ORGANIC CHEMISTRY

XIII (ALL)

ALKYL HALIDE & GRIGNARD REAGENT

PART-II

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PART-II: ALKYL HALIDE

EXERCISE-I

- 1. A gem dichloride is formed in the reaction except:
 - (A) CH₃CHO and PCl₅

(B) CH₃COCH₃ and PCI₅

(C)
$$\longrightarrow$$
 OH \longrightarrow OH

- $(D) \stackrel{O}{\downarrow} \bigwedge \stackrel{PCl_5}{\longrightarrow}$
- 2. Which of the following nucleophile
- will show minimum reactivity towards S_N2 reaction:

$$(C)$$
 \bigcup_{O}

(D) Me₂CHO

3.

x = moles of HI consumed.

value of x is

(D) 6

 $CH_3 - CH_2 - O - C = CH_2 \xrightarrow{H_3O^{\oplus}}$ Products are CH_3

5. HO OH
$$\xrightarrow{\text{Conc.H}_2SO_4} A$$

Final product A is

(A)
$$HO \longrightarrow O$$
 (B) $CH_2 = C = CH_2$ (C)

(B)
$$CH_0 = C = CH$$

- $\begin{array}{c|c} H & \xrightarrow{Et} & \xrightarrow{alc. \, KOH} & \text{major product is :} \\ Br & \xrightarrow{\Delta} & \end{array}$ 6.

Total number of $SN_1 + E_1$ products obtained will be -

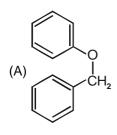
- (B) 6
- (C)7
- (D)8

8.
$$-N_2^{\bigoplus}$$
 - OTf, - OTs

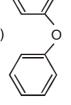
Which of the following orders is correct about leaving ability of these groups in nucleophilic substitutions?

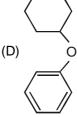
- (B) III > II > I
- (C) | | | > | > | |
- (D) II > III > I

- 9. Which of the following ethers
- is unlikely to be cleaved by hot conc. HBr?

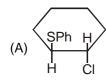


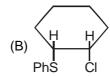
$$(B) \bigcirc C_2H_5$$

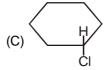




10. Which of following compounds will show NGP?





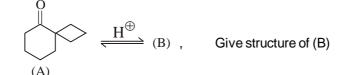




(x) conc. HI

Value of x in above reaction is

- (A)2
- (B)3
- (C)4
- (D) 5
- In the given reaction: $CH_3 CH_2 \overset{*}{O} \overset{*}{C}H_2 CH_2 Br \xrightarrow{HOH} [X]$, [X] will be: 12.
 - (A) $CH_3 CH_2 S \overset{*}{C}H_2 CH_2 OH$ (B) $CH_3 CH_2 S CH_2 \overset{*}{C}H_2 OH$
 - (C) 1:1 mixture of (A) and (B)
- (D) 2: 1 mixture of (A) and (B)
- In the given reaction $CH_3 CH CH_2 CH_2 CH CH_3 \xrightarrow{\text{(i) SH (one equivalent)}} [X], [X] \text{ will be:}$ 13.





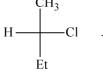






15.

Reaction :-1 $CH_3-CH_2-CH_2-CH_3-\frac{Cl_2}{hv}$ Optically active monochloro product(s) are **(R)**



Reaction :–2 H \longrightarrow Cl $\xrightarrow{\text{Cl}_2}$ Optically active di-chloro product(s) are **(S)**

S-2-chlorobutane

Reaction:-3



Reaction :-4 2-methoxy propane $\xrightarrow[hv]{\text{Cl}_2}$ Optically active mono chloro product(s) are **(Q)**

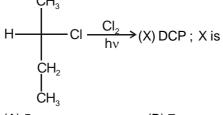
Sum of P + Q + R + S is

8 (A)

(C) 10

(D) 11

16.



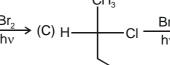
(A)5

(C) 9

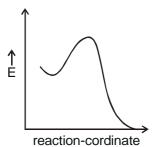
(D) 11

17. In-which of following reaction diastereomer will form.

(A)
$$H \xrightarrow{CH_3} CI \xrightarrow{CI_2} hv$$
 (B) $CI \xrightarrow{Br_2} hv$ (C) $H \xrightarrow{CH_3} CI \xrightarrow{Br_2} hv$



18.



