} CH_3-\overset{OH}{\overset{|}{C}}H-Ph \quad (d+\ell)$$

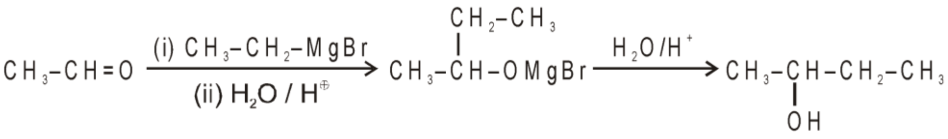
P can be :

(1) CH_3COOH (2) $H-COOCH_3$ (3) CH_3-COCl (4*) $CH_3-CH=O$

Sol.



+ Mg(OH)Br



$$CH_3-CH=O \xrightarrow[\text{(ii) } H_2O / H^{\oplus}]{\text{(i) } CH_3-CH_2-MgBr} CH_3-\underset{CH_2-CH_3}{CH}-OMgBr \xrightarrow{H_2O/H^+} CH_3-\underset{OH}{CH}-CH_2-CH_3$$

C-13. **Sol.**

It is a nucleophilic addition of Grignard reagent to carbonyl group.

C-14. **Sol.** As steric hinderance increases around carbonyl group, the rate of nucleophilic addition reaction decreases.

C-15. **Sol.** Electron withdrawing (–I, –M) groups (eg. NO_2) increases reactivity towards nucleophilic addition reaction.

C-17. **Sol.** Reactivity of Neucleophilic addition reaction $\propto$ EWG.

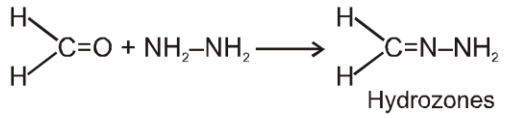
Section (D) : Addition Elimination reactions of aldehydes & ketones

D-1. **Sol.** $R–CHO + NH_2OH \xrightarrow[\Delta]{H^-} R–CH=N–OH$
(Hydroxylamine) (Oxime)

D-2. **Sol.** $CH_3–CH=O + NH_2–NH–CO–NH_2 \xrightarrow[\Delta]{H^-} CH_3CH = NNHCONH_2$

D-3. **Sol.** Here 1, 2, 3 give addition-elimination reaction, while 4 gives only addition reaction with aldehyde and ketone.

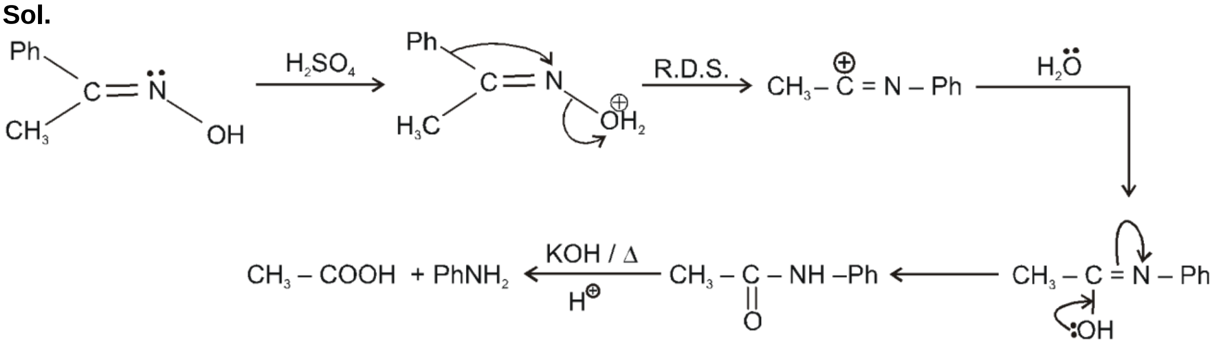
D-4. **Sol.**



D-5. **Sol.** $R–CH=O + R–NH_2 \xrightarrow[-H_2O]{} \underset{\text{imine}}{R-CH=N-R}$ [Schiff's base]

D-6. **Sol.** It is Beckmann's rearrangement

D-7. **Sol.**



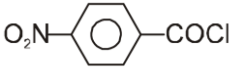
D-8. **Sol.** Basic Information.

