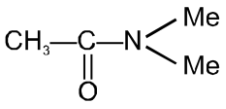
Exercise-1

Marked Questions may have for Revision Questions.

OBJECTIVE QUESTIONS

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

A-1. Which of the following is aprotic solvent ?
(1*) C_6H_6 (2) NH_3 (3) H_2O (4) CH_3COOH

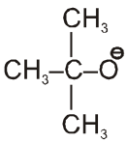
A-2. Which of the following is polar protic solvent ?
(1) CH_3COCH_3 (2*) C_2H_5–OH (3) CH_3SOCH_3 (4) 

A-3. Electrophiles are
(1) Electron deficient species (2) having vacant p or d-orbital
(3) Electron rich species (4*) (1) & (2) both

A-4. Which of the following is an electrophile?
(i) H_2O (ii) OH^- (iii) NO_2^+ (iv) SO_3 (v) PCl_5
(1) i, ii (2) i, iii (3*) iii, iv, v (4) i, ii, iv, v

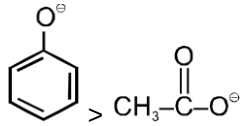
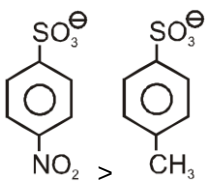
A-5. Which of the following is not an electrophile?
(1*) CN^- (2) H^+ (3) Br^+ (4) $AlCl_3$

A-6. Which of the following statement is correct for nucleophile ?
(1) Electron rich species are called nucleophile.
(2) Nucleophiles are Lewis bases.
(3) Nucleophile donates lone pair of electrons to vacant orbital of carbon atom.
(4*) All are correct.

A-7. Which one of the following has maximum nucleophilicity :
(1*) (2) (3) (4) 

A-8. Which among the following species is an ambident nucleophile ?
(1) Ethene (2) Benzene (3*) Cyanide ion (4) Acetone

A-9. According to Lewis concept of acids and bases, ethers are :
(1) Acidic (2*) Basic (3) Neutral (4) Amphoteric

A-10. Which of the following is **incorrect** order for leaving group ability in S_N reaction ?
(1*)  (2) $Cl^\theta > F^\theta$ (3) $CF_3SO_3^\theta > CH_3SO_3^\theta$ (4) 

A-11. Which of the following is not a lewis base?
(1*) SO_3 (2) $(CH_3)_2$ NH (3) C_2H_5OH (4) $C_2H_5–O–C_2H_5$

A-12. Which of the following is not a nucleophile?
(1) CH_3ONa (2) PhLi (3) PH_3 (4*) $\overset{\oplus}{N}H_4$

A-13. Which one of the following has maximum nucleophilicity :
(1*) $CH_3S^{\ominus}$ (2) $C_6H_5–\overset{\ominus}{O}$ (3) Et_3N (4) $F^{\ominus}$

A-14. For the following the increasing order of nucleophilicity would be :
(i) I^- (ii) Cl^- (iii) Br^-
(1) $I^- < Cl^- < Br^-$ (2) $Br^- < Cl^- < I^-$ (3) $I^- < Br^- < Cl^-$ (4*) $Cl^- < Br^- < I^-$

A-15. Correct arrangement of the following nucleophiles in the order of their nucleophilic strength is :
(1) $C_6H_5O^- < CH_3O^- < CH_3COO^- < OH^-$ (2) $CH_3COO^- < C_6H_5O^- < CH_3O^- < OH^-$
(3) $C_6H_5O^- < CH_3COO^- < CH_3O^- < OH^-$ (4*) $CH_3COO^- < C_6H_5O^- < OH^- < CH_3O^-$

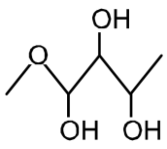
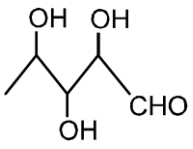
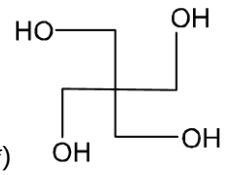
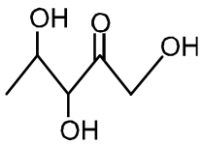
A-16. The correct order of leaving group ability is/are :
(1) $Ph–COO^- > CH_3SO_3^-$ (2*) $\overset{\ominus}{C}F_3SO_3 > \overset{\ominus}{C}Cl_3SO_3$
(3) $\overset{\ominus}{C}N > I^{\ominus}$ (4) $\overset{\ominus}{N}H_2 > \overset{\ominus}{O}H$

Section (B) : Reaction of acidic Hydrogen

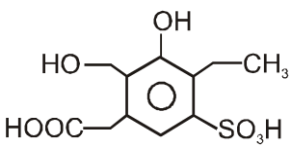
B-1. A five carbon atoms alkyne forms a sodium salt and gives H_2 gas on treatment with sodamide. The alkyne may be
(1) $CH_3CH_2CH_2C{\equiv}CH$ (2) $CH_3C{\equiv}CCH_2CH_3$ (3) $(CH_3)_2CHC{\equiv}CH$ (4*) Either (1) or (3).

B-2. $C_6H_5COOH + CH_3MgI \longrightarrow$?
(1) $C_6H_5COOMgI$ (2) CH_4 (3*) Both (1) & (2) (4) none

B-3. $(CH_3)_3CMgCl$ on reaction with D_2O produces :
(1*) $(CH_3)_3CD$ (2) $(CH_3)_3COD$ (3) $(CD_3)_3CD$ (4) $(CD_3)_3COD$

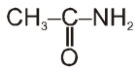
B-4. A compound X ($C_5H_{12}O_4$) upon treatment with CH_3MgX gives 4 mole of methane. Identify the structure of (X).
(1)  (2)  (3*)  (4) 

B-5. How many functional group produced CH_4 gas by the reaction of compound (I) with CH_3MgBr.

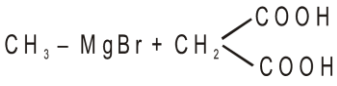


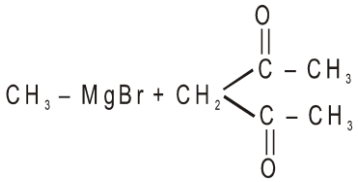
(I)
(1) 3 (2*) 4 (3) 5 (4) 6

B-6. Which of the following does not liberate hydrogen gas with NaH.