Above is energy profile for. r.d.s of

(A) Iodination of alkane

(B) Chlorination of alkane

(C) Bromination of alkane

(D) Cannot predict

19. Which of the following reaction has (Ea = Δ H).

(A)
$$Cl' + H - CH_3 \longrightarrow HCl + \dot{C}H_3$$

(B) Cl· + Cl·
$$\longrightarrow$$
 Cl₂

(C)
$$Cl_2 \xrightarrow{hv} 2Cl$$

(D) Et'+ H – CH₃
$$\longrightarrow$$
 Et–H + $\dot{C}H_3$

20. Which of following reaction has $\Delta(Ea = 0)$

(A)
$$Cl' + H - CH_3 \longrightarrow HCl + \dot{C}H_3$$

(B) Cl· + Cl·
$$\longrightarrow$$
 Cl₂

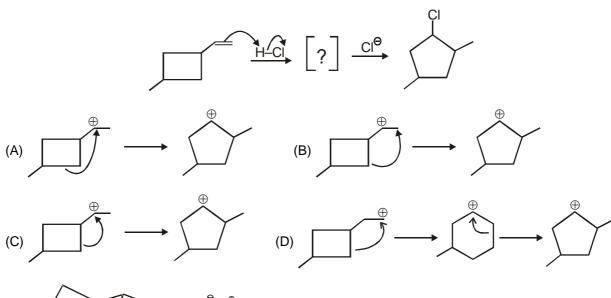
(C)
$$Cl_2 \xrightarrow{hv} 2Cl^{-1}$$

(D) Et'+ H – CH₃
$$\longrightarrow$$
 Et–H + $\dot{C}H_3$

21. 1-Penten-4-yne reacts with bromine at – 80°C to produce:

- (A) 4, 4, 5, 5-Tetrabromopentene
- (B) 1, 2-Dibromo-1, 4-pentadiene
- (C) 1, 1, 2, 2, 4, 5-hexabromopentane
- (D) 4, 5-dibromopentyne

22. Write mechanism best accounts for the transformation in the brackets?



23. $t\text{-Bu} \longrightarrow OTs \xrightarrow{AcO^{\Theta}Na^{\Theta}} (A)$

Major-product (A) is

24. $\underbrace{ \begin{array}{c} OH \\ \\ O \end{array}}_{O} \xrightarrow{H_2SO_4} X, \quad X \text{ is }$

25.
$$Me$$
 Me
 Me
 $Conc.H_2SO_4$
 Δ
 $A.$

Product A is:

The major product obtained when this substrate is subjected to E2 reaction under the treatment of potassium tert-butoxide will be

(A)
$$CH_2$$
 (B) CH_3 (C) both in equal proportions (D) none of these

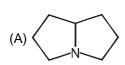
28. Which of the following isomeric hexachlorocyclohexanes is least reactive in β-dehydrochlorination (β-) on treatment with strong base ?

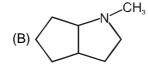
29. If the following E2 reaction proceeds through an anti-periplanar transition state, what product or products are expected?

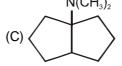


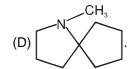
- (A) Only 3-methylcyclohexene
- (B) Only 1-methylcyclohexene
- (C) The major product is 3-methylcyclohexene and the minor product is 1-methyl cyclohexene
- (D) The major product is 1- methylcyclohexene and the minor product is 3-methyl cyclohexene
- **30.** The nitrogen atom in each of the following tertiary amines may be removed as trimethyl amine by repeated Hofmann eliminations (exhaustive methylation followed by heating with AgOH).

Which of the amines requires the greater number of Hofmann sequences to accomplish this?







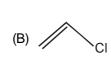


EXERCISE-II

Choose the correct option. One or more than one are correct

1. Which of the following compound will not undergo Nucleophilic substitution reaction









Consider the given reaction: H-C-OTs 2. CH₃

Which of following statements are correct for above reaction.

- (A) Product formation takes place due to the breaking of O-Ts
- (B) The reaction is S_{N^2}

(C) The reaction is S_{N1}

(D) Configuration

of product is (R)

3. Rate of S_N2 will be negligible in



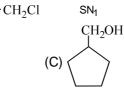




4. Which are possible products in following







moist Ag₂O

S_N1 & S_N2 product are same in (excluding stereoisomer) 5.