D-9. **Sol.** $C_6H_5CHO + C_6H_5NH_2 \xrightarrow{\Delta} Ph–CH=N–Ph$
Schiff's base

Section (E) : S_N2Th reaction of acid and acid derivatives (with nucleophiles PCl_5 , $SOCl_2$, R-MgX ,ROH, Amines, OH^-, H^+/H_2O)

E-1. **Sol.** The reactivity towards nuecleophilic substitution reaction is
Acyl chloride > Acid anhydride > Ester > Amide

E-2. **Sol.** Decreasing order of their reactivity toward hydrolysis is :



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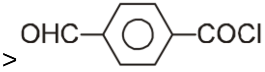
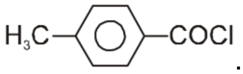


> C_6H_5COCl >



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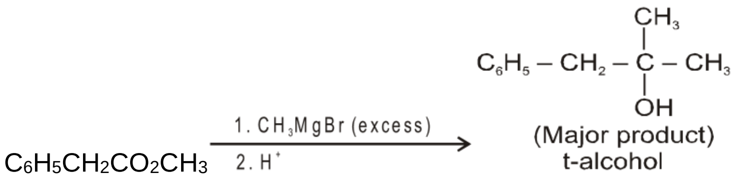
E-3. **Sol.** $RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$

$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$

$RCOOH + PCl_3 \longrightarrow RCOCl + H_3PO_3$

E-4. **Sol.** Reactivity $\propto$ Partial positive charge on C=O carbon.

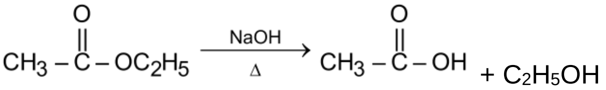
E-5. **Sol.** 

$$C_6H_5CH_2CO_2CH_3 \xrightarrow[2.\ H^+]{1.\ CH_3MgBr\ (excess)} C_6H_5-CH_2-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

(Major product)
t-alcohol

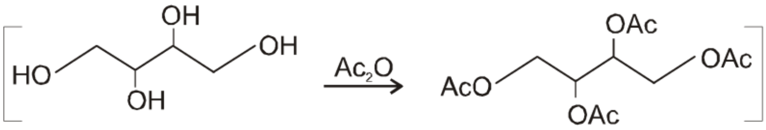
E-6. **Sol.** $CH_3CH_2CH_2CONH_2 \xrightarrow[\Delta]{NaOH} CH_3CH_2CH_2COO^- \xrightarrow{HCl} CH_3CH_2CH_2COOH + NH_4Cl$

E-7. **Sol.** $CH_3CONH_2 \xrightarrow[\Delta]{NaOH} NH_3\uparrow + CH_3COO^-$



$$CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[\Delta]{NaOH} CH_3-\overset{O}{\overset{\|}{C}}-OH + C_2H_5OH$$

E-8. **Sol.** $C_4H_{10}O_4 \xrightarrow{Ac_2O} C_{12}H_{18}O_8$



Exercise-2

Marked Questions may have for Revision Questions.

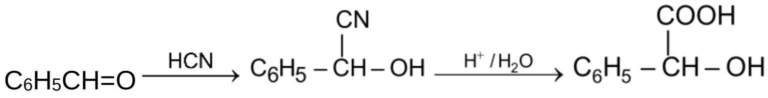
PART - I : OBJECTIVE QUESTIONS

Section (A): Reagents (Electrophiles, Nucleophiles, Carbene),Solvents, leaving group:

1. **Sol.** Strength of nucleophile generally increases on going down a group in the periodic table, because polarising strength of anion increases.

2. **Sol.** $:CCl_2$ is electron deficient specie thus it is a Lewis acid.