(1) $CH_3–COOH$ (2)  (3) $CH_3–C\equiv CH$ (4*) $CH_3–CH_2–NH_2$

B-7. In which of the following reaction CH_4 will be obtained.

(i) $CH_3–MgBr + CH_3–C\equiv CH$ (ii) 



(iii) $CH_3–MgBr + HCN$ (iv)

(1) (i), (ii) & (iii) (2*) (i), (ii), (iii) & (iv) (3) (iii) & (iv) (4) (iii) & (i), (iv)

B-8. The product X formed in the following reaction is

$C_6H_5MgBr + CH_3OH$ □ X

(1*) benzene (2) methoxybenzene (3) phenol (4) toluene

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

C-1. The typical reaction of aldehydes and ketones is :

(1) Nucleophilic substitution (2*) Nucleophilic addition

(3) Electrophilic substitution (4) Electrophilic addition

C-2. Ketones are less reactive than aldehydes because

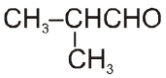
(1) the + I-effect of the alkyl groups increases the electron deficiency of the carbonyl carbon.

(2) the + I-effect of the alkyl groups decreases the electron deficiency of the carbonyl carbon.

(3) steric hindrance to the attacking nucleophile.

(4*) both (2) and (3) are correct.

C-3. Which can give nucleophilic addition most easily ?

(1) CH_3CHO (2) CH_3CH_2CHO (3)  (4*) HCHO

C-4. HCN reacts fastest with :

(1) Acetone (2*) Ethanal (3) Benzophenone (4) cyclohexanone

C-5. The correct order of reactivity of PhMgBr with given compounds is :

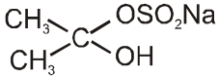
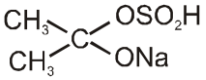
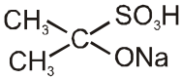
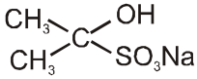
(i) $(C_6H_5)_2CO$ (ii) PhCHO (iii) $Ph–COCH_3$

(1) i > ii > iii (2*) ii > iii > i (3) iii > ii > i (4) i > iii > ii

C-6. Which of the following can form stable hydrate ?

(1) CH_3COCH_3 (2) CH_3CHO (3*) Cl_3CCHO (4) HCHO

C-7. The structure of the addition product formed when acetone reacts with a concentrated aqueous solution of sodium bisulphite is :

(1)  (2)  (3)  (4*) 

C-8. Aldehydes react with alcohols in presence of dry HCl gas to form

(1) Aldols (2*) Acetals (3) Ketals (4) None of these .

C-9. The product of the reaction $Ph_2C{=}O \xrightarrow[H_3O^{\oplus}]{LiAlD_4}$ is

(1*) $Ph_2CD(OH)$ (2) $Ph_2CH(OD)$ (3) $Ph_2CD(OD)$ (4) None (dksbZ ugha)

C-10. Hydrolysis product which is formed by reaction between ketone and Grignard reagent will be :

(1*) $(CH_3)_3COH$ (2) C_2H_5OH (3) $PhCH_2CH_2OH$ (4) $(CH_3)_2CHOH$

C-11. $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr}$ Product is :

(1*) $CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (2) $CH_3-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{CH}}-CH_2$

(3) $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$ (4) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

C-12. P $\xrightarrow{PhMgBr} \xrightarrow{H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-Ph$ $(d+\ell)$

P can be :

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

C-13. Butan-2-ol is obtained by using carbonyl compound and Grignard reagent as :

(1*) $CH_3-CH{=}O \xrightarrow[(ii)\ H_2O/H^{\oplus}]{(i)\ CH_3-CH_2-MgBr}$

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

(3) $\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>\!C{=}O \xrightarrow[(ii)\ H_2O/H^{\oplus}]{(i)\ CH_3-MgBr}$

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

C-14. The general order of reactivities of given carbonyl compounds towards nucleophilic addition reaction is :

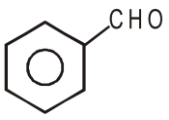
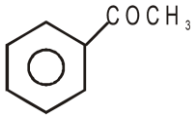
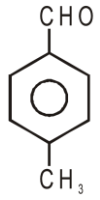
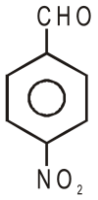
(1) $H_2C{=}O > (CH_3)_2C{=}O > Ar_2C{=}O > CH_3CHO > ArCHO$.

(2*) $H_2C{=}O > CH_3CHO > ArCHO > (CH_3)_2C{=}O > Ar_2C{=}O$.

(3) $ArCHO > Ar_2C{=}O > CH_3CHO > (CH_3)_2C{=}O > H_2C{=}O$.

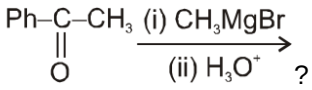
(4) $Ar_2C{=}O > (CH_3)_2C{=}O > ArCHO > CH_3CHO > H_2C{=}O$.

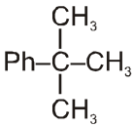
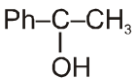
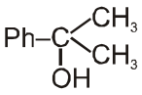
C-15. Which one is most reactive towards nucleophilic addition reaction ?

(1)  (2)  (3)  (4*) 

C-16. $Ph-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[(ii)\ H_3O^{+}]{(i)\ CH_3MgBr}$?

The product is :



(1) $Ph–CH_2–CH_3$ (2)  (3)  (4*) 

C-17. Give the decreasing order of nucleophilic addition reaction of the following :
(i) HCHO (ii) PhCHO (iii) Chloral ($Cl_3C–CH=O$)(iv) Acetophenone
(1*) iii > i > ii > iv (2) iv > ii > i > iii (3) i > iii > ii > iv (4) iii > i > iv > ii

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

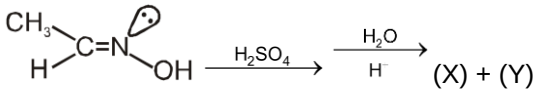
D-1. Oximes are formed by the reaction of aldehydes and ketones with :
(1) NH_3 (2) NH_2NH_2 (3*) NH_2OH (4) $NH_2CONHNH_2$