On moving 1° to 3° alkyl halide rate of E₂ increases while rate of S_N2 decreases 6.

CH₃

Statement 2: E₂ reaction give elemental effect with respect to halogen.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.
- $CH_3 CH_2 O CH_3 \xrightarrow{PCl_5}$ 7. Products are:
 - (A) CH₃ CI

- 8.
- $\begin{array}{c}
 O \\
 Ph C CH_3 \\
 CI \\
 (A) Ph C CH_3
 \end{array}$ $\begin{array}{c}
 CI \\
 CI \\
 CI
 \end{array}$ $\begin{array}{c}
 CI \\
 CI \\
 CI
 \end{array}$ $\begin{array}{c}
 CI \\
 CI \\
 CI
 \end{array}$ $\begin{array}{c}
 CI \\
 CI$ CI CI

$$9. \qquad (p) \xrightarrow{Zn-dust} /$$

compound (p) is

$$(A) \begin{array}{c} CH_3 \\ H \\ \hline \\ CH_2 \end{array}$$

$$(B) \begin{array}{c} CH_3 \\ H \\ \hline \\ CH_3 \end{array}$$

$$(C) \begin{array}{c} Br \\ Br \\ Br \end{array}$$

$$(D) \begin{array}{c} Br \\ Br \\ CH_3 \end{array}$$

10.
$$\begin{array}{c|c} CH_3 \\ H & Br \\ Br & H \\ CH_3 \end{array}$$
 (p). The product (p) is

Paragraph for Question Nos. 11 to 13 (3 questions):

Dehydration require an acid catalyst to protonate the hydroxy group of the alcohol and convert it into good . Loss of water followed by a loss of a proton, given the alkene an equilibrium leaving group is established between reactants and products.

$$\begin{array}{c} \text{OH} \\ \hline \\ \hline \\ \hline \\ \hline \\ \end{array} \text{CH}_3\text{-CH=CH}_2$$

Mechanism

OH +
$$H_2SO_4$$
 \longrightarrow H_3O_4 \longrightarrow H_2O \longrightarrow H_2O \longrightarrow H_2O \longrightarrow H_2O \longrightarrow H_3O_4 \longrightarrow \longrightarrow H_3O_4 \longrightarrow \longrightarrow

- 11. To improve the yield of above reaction which of following is **correct**.
 - (A) High temperature (B) Distillation
- (C) Addition of H₂O (D) Both (A) and (B)

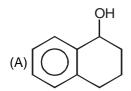
12. (i)
$$\xrightarrow{OH} \xrightarrow{H^+} (A) \text{ Major}$$

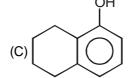
$$\begin{array}{c}
 & \xrightarrow{H^{+}} \\
 & \xrightarrow{\Delta}
\end{array}$$
(A) Major
(ii)
$$\begin{array}{c}
 & \xrightarrow{H^{+}} \\
 & \xrightarrow{\Delta}
\end{array}$$
(B) Major

(iii)
$$\xrightarrow{H^+}_{\Delta}$$
 (C) Major

total number of α -hydrogen in A + B + C is

- (A) 23
- (C) 37
- Which alcohol is most reactive towards dehydration of alcohol in acid catalyzed reaction. 13.





MATRIX

1. Column I

Primary alkyl bromide

(A)
$$CH_3 - CH_2 - Br$$

(B)
$$Me - CH_2 - CH_2 - Br$$

(C)
$$\begin{array}{c} \operatorname{Me}-\operatorname{CH}-\operatorname{CH}_2-\operatorname{Br} \\ | \\ \operatorname{Me} \end{array}$$

$$\begin{array}{c} \operatorname{Me} \\ \mid \\ \operatorname{Me} - \operatorname{C} - \operatorname{CH}_2 - \operatorname{Br} \\ \mid \\ \operatorname{Me} \end{array}$$

Column II

SN₂ relative rate

2. Column I

Alkyl-P-toluene sulfonate

(A)
$$CH_3 - CH_2 - OTs$$

(B)
$$H_2C = CH - CH_2 - OTs$$

(C)
$$Ph - CH_2 - OTs$$

(E)
$$Ph_{s}C - OTs$$
.