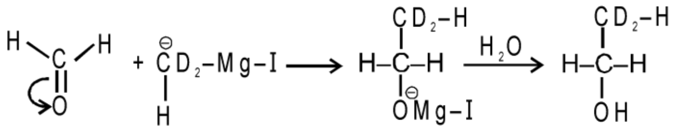
Section (C) : Nucleophilic addition of carbonyl compounds

5. **Sol.** 

$$C_6H_5CH{=}O \xrightarrow{HCN} C_6H_5-\overset{CN}{\overset{|}{C}H}-OH \xrightarrow{H^+/H_2O} C_6H_5-\overset{COOH}{\overset{|}{C}H}-OH$$

Cyanohydrin Mandelic acid

6. **Sol.** –I and –M group increase electrophilicity on –CHO group so rate of nucleophilic addition reaction increases.

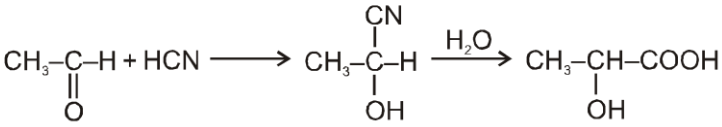
7. **Sol.** 

10. **Sol.** Order of Rate of functional group with RMgX : (RMgX ds lkFk fØ;kRed lewg dh nj dk Øe)

–OH > –CH=O > >C=O > –COOR

11. **Sol.** Rate of esterification $\propto \dfrac{1}{\text{Steric crowding}}$.

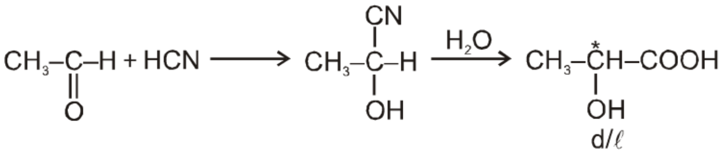
12. **Sol.**



$$CH_3-\underset{\underset{O}{\|}}{C}-H + HCN \longrightarrow CH_3-\overset{CN}{\underset{OH}{C}}-H \xrightarrow{H_2O} CH_3-\underset{OH}{CH}-COOH$$

(Lactic acid)

13. **Sol.**

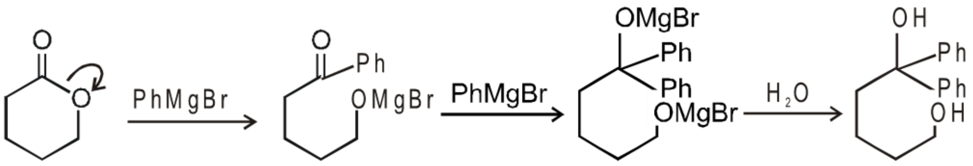


$$CH_3-\underset{\underset{O}{\|}}{C}-H + HCN \longrightarrow CH_3-\overset{CN}{\underset{OH}{C}}-H \xrightarrow{H_2O} CH_3-\underset{\underset{d/\ell}{OH}}{\overset{*}{CH}}-COOH$$

(Lactic acid)

14.

Sol.



PART - II : MISCELLANEOUS QUESTIONS

Section (A) : ASSERTION/REASONING

A-1. **Ans.** (2)
Sol. Carbonyl compounds have polar double bond (>C=O) so give nucleophilic addition reaction.

A-2. Ans. (1)
Sol. Because of less steric hindrance around >C=O group in cyclopropanone rate of addition reaction is faster.

A-3. **Ans.** (1)
Sol. S_N2 Th is a sterically as well as electronically controlled reaction i.e., steric crowding around acyl carbon decreases rate of reaction and inerease in +ve charge centre around acyl carbon increases rate of reaction :

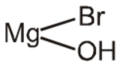
A-4. **Ans.** (4)
Sol. G.R. can not be prepare in aqueous solution due to acid base reaction.