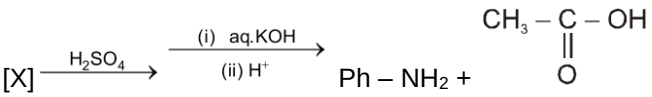
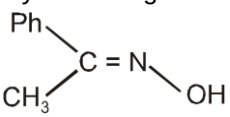
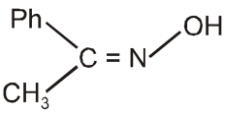
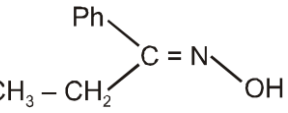
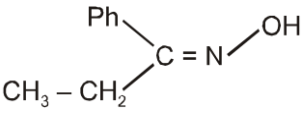
D-2. The structure for acetaldehyde semicarbazone is
(1) $CH_3CH=NCONHNH_2$ (2*) $CH_3CH=NNHCONH_2$
(3) $CH_3CH=NOH$ (4) $CH_3CH=NNH_2$

D-3. Which gives only addition reaction with aldehyde and ketone :
(1) $NH_2–NH_2$ (2) $NH_2NHCONH_2$ (3) $C_6H_5NHNH_2$ (4*) HCN

D-4. Aldehyde with $NH_2–NH_2$ forms :
(1*) hydrazones (2) aniline (3) oxime (4) imine

D-5. Which functional group is formed by the reaction of primary amine with aldehyde?
(1) Amino (2*) Imine (3) hydrazone (4) Nitrito

D-6. 
Product (X) and (Y) are:
(1) NH_3 + HCOOH (2) CH_3 NH_2 + CH_3COOH
(3*) CH_3NH_2 + HCOOH (4) $CH_3CH_2NH_2$+ CH_3COOH

D-7. 
Identify the configuration of compound [X] :
(1*)  (2) 
(3)  (4) 

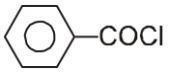
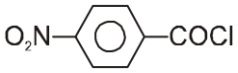
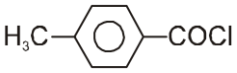
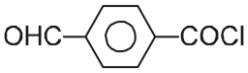
D-8. Schiff's reagent is :
(1*) Magenta solution of p-Rosaniline hydrochloride decolourised with sulphurous acid
(2) Magenta solution of p-Rosaniline hydrochloride decolourised with chlorine
(3) Ammonical cobalt chloride solution
(4) Ammonical manganese sulphate solution.

D-9. When $C_6H_5NH_2$ heated with C_6H_5CHO the product is :
(1*) Schiff's base (2) Amide (3) Azoxy benzene (4) Unsaturated acid

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. The relative reactivity of acyl compounds towards nucleophilic substitution are in the order of :
(1) Acid anhydride > Amide > Ester > Acyl chloride
(2) Acyl chloride > Ester > Acid anhydride > Amide
(3*) Acyl chloride > Acid anhydride > Ester > Amide
(4) Ester > Acyl chloride > Amide > Acid anhydride

E-2. Consider the following compounds :

(i)  (ii)  (iii)  (iv) 

The correct order of reactivity towards hydrolysis is :
(1) (i) > (ii) > (iii) > (iv) (2) (iv) > (ii) > (i) > (iii) (3*) (ii) > (iv) > (i) > (iii) (4) (ii) > (iv) > (iii) > (i)

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

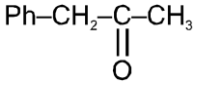
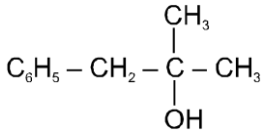
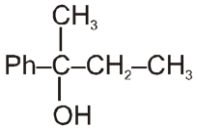
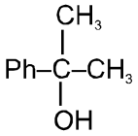
(1) $RCOOH + SOCl_2 \longrightarrow$ (2) $RCOOH + PCl_5 \longrightarrow$

(3*) $RCOOH + Cl_2 \longrightarrow$ (4) $RCOOH + PCl_3 \longrightarrow$

E-4. The decreasing order of reactivity towards nucleophilic acyl substitution is
(i) CH_3COCl (ii) $CH_3COOC_2H_5$, (iii) CH_3CONH_2 (iv) $(CH_3CO)_2O$
(1) (i) > (iv) > (iii) > (ii) (2*) (i) > (iv) > (ii) > (iii) (3) (iv) > (iii) > (i) > (ii) (4) (iii) > (i) > (iv) > (ii)

E-5. Predict the major product in the following reaction:

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

(1)  (2*)  (3)  (4) 

E-6. $CH_3CH_2CH_2CONH_2$ is boiled with aqueous NaOH, then the reaction mixture is acidified with HCl. The products obtained are
(1) $CH_3CH_2CH_2COO^- + NH_3$ (2) $CH_3CH_2CH_2COONa + NH_3$
(3*) $CH_3CH_2CH_2COOH + NH_4Cl$ (4) $CH_3CH_2CH_2COO^- + NH_4Cl$.

E-7. Acetamide and ethyl acetate can be distinguished by reacting with
(1) Aqueous HCl and heat (2*) Aqueous NaOH and heat
(3) Acidified $KMnO_4$ (4) Bromine water.

E-8. A compound with molecular formula $C_4H_{10}O_4$ on acylation with acetic anhydride gives a compound with molecular formula $C_{12}H_{18}O_8$. How many hydroxyl groups are present in the compound ?
(1) one (2) Two (3) Three (4*) Four

Exercise-2

Marked Questions may have for Revision Questions.

PART - I : OBJECTIVE QUESTIONS

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

1. Which of the following statement is not true?
(1) Nucleophiles possess unshared pairs of electron which are utillized in forming bonds with electrophilic substrate.
(2) The cyanide ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its carbon atom or nitrogen atom.
(3) The nitrite ion is an ambident nucleophile and causes nucleophilic substitution of alkyl halide by either of its oxygen atom or nitrogen atom.
(4*) Strength of nucleophile generally decreases on going down a group in the periodic table.