Column II

Ethanolysis

relative rate (50°C)

3. Substrate

E, elimination

SN₂-substitution

(A)
$$CH_3 - CH_2 - Br$$

(C)
$$(CH_3)_3 CBr$$

(P) 1

- (W) ≈0
- (X)20
- (Y) 90

4. Reaction

(B)

(A)
$$HO^{\Theta_+}R-CH_2-I\longrightarrow$$

 $(CH_3)_2 CH - Br$

(B)
$$HO^{\Theta_+}R-CH_2-Br\longrightarrow$$

(C)
$$HO^{\Theta_+}R - CH_2 - CI \longrightarrow$$

(D)
$$HO^{\Theta_+}R - CH_2 - F \longrightarrow$$

Relative rate of reaction

- (P) 1
- (Q) 200
- (R) 10,000
- (S) 30,000

5. Column I

Alkyl-bromide

(A)
$$CH_3 - C - Br$$
 $CH_3 - C - Br$
 CH_3

(B)
$$CH_3 - CH - Br$$

 CH_3

(C)
$$CH_3-CH_2-B$$

Column II

Relative rate of SN1

)

- (A) 100 % water
- (B) 80% water + 20% ethanol
- (C) 50% water + 50% ethanol
- (D) 20% water + 80% ethanol
- (E) 100% ethanol

- 1200 (P)
- 400
- (R) 60

(Q)

- (S) 10
- (T) 1
- Match List-I with List-II for given S_{N^2} reaction & select the correct answer from the codes given below 7.

$$Z-CH_2Br + CH_3O^{\Theta} \longrightarrow Z-CH_2-OCH_3 + Br^{\Theta}$$

List-I

List-II (relative reactivity/

- (A) H-
- (B) CH₃-
- (C)
- $C_{2}H_{5}-$

- 0.1 (P)
- (Q) 3
- (R)

(D)
$$CH_3$$
 CH —

- (S) 100
- 8. Match List I with List II and select the correct answer from the codes given below:

List II

- $CH_3-O-SO_2CH_3 + C_2H_5 \overset{\Theta}{O}$ $CH_3-CH_2-I+PH_3$ (A)
- $\mathsf{CH}_{3}\!\!-\!\!\mathsf{CH}_{2}\!\!-\!\!\mathsf{PH}_{2}$

- $\Theta \Theta$ $HC \equiv C \text{ Na} + CH_3 CH_2 Br$ (C)
- CH₃-O-CH₃ (R)

(P)

CH₃-CI + CH₃-O (D)

- CH=C-CH₂-CH₃ (S)
- 9. Column-I and Column-II contains four entries each. Entries of column-I are to be matched with one entry of column-II. single choice question.

(one to one matching)

Column-I

Column-II

S_N2 reaction

- CH_3 $CH_3 CH CH_2Br \xrightarrow{EtO^{\Theta}}$
- E₁ reaction (Q)
- $\begin{array}{ccc} CH_3 & & CH_3 \\ & & CH_3 & & CH_3OH \\ & & & \Delta \end{array}$ (C)
- E2 reaction (R)
- $CH_{3} \xrightarrow{CH_{3}-CH-Cl} \xrightarrow{CH_{3}-C-O^{\Theta}}$ (D)
- (S) S_N1 reaction

10. $Nu^{\Theta} + Me-OTs \xrightarrow{DMF} Me-Nu + TsO^{\Theta}$

This is a S_N^2 reaction where nucleophile attack Me–OTs in the rate determining step to give the product. Rate of this reaction increases with concentration as well as nucleophilicity of the nucleophile. Match the column I with column II for the above reaction

(Column I	Column II				
(N	ucleophile)	(Rel	ative rate)			
(A)	F [⊖]	(P)	3.25			
(B)	Cle	(Q)	6.25			
(C)	Br [⊖]	(R)	1.0			
(D)	lΘ	(S)	7.75			