Section (B) : MATCH THE COLUMN

B-1. **Ans.** (A : s) ; (B : q) ; (C : r) ; (D : p)

Section (C) : ONE OR MORE THAN ONE OPTIONS CORRECT

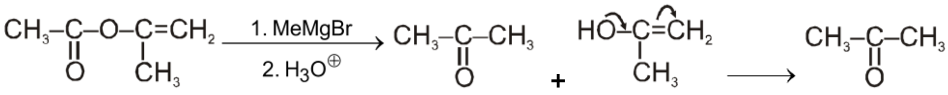
C-1. **Sol.** (2) $PhMgBr + H_2O \longrightarrow Ph-H +$



$$Mg\begin{matrix}Br\\OH\end{matrix}$$

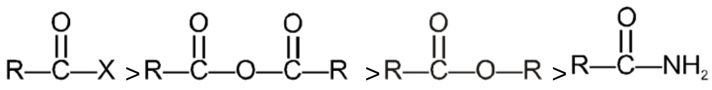
(4) $PhMgBr + CH_3-C\equiv C-H \longrightarrow Ph-H + CH_3-C\equiv C-MgBr$

C-2. **Sol.**



$$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{CH_3}{C}=CH_2 \xrightarrow[2.\ H_3O^{\oplus}]{1.\ MeMgBr} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + HO-\underset{CH_3}{C}=CH_2 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

C-4. **Sol.** Hydrolysis of acid derivatives is S_N2Th reaction and the reactivity of acid derivatives toward S_N2Th is



$$R-\overset{\overset{O}{\|}}{C}-X > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R > R-\overset{\overset{O}{\|}}{C}-O-R > R-\overset{\overset{O}{\|}}{C}-NH_2$$

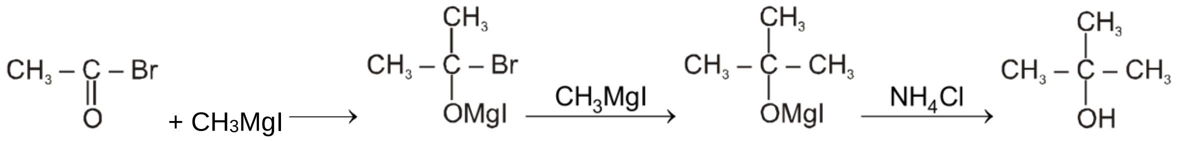
C-5. **Sol.** Product must have two identical alkyl/aryl groups.

Exercise-3

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

1.

Sol.

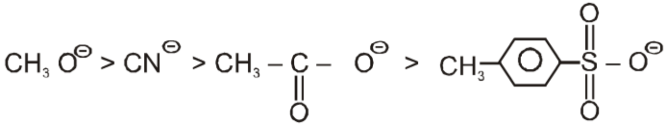


2-Methyl-2-propanol

2. **Sol.** Among the given option Cl^- is the best leaving group hence the rate of reaction will be fastest in case of RCOCl.

3. **Sol.** No reaction occurs on mixing NaCl and ethyl acetate.

4. **Sol.** Nucleophilicity order



5. **Sol.** $CH_3OH + C_6H_5MgBr \rightarrow C_6H_6 + Mg(OCH_3)Br$

methanol phenylmagnesium bromide benzene

6. **Sol.** If the nucleopilic atom or the centre is same, nucleophilicity parallels basicity, i.e., more basic the species stronger is the nucleophile.

$CH_3O^- > HO^- > PhO^- > AcO^-$

Here, the nucleophilic atom i.e. O is the same in all these species, This order can be easily explained on the general concept that a weaker acid has a stronger conjugate base.

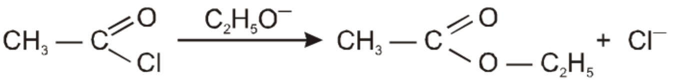
7. **Sol.** As increase steric hinderance around carbonyl group then rate of nucleophilic addition reaction decreases.

8. **Sol.** $CH_3MgX + CH_3-C\equiv CH \longrightarrow CH_4 + CH_3-C\equiv C-MgX$

9. **Sol.** $CH_3COOH + C_2H_5OH \xrightarrow{H_2SO_4} CH_3COOC_2H_5 + H_2O$

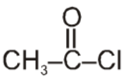
Ester (Fruity smell)

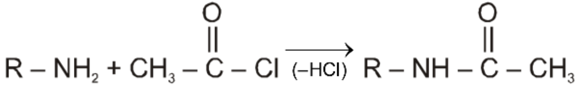
10. **Sol.** RS^θ is more nucleophilic than RO^θ due to larger size of orbitals and polarization but RS^θ is less basic than RO^θ as the negative charge get stabilized due to larger size of sulphur atom.