2. Which of the following is not a nucleophile ?
(1*) $:CCl_2$ (2) $(CH_3)_2$ NH (3) C_2H_5OH (4) H_2O

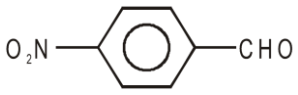
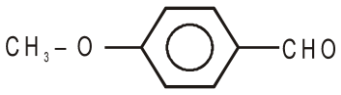
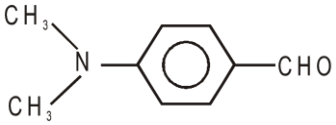
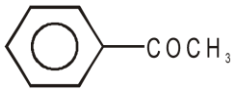
3. Out of the followings best leaving group is :
(1) F^- (2) Cl^- (3) Br^- (4*) I^-

4. Which of the following reactions is not feasible ?

(1) $PhSO_3H + NaHCO_3 \longrightarrow$ (2) $Ph–OH + NaNH_2 \longrightarrow$

(3*) $CH_3–NH_2 + NaOH \longrightarrow$ (4) $Ph–C\equiv CH + NaH \longrightarrow$

5. $C_6H_5CHO \xrightarrow{HCN} X \xrightarrow{H^+/H_2O} Y$
In the above sequence, Y is
(1) Lactic acid (2*) Mandelic acid (3) Malic acid (4) Cinnamic acid

6. Cyanohydrin formation constant will be highest for ?
(1*) 
(2) 
(3) 
(4) 

7. $CH_2O \xrightarrow[H_3O^{\oplus}]{CHD_2MgI} X$
In the above reaction compound X will be :
(1) $CH_3–CHD–OH$ (2) $CH_2D–CH_2–OH$ (3*) $CHD_2–CH_2–OH$ (4) $\begin{matrix} CHD-CH_2-OH \\ | \\ OH \end{matrix}$

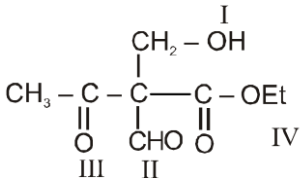
8. Carbonyl compounds undergo nucleophilic addition because of
(1) electronegativity difference of carbon and oxygen atoms
(2) electromeric effect
(3) more stable anion with negative charge on oxygen atom and less stable carbonium ion.

(4*) All

9. The reagent used for the separation of acetaldehyde from acetophenone is :

(1*) $NaHSO_3$ (2) $C_6H_5NHNH_2$ (3) NH_2OH (4) $NaOH + I_2$

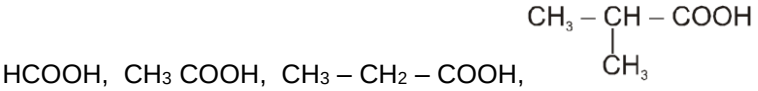
10.



Above compound contains four different functional group the rate of reaction with RMg-X will be :

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

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



HCOOH, CH_3COOH, $CH_3 - CH_2 - COOH$, $CH_3 - CH(CH_3) - COOH$

I II III IV

(1) I = II = III = IV (2*) I > II > III > IV (3) I < II < III < IV (4) I > IV > III > II

12. The cyanohydrin of a carbonyl compound on hydrolysis gives lactic acid. The carbonyl compound is

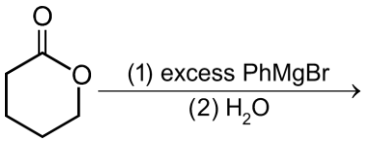
(1) HCHO (2*) CH_3CHO (3) CH_3COCH_3 (4) $CH_3COCH_2CH_3$

13. Reaction of acetaldehyde with HCN followed by hydrolysis gives a compound which shows.

(1*) Optical isomerism (2) Geometrical isomerism

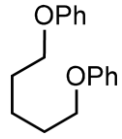
(3) Metamerism (4) Tautomerism

14.

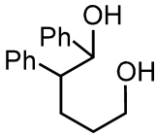


X , X is

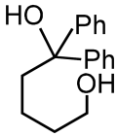
(1)



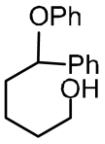
(2)



(3*)



(4)



15. Which of the following compounds would react with PhMgBr subsequently yield Ph_3COH?

(1) a ketone (2) an ester other than formate ester

(3) diethyl carbonate (4*) all of these.

16. The relative reactivity of following compounds towards nucleophile :

(1*) $CH_3CHO > CH_3COCH_3 > CH_3COOCH_3 > CH_3CONH_2$

(2) $CH_3COOCH_3 > CH_3CONH_2 > CH_3CHO > CH_3COCH_3$

(3) $CH_3CONH_2 > CH_3CHO > CH_3COCH_3 > CH_3COOCH_3$

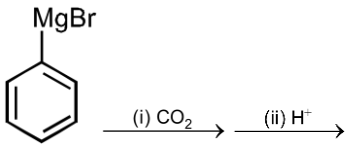
(4) $CH_3CHO > CH_3COOCH_3 > CH_3CONH_2 > CH_3COCH_3$.

17. In the reactions $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN \xrightarrow{H_3O^+} CH_3CH(OH)COOH$,

the acid obtained is:

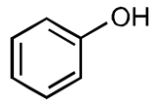
(1) D-isomer (2) L-isomer

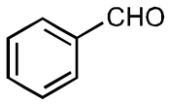
(3) 80% D + 20% L mixture (4*) 50% D + 50% L mixture.

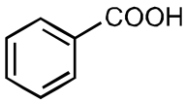
18. 

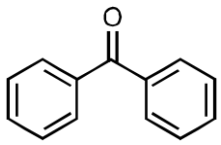
product

The product in this reaction will be

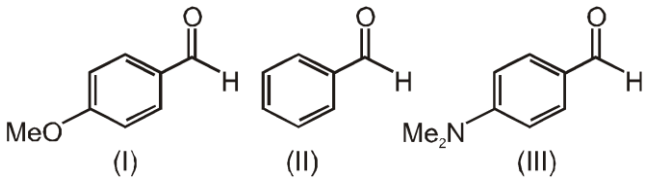
(1) 

(2) 

(3*) 

(4) 

19. The K_{eq} values in HCN addition to following aldehydes are in the order :



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

20. Identify the ester which upon addition of excess Grignard's reagent will provide a secondary alcohol :

(1) CH_3CO_2Et (2) $(CH_3)_2CHCO_2Et$ (3*) HCO_2Et (4) $C_6H_5CO_2Et$

PART - II : MISCELLANEOUS QUESTIONS

Section (A) : ASSERTION/REASONING

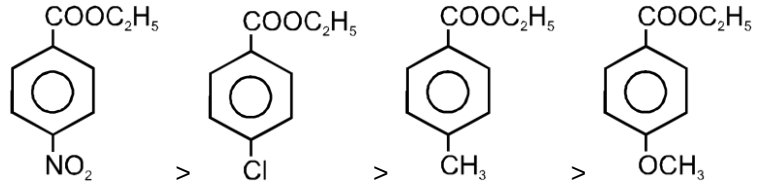
DIRECTIONS : Each question has 4 choices (1), (2), (3) and (4) out of which ONLY ONE is correct.