11. Match List-I with List-II (no. of structural isomers produced in β -E₂ elimination) and select the correct answer.

List-II List-II

(a)
$$H_3C$$
 CH_3 CH_3

(i) Three

(b)
$$H_3C \xrightarrow{Br} CH_3$$
 CH_3

(ii) Zero

(c)
$$H_3C$$
 H_3C CH_3 CH_3

(iii) One

(d)
$$H_3C \xrightarrow{CH_3} Br$$

(iv) Two

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

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

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

12. Match the column

$$(A) \bigcirc O - CH_2 - CH_3 \quad \underline{H_3O}$$

(P) One of product is Ph – OH

$$(B) \bigcirc \bigcirc \bigcirc \bigcirc \qquad \underline{H_3O} \bigcirc \bigcirc$$

(Q) One of product is $CH_3 - CHO$

(R) One of product is 2° alcohol

(S) No-reaction

13. Column I

Column II

(A)
$$O \longrightarrow H_3O^{\oplus}$$

(P) No-reaction

(Q)

is one of the product of the reaction

(R) OH

is one of the product of the reaction

(D)
$$\begin{array}{c} & & \\$$

$$\begin{array}{ccc} \text{(S)} & & \text{CH}_3 - \text{CH} - \text{OH} \\ & & \text{|} \\ & & \text{CH}_3 \end{array}$$

is one of the product of the reaction

Column-I

Column-II

(A)
$$CH_3$$
 $C - CCH_3$ CH_3 CH_3

(P) Pinacol fashion reaction

(B)
$$CH_3 \xrightarrow{CH_3} CH_3 \xrightarrow{H_2SO_4} CH_3 \xrightarrow{H_2SO_4} OH OH$$

(Q) Pinacolic Diazotization reaction

(R) Pinacol-Pinacolone reaction

$$(D) \xrightarrow{\qquad \qquad } \frac{TsCl}{Pyridine} \rightarrow$$

(S) Product formed is $CH_3 - C - CH - CH_3$

(T) Semipinacol reaction

15. Column-I

Column-I

(A) Best leaving group

- (P) F^Θ
- (B) Best nucleophile in polar protic solvent
- (Q) CI^Θ
- (C) Best nucleophile in polar aprotic solvent
- (R) Br[⊖]

(D) Weakest base

(S) I[⊖]

16. Substitution Logistics :

You were asked to run a series of reactions in the lab with different experimental conditions. Based on the experimental observations you gathered (listed below), indicate which mechanism this evidence supports. (Check the appropriate box to correspond to your answer.)

S.No.	Observation	SN1	SN2	Both
1	The rate of the reaction decreased when the concentration of the Nu is decreased.			
2	The rate of the reaction increased when the concentration of the RX was increased.			
3	The rate increased when the X was changed from CI to I.			
4	The products showed a skeletal rearrangement.			
5	The product showed inversion of configuration.			
6	The Nu was changed from methoxide to isopropoxide and the rate descreased.			
7	The RX was changed from 2° alkyl halide to a 2° allyl halide and the rate increased.			
8	The solvent was switched from ethanol to acetone and the rate decreased.			

EXERCISE-III

SUBJECTIVE PREVIOUS YEAR QUESTIONS

- Suggest a reason for the large difference between the boiling points of butanol and butanal, although they have almost the same solubility in water.

 [IIT 1985]
- 2. Write the structure of the major organic product expected from each of the following reaction:

(i)
$$CH_3CH_2CHCI_2 \xrightarrow{Boil(aq)}$$
 alkali [IIT 1992]

- 3. Fill in the blanks:
 - (a) Butane nitrile can be prepared by heating _____with alcohalic KCN. [IIT 1992]
 - (b) Amongst three isomers of nitrophenol, the one that is least soluble in water is____ [IIT 1992]

Cl

$$(CH_3)_2C - CH_2CH_3 \xrightarrow{\text{alc.KOH}} ?$$
 [IIT 1992]

- 5. Aryl halides are less reactive than alkyl halides towards nucleophilic reagents. Give reason. [IIT 1994]
- Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly.
- 7. An alkyl halide X of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3–dimethylbutane. Predict the structures of X, Y and Z. [IIT 1996]
- 3, 3-dimethylbutan-2-ol losses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism. [IIT 1996]
- 9. An alkyl halide, (X) of formula $C_6H_{13}CI$ on treatment with potassium tertiary butoxide gives two isomeric alkenes (Y) and (Z) (C_6H_{12}). Both alkenes on hydrogenation give 2, 3–dimethylbutane. Predict the structures of (X), (Y) and (Z) [IIT 1996]
- **10.** 2, 2-dimethyloxirane can be cleaved by dil. acid. Write mechanism. **[IIT 1997]**
- 11. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