Ethylethanoate

11. **Sol.**

12. **Sol.** By reaction with one mole of  $CH_3-\overset{\overset{O}{\|}}{C}-Cl$ with one $-NH_2$ group the molecular mass increases with 42 unit. Since the mass increases by (390 – 180) = 210 hence the number of $-NH_2$ groups is 5.



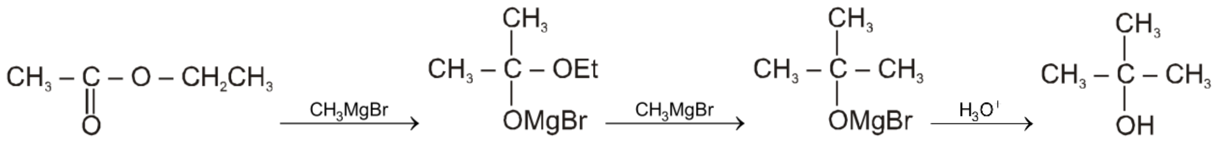
$$R-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[(-HCl)]{} R-NH-\overset{\overset{O}{\|}}{C}-CH_3$$

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

Marked Questions may have more than one correct option.

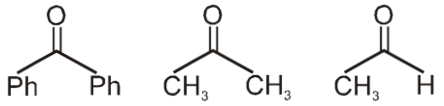
1.

Sol.



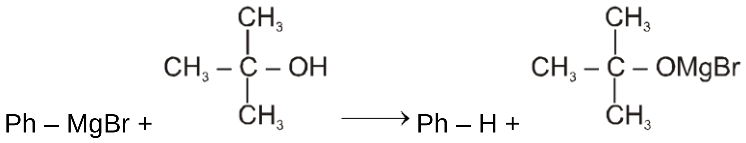
$$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OMgBr}{|}}{C}}-OEt \xrightarrow{CH_3MgBr} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OMgBr}{|}}{C}}-CH_3 \xrightarrow{H_3O^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

2. **Sol.**



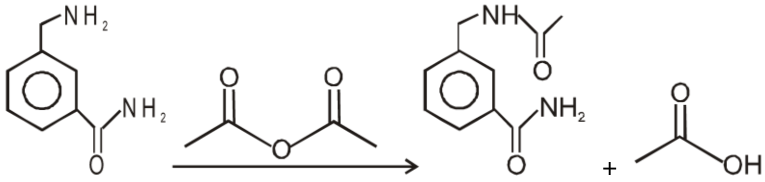
III < I < II

3. **Sol.**



$$Ph-MgBr + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \longrightarrow Ph-H + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OMgBr$$

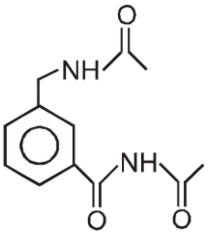
4. **Sol.**



since $-CH_2-NH_2$ is more basic.

The resulting amide will fail to react further. Had it been possible, imied formation would have occured at both the sites.

∴



also results.

Additional Problems For Self Practice (APSP)

Marked Questions may have for Revision Questions.

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

2. **Sol.** The nucleophilicity order is $R^{\ominus} > \overset{\ominus}{N}H_2 > CH_3O^{\ominus} > OH^{\ominus}$

4. **Sol.** Ph–COCl $\xrightarrow{NH_3}$ Ph–CONH$_2$ + HCl

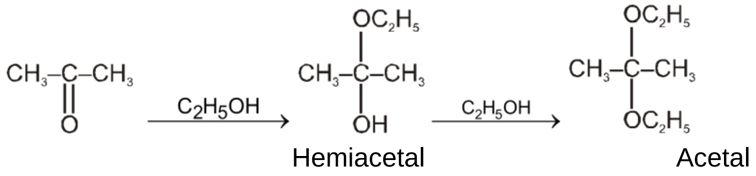
5. **Sol.** The species with complete octet can act as nucleophile.