(1) Both assertion and reason are correct, and the reason is the correct explanation for the assertion
(2) Both assertion and reason are correct, but the reason is not the correct explanation for the assertion
(3) The assertion is incorrect, but the reason is correct
(4) Both are assertion and reason are incorrect

A-1. **Assertion :** Carbonyl compounds take part in nucleophilic addition reactions generally.
Reason : These reactions are initiated by nucleophilic attack at the electron deficient carbon atom.

A-2. **Assertion :** Cyclopropanone undergoes addition with HCN more easily in comparision to acetone
Reason : Cyclopropanone contains strained ring and also has less steric crowding.

A-3. **Assertion :** The order of base catalysed hydrolysis of ester is
(1) $CH_3–COOCH_3 > CH_3–COOC_2H_5 > CH_3–COOCH(CH_3)_2$.

(2) 

Reason : S_N2 Th reaction is sterically as well as electronically controlled reaction.

A-4. **Assertion :** CH_3MgBr is prepared in cold aqueous solution.
Reason : Water molecule stablise Grignard reagent by H-bonding.

Section (B) : MATCH THE COLUMN

Note : Only one answer type (1 × 1)

B-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**

(A) $CH_3COCH_3 + CH_3MgBr \xrightarrow{Ether}$ (p) $CH_3–CH_2–CH_2–OH$

(B) $CH_3–\underset{\underset{O}{\|}}{C}–CH_3 + NaBH_4 \xrightarrow{EtOH}$ (q) $CH_3–\underset{\underset{OH}{|}}{CH}–CH_3$

(C) $CH_3–\underset{\underset{O}{\|}}{C}–CH_2CH_3 + CH_3MgBr \xrightarrow{Ether} \xrightarrow{H_2O}$ (r) $CH_3–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_2–CH_3$

(D) $CH_3–CH_2–\underset{\underset{O}{\|}}{C}–OCH_3 + LiAlH_4 \xrightarrow{Ether} \xrightarrow{H_2O}$ (s) $CH_3–\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}–CH_3$

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

C-1. Which of the following reactions yield benzene?

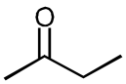
(1) PhMgBr + $CH_3–Br$ (2*) PhMgBr + H_2O (3) PhBr + H_2O (4*) PhMgBr + $CH_3–C\equiv CH$

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

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

(1) R is H (2*) R′ is $–\underset{\underset{CH_2}{||}}{C}–CH_3$ (3) R′ is $–\underset{\underset{CH_3}{|}}{CH}–CH_2$ (4*) R is CH_3

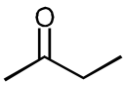
C-3. 2-Phenylbutan-2-ol can be prepared by :

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

(2*) $CH_3MgBr + Ph–\underset{\underset{O}{\|}}{C}–C_2H_5 \xrightarrow{ether} \xrightarrow{H^{\oplus}}$

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

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

(1*) PhMgBr +  $\xrightarrow{benzene} \xrightarrow{H^{\oplus}}$

(2*) $CH_3MgBr + Ph–\underset{\underset{O}{\|}}{C}–C_2H_5 \xrightarrow{benzene} \xrightarrow{H^{\oplus}}$

(3*) $C_2H_5MgBr + Ph–\underset{\underset{O}{\|}}{C}–CH_3 \xrightarrow{benzene} \xrightarrow{H^{\oplus}}$

(4) $CH_3CH_2CH_2MgBr + PhCHO \xrightarrow{benzene} \xrightarrow{H^{\oplus}}$

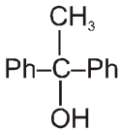
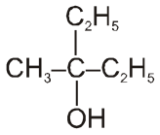
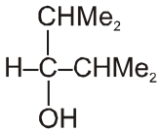
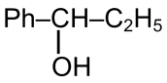
C-4. The correct decreasing reactivity order of the given compound(s) towards hydrolysis under identical condition is/are:

(1*) $CH_3COCl > CH_3CONH_2$ (2*) $CH_3COCl > (CH_3CO)_2O$

(3) $CH_3COOCH_3 > CH_3COCl$ (4*) $(CH_3CO)_2O > CH_3CONH_2$

C-5. X (an ethyl ester) $\xrightarrow[(ii)H_3O^{\oplus}]{(i)\text{Grignard's reagent (Y) (execess)}}$ product

The product(s) may be :

(1*)  (2*)  (3*)  (4) 

Exercise-3

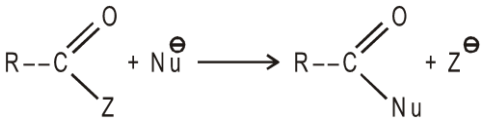
PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives

[AIEEE-2004, 3/225]

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

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



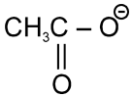
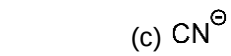
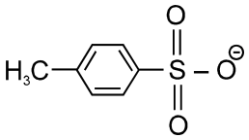
(1*) Cl (2) $OCOCH_3$ (3) OC_2H_5 (4) NH_2

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

(1*) $CH_3COOC_2H_5 + NaCl$ (2) $CH_3Cl + C_2H_5COONa$

(3) $CH_3COCl + C_2H_5OH + NaOH$ (4) $CH_3COONa + C_2H_5OH$

4. The decreasing order of nucleophilicity among the following nucleophiles : **[AIEEE-2005, 3/225]**

(a)  (b)  (c)  (d) 

(1) (c), (b), (a), (d) (2*) (b), (c), (a), (d) (3) (d), (c), (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. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is:

[AIEEE-2006, 3/165]

[Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-]

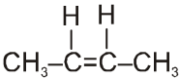
$CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$

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

(a) HCHO (b) CH_3COCH_3 (c) $PhCOCH_3$ (d) PhCOPh

(1) d > b > c > a (2) d > c > b > a (3) c > d > b > a (4*) a > b > c > d

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

(1) $CH_3C{\equiv}C{-}CH_3$ (2)  (3*) CH_4 (4) $CH_3{-}CH{=}CH_2$

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

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

10. Consider thiol anion (RS^{Θ}) and alkoxy anion (RO^{Θ}). Which of the following statement is correct ?

(1*) RS^{Θ} is less basic but more nucleophilic than RO^{Θ}. **[AIEEE-2011, 4/120]**

(2) RS^{Θ} is more basic and more nucleophilic than RO^{Θ}.