6. **Sol.** Except HCHO all given carbonyl compound will give racemic mixture.

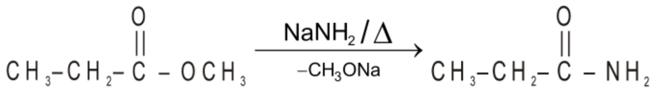
8. **Sol.** Weaker bases are better leaving group.

9. **Ans.** (4)

Sol.

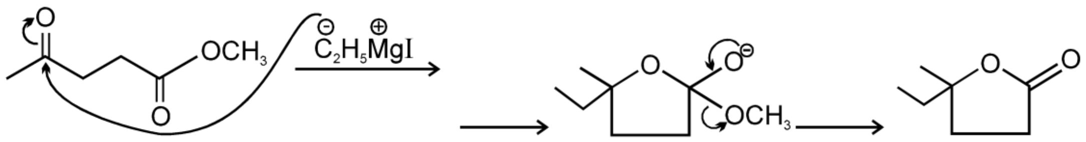


11. **Sol.**

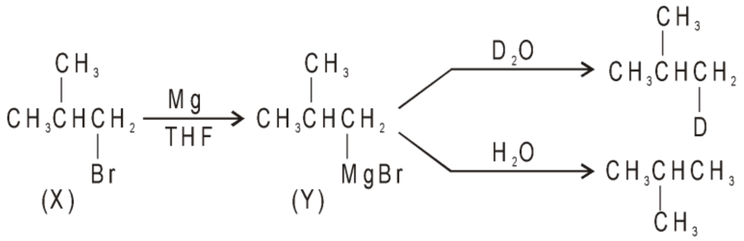


$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-OCH_3 \xrightarrow[-CH_3ONa]{NaNH_2/\Delta} CH_3-CH_2-\overset{\overset{O}{||}}{C}-NH_2$$

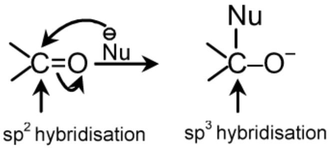
12. **Sol.**



16. **Sol.**

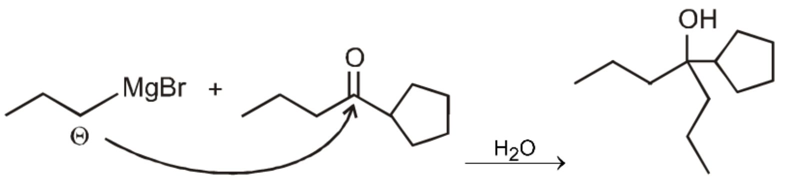


18. **Sol.**

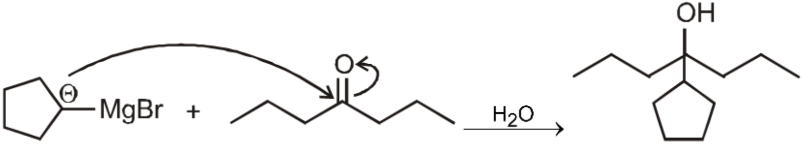


19. **Sol.** Nucleophiles are electron rich species.

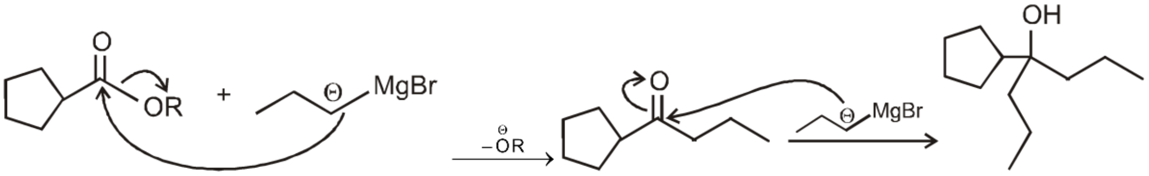
21. **Sol.** (2)