(3) RS^{Θ} is more basic but less nucleophilic than RO^{Θ}.

(4) RS^{Θ} is less basic and less nucleophilic than RO^{Θ}.

11. 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

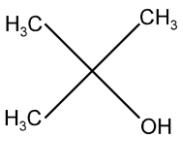
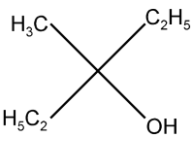
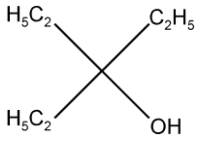
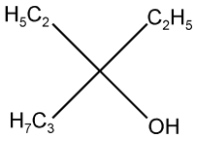
12. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is :

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

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

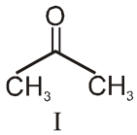
*** Marked Questions may have more than one correct option.**

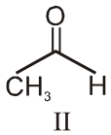
1. Ethylester $\xrightarrow[\text{excess}]{CH_3MgBr}$ P. The product P will be **[JEE-2003, 3/84]**

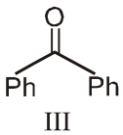
(A*)  (B)  (C)  (D) 

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

[JEE-2004, 3/84]

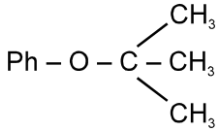
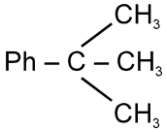

I


II

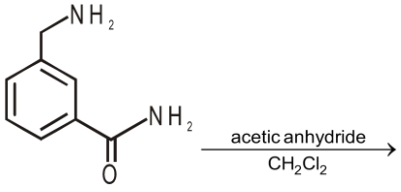

III

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

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

(A) Ph–OH (B*) Ph–H (C)  (D) 

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



product(s)

Additional Problems For Self Practice (APSP)

Marked Questions may have for Revision Questions.

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

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

Max. Marks : 120 **Max. Time : 1 Hr.**

Important Instructions

1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
   ¼ (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.
5. 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.

1. Which solvent is non-polar solvent?
(1) $CH_3-CO-CH_3$ (2) $CH_3-SO-CH_3$ (3) CH_3COOH (4*) Cyclohexane

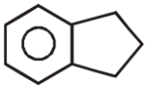
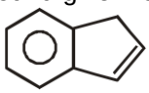
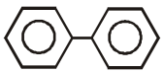
2. Which one of the following has minimum nucleophilicity?
(1) $(CH_3)_3CLi$ (2) $NaNH_2$ (3) CH_3ONa (4*) NaOH

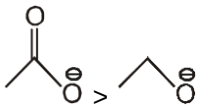
3. Which of the following compound gives fastest nucleophilic addition reaction :
(1) Ph–CHO (2) Ph–COPh (3*) CH_3–CHO (4) $CH_3-CO-CH_3$

4. Benzoyl chloride on treatment with ammonia gives
(1*) Benzamide (2) Acetamide (3) Benzylamine (4) Benzoic acid

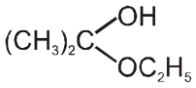
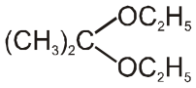
5. Which of the following is a nucleophile?
(1) $\overset{\bullet}{C}H_3$ (2) $CH_2^{\bullet\bullet}$ (3) $CH_3-\ddot{N}^{\bullet\bullet}$ (4*) $CH_3-\ddot{N}H_2$

6. Which of the following reactants will give only one organic product when reacted with NaCN / H_2SO_4 (small amounts) (No other isomer is obtained)
(1) CH_3CHO (2*) HCHO (3) PhCHO (4) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

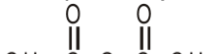
7. Which of the following compound give methane on treatment with CH_3MgI.
(1)  (2*)  (3)  (4) 

8. The correct order of leaving ability is :
(1) $\overset{\ominus}{O}H > H_2O$ (2) $\overset{\ominus}{O}H > \overset{\ominus}{S}H$ (3*)  (4) $\overset{\ominus}{Cl} > \overset{\ominus}{I}$

9. Acetone is treated with excess of ethanol in the presence of hydrochloric acid. The product obtained is :
(1) $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (2) $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

(3)  (4*) 

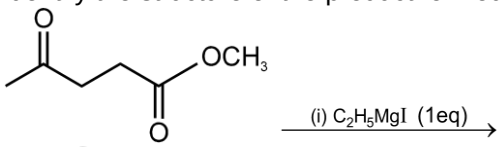
10. Which of the following is the most reactive towards nucleophilic acyl substitution?

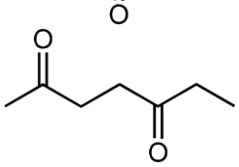
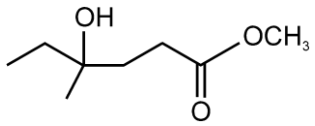
(1)  (2*)  (3)  (4) $CH_3COOC_2H_5$

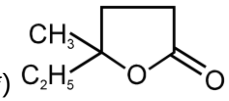
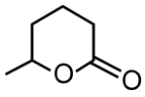
11.  X, X is

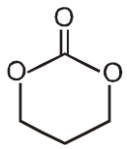
(1)  (2*)  (3)  (4)

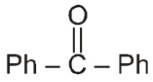
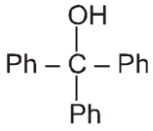
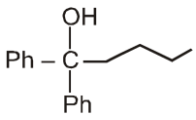
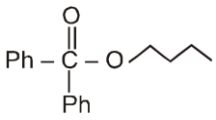
12. Identify the structure of the product formed in the following reaction.

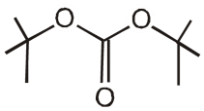
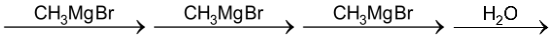


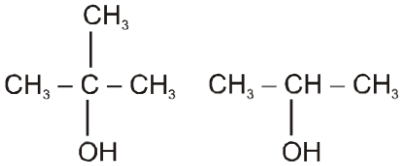
(1)  (2) 

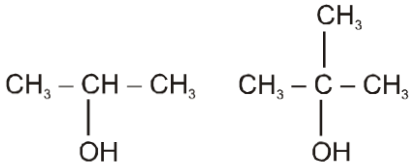
(3*)  (4) 

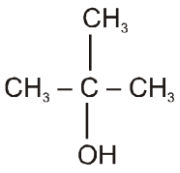
13. PhMgBr excess +   (A). Main Product (A) is :

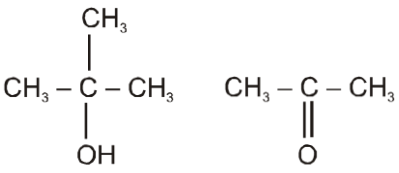
(1)  (2*)  (3)  (4) 

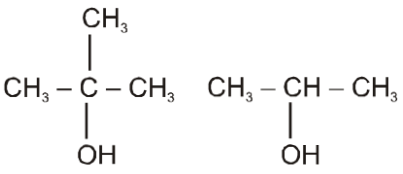
14.   Product

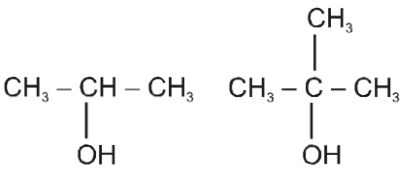
(1)  (2mol) + (1mol)

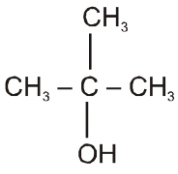
(2)  (2mol) + (1mol)

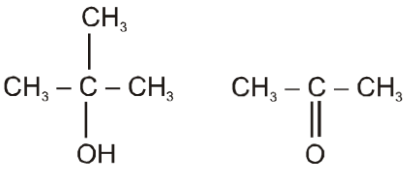
(3*)  (3mol)

(4)  (2mol) + (1mol)

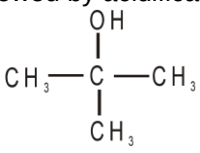
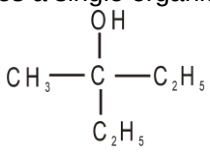
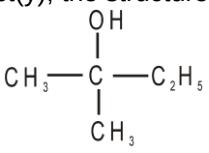
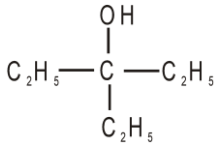
(1)  (2 मोल) + (1मोल)

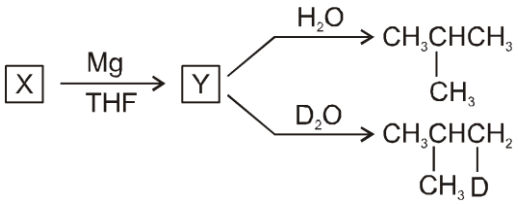
(2)  (2मोल) + (1मोल)

(3*)  (3मोल)

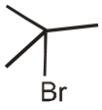
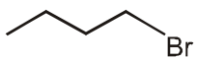
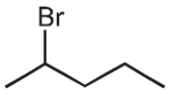
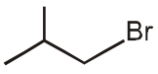
(4)  (2मोल) + (1मोल)

15. A sweet smelling compound(x) with molecular formula $C_8H_{16}O_2$ on reaction with excess of CH_3MgBr followed by acidification gives a single organic product(y), the structure of (y) can be :

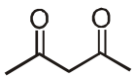
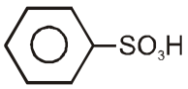
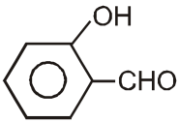
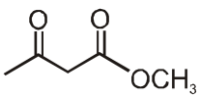
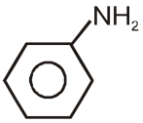
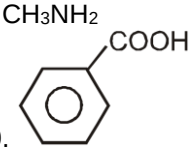
(1)  (2)  (3*)  (4) 

16. 

Give the structure of X.

(1)  (2)  (3)  (4*) 

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

1. 
2. 
3. 
4. $CH_3–C\equiv CH$
5. 
6. CH_3NH_2
7. 
8. 
9. CH_3SH
10. 

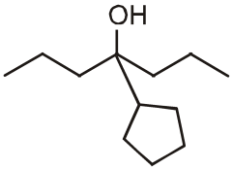
(1) 2,3,4,5 (2) 7,8,9 (3) 2,4,5,7,10 (4*) All

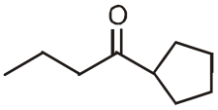
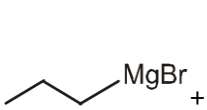
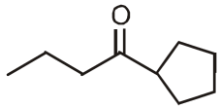
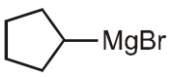
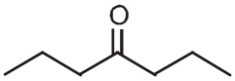
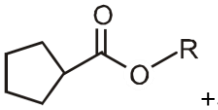
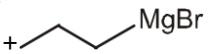
18. When a nucleophile attacks on a carbonyl group to form an intermediate, the hybridisation of the carbon atom changes from
(1) sp^3 to sp^2 (2) sp^2 to sp (3) sp to sp^2 (4*) sp^2 to sp^3

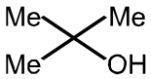
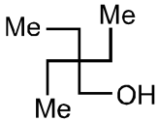
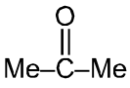
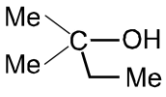
19. Which of these statements is incorrect about nucleophiles ?
(1) Nucleophiles have an unshared electron pair and can make use of this to react with an electron deficient species.
(2) The nucleophilicity of an element (as electron donor) generally increases on going down a group in the periodic table.
(3*) A nucleophile is electron-deficient species
(4) All good nucleophiles are good bases when we deal across the period.