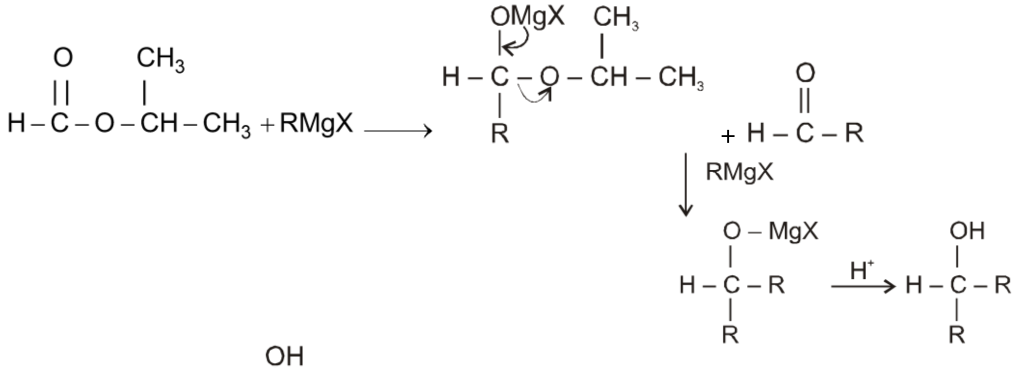
(3)



(4)



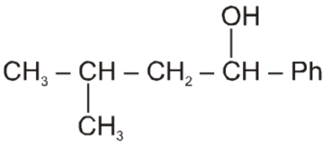
25. **Sol.**



$$H-\overset{\overset{\displaystyle O}{||}}{C}-O-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 + RMgX \longrightarrow H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-O-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$$

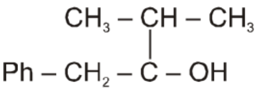
$$+\ H-\overset{\overset{\displaystyle O}{||}}{C}-R \xrightarrow{RMgX} H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O-MgX}{|}}{C}}-R \xrightarrow{H^+} H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R$$

26. **Sol.** (1)



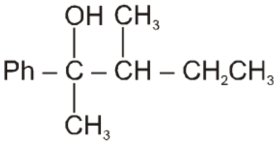
$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{C}H-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-Ph$$

(2)



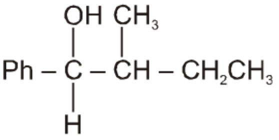
$$\begin{array}{c} CH_3-CH-CH_3 \\ | \\ Ph-CH_2-C-OH \end{array}$$

(3)



$$Ph-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2CH_3$$

(4)



$$Ph-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2CH_3$$

28. **Sol.** Acid hydrolysis of an ester gives two different organic compounds.

$CH_3COOC_2H_5 + H_3O^+ \longrightarrow CH_3COOH + C_2H_5OH$

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

$CH_3CONH_2 + H_3O^+ \longrightarrow \underset{\text{organic compound}}{CH_3COOH} + \underset{\text{Inorganic compound}}{NH_3}$

29. **Hint** : Conjugated base of strong acid is weak base and behave as better leaving group.

30. **Ans.** **(4)**

Sol. $R-CH=O + H_2N-NH_2 \longrightarrow R-CH=N-NH_2$

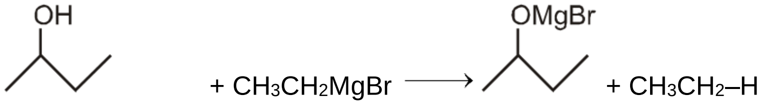
It is a Nucleophilic addition-elimination reaction.

PART - II : PRACTICE QUESTIONS

3. **Sol.** weak bases are best leaving group.

5. **Sol.** Leaving group abilibity ∝ size of leaving atom.

11. **Sol.** It is acid base reaction.



+ $CH_3CH_2MgBr \longrightarrow$ + CH_3CH_2–H

12. **Sol.** A Catalyst provide alternate path thereby decreasing the transition state and accelerates a reaction.

13. **Sol.** Reaction mechanism does not provide the information regarding the energy content of the reacting species.