20. Which of the following reaction is substitution reaction ?
(1) $CH_3–CHO \xrightarrow[H^{\oplus}]{KCN} CH_3-\underset{CN}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH$ (2) $CH_3–CH=CH_2 \xrightarrow{HCl} CH_3-\underset{Cl}{CH}-CH_3$
(3) $CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow{Alc.KOH} CH_3–CH=CH_2$ (4*) $CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[H^+]{CH_3OH} CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$

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



(1*) CH_3MgBr (excess) + 
(2)  + 
(3)  + 
(4)  +  (excess)

22. When ethyl ethanoate is treated with excess of MeMgBr followed by hydrolysis, the product is :
(1*)  (2)  (3)  (4) 

23. What product is formed when acetic acid heated with PCl_5.
(1) Acetic anhydride (2) Acetate ester (3*) Acetyl chloride (4) Ethylchloride

24. Which species will not be considered as an electrophile ?
(1) $CH_3-CH_2^{\oplus}$ (2) $AlCl_3$ (3*) NH_3 (4) SO_3

25. When grignard reagent is treated with isopropyl formate followed by acid hydrolysis we get :
(1) Aldehyde (2*) 2º alcohol (3) 3º alcohol (4) 1º alcohol

26. Compound $CH_3-CH_2-\underset{Ph-CH-OH}{\underset{|}{CH}}-CH_3$ can be prepared by :

(1) $CH_3-\underset{CH_3}{CH}-CH_2-CHO \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ PhMgBr}$ (2) $CH_3-\underset{MgBr}{CH}-CH_3 \xrightarrow[(ii)\ H_3O^{\oplus}]{(i)\ PhCH_2CHO}$

(3) Ph – $COCH_3$ $\xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-MgBr}$

(4*) PhCHO $\xrightarrow[\text{(ii) } H_3O^{\oplus}]{\text{(i) } CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-MgBr}$

27. Identify the correct set of aprotic solvent .
(1) Water, DMSO (2*) DMSO, Acetone
(3) Ethanol, Acetone (4) Diethylether, Methyl amine

28. Acid hydrolysis of which of the following compounds yields two different organic compounds?
(1) CH_3COOH (2) CH_3CONH_2 (3*) $CH_3COOC_2H_5$ (4) $(CH_3CO)_2O$

29. Leaving group ability order amongst the following
(I) $C_6H_5O^-$ (II) p-$(CH_3)C_6H_4O^-$ (III) p-$(OCH_3)C_6H_4O^-$ (IV) p-$(NO_2)C_6H_4O^-$
(1) I > II > III > IV (2) III > II > I > IV
(3*) IV > I > II > III (4) IV > III > II > I

30. Consider the reaction :

$$RCHO + NH_2NH_2 \rightarrow RCH = N–NH_2$$

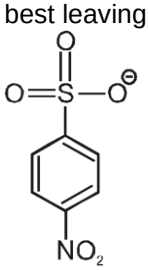
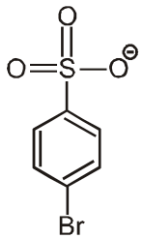
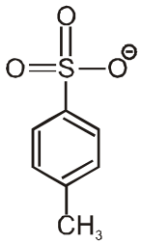
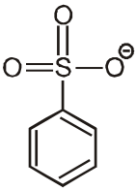
What sort of reaction is it ?
(1) Electrophilic addition - elimination reaction
(2) Free radical addition - elimination reaction
(3) Electrophilic substitution - elimination reaction
(4*) Nucleophilic addition - elimination reaction

Practice Test (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.										

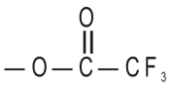
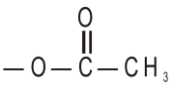
PART - II : PRACTICE QUESTIONS

1. The best leaving group is :

(1*)  (2)  (3)  (4) 

2. $CH_3-\overset{\ominus}{S}Na^{\oplus} + CH_3-CH_2-X \longrightarrow$

The reaction is fastest when X is

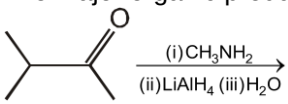
(1) –OH (2) –F (3*)  (4) 

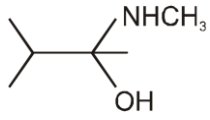
3. The weakest nucleophile but best leaving group is
(1*) $CF_3SO_3^{\ominus}$ (triflate ion) (2) $CH_3SO_3^{\ominus}$ (3) $CH_3COO^{\ominus}$ (4) $PhO^{\ominus}$

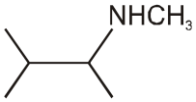
4. The reagent with which both acetaldehyde and acetone react easily is
(1) Tollen's reagent (2) Schiff's reagent (3*) Grignard reagent (4) Fehling reagent

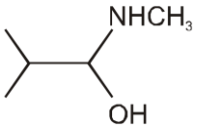
5. The best leaving group (nucelofuge) is :
(1*) $(CH_3)_2S$ (2) $(CH_3)_2NH$ (3) $(CH_3)_2O$ (4) CH_3OH

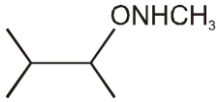
6. The major organic product formed from the following reaction is :



(1) 

(2*) 

(3) 

(4) 

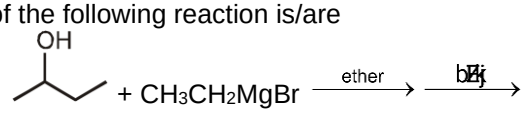
7. Which of the following is NOT a nucleophile ?
(1*) B_2H_6 (2) CH_3OH (3) H_2O (4) NH_3

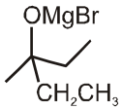
8. Absolutely pure hydrogen cyanide fails to react with aldehydes because
(1) hydrogen cyanide is not a strong nucleophile
(2) hydrogen cyanide is undissociated when pure
(3) hydrogen cyanide cannot add to the carbonyl group on its own
(4*) all the above are correct.

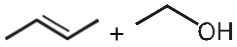
9. The non-nucleophilic base is
(1) CN^- (2*) $^-OC(Me)_3$ (3) HO^- (4) MeO^-

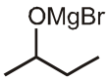
10. Which of the following series contains only nucleophiles ?
(1*) NH_3, H_2O, CN^-, I^- (2) $AlCl_3$, NH_3, H_2O, I^-
(3) $AlCl_3$, BF_3, H_2O, NH_3 (4) $AlCl_3$, BF_3, NO_2^+, NH_3

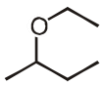
11. The product/s of the following reaction is/are



(1) 

(2) 

(3*) 

+ CH_3CH_3
(4) 

12. A catalyst accelerates a reaction primarily by stabilizing the
(1) substrate (2) product (3) intermediate (4*) transition state

13. Which of the following information is not provided by a reaction mechanism?
(1) Which bonds are formed and which bonds are broken
(2) Which intermediates and transition states are formed
(3*) Energy content of the reacting species
(4) Which is the slowest step