(i)
$$(CH_3)_3 CBr + NaOMe \longrightarrow$$
 (ii) $CH_3Br + t - BuO^-Na^+ \longrightarrow$ [IIT 1997]

12. Give reasons for the following in one or two sentences. "Acid catalysed dehydration of t-butanol is faster than that of n-butanol. [IIT 1998]

13. (a)
$$C_6H_5CH_2CHC1 \xrightarrow{Alcohalic KOH} A + B$$
 Write structures of (A) and (B).
(b) $(CH_3)_2CHOCH_3 \xrightarrow{HI(excess)} A + B$ Write structures of A and B. [IIT 1998]

14. What would be the major product in each of the following reactions? [IIT 2000]

$$\begin{array}{c} \operatorname{CH_3} \\ | \\ \operatorname{CH_3} - \operatorname{C-CH_2Br} \xrightarrow{\operatorname{C_2H_5OH}} \\ | \\ \operatorname{CH_3} \end{array}$$

in 190	15.	is most acidic. (Ethane, Ethene, Ethyne)	[IIT 198 ⁻	IJ
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- **16.** Give reasons for the following in one or two sentences:
 - (i) Methane does not react with chlorine in the dark.
 - (ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide. [IIT 1983]
- 17. The terminal carbon atom in 2-butene is hybridised. [IIT 1985]
- **18.** Write the balanced chemical equation for the following "Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate." **[IIT 1991]**
- **19.** Write down the structures of the stereoisomers formed when cis–2–butene is reacted with bromine.

[IIT 1995]

- 20. An organic compound $E(C_5H_8)$ on hydrogenation gives compound $F(C_5H_{12})$. Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. **[IIT 1995]**
- 21. One mole of the compound A (molecular formula C_8H_{12}), incapable of showing stereoisomerism, reacts with only one mole of H_2 on hydrogenation over Pd. A undergoes ozonolysis to give a symmetrical diketone B ($C_8H_{12}O_2$). What are the structure of A and B? [IIT 1997]
- 22. The central carbon–carbon bond in 1, 3–butadiene is shorter than that of n–butane. Why? [IIT 1998]
- 23. $CH_2=CH^-$ is more basic than $HC=C^-$ [IIT 2000]

- **25.** The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is: **[IIT 2011]**
- **26.** The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is **[IIT 2011]**

27. The number of resonance structures for N is

[IIT Advanced 2015]

$$\stackrel{\mathsf{OH}}{\longrightarrow} \mathsf{N}$$

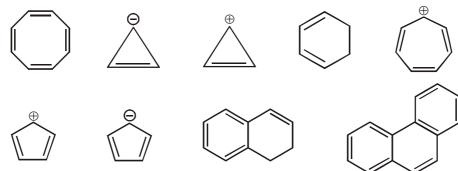
28. In the following monobromination reaction, the number of possible chiral products is:

[JEE-Advanced-2016]

(enantiomerically pure)

29. Among the following, the number of aromatic compound(s) is:

[IIT Advance - 2017]



ANSWER KEY

EXERCISE - I

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

EXERCISE - II

1.	ABD	2.	BD	3.	ABC	4.	AB	5.	BC	6.	В	7.	AB
8.	Α	9.	Α	10.	В	11.	D	12.	D	13.	Α		

MATRIX

- 1. $A \rightarrow S$; $B \rightarrow R$; $C \rightarrow Q$; $D \rightarrow P$
- 3. $A \rightarrow P,Y ; B \rightarrow Q, X ; C \rightarrow R,W$
- 5. $A \rightarrow R ; B \rightarrow Q ; C \rightarrow P$
- 7. $A \rightarrow S ; B \rightarrow Q ; C \rightarrow R ; D \rightarrow P$
- 9. $A \rightarrow S$, $B \rightarrow R$, $C \rightarrow Q$, $D \rightarrow P$
- **11.** B

16.

- 13. $A \rightarrow P$; $B \rightarrow Q$, S; $C \rightarrow Q$, R; $D \rightarrow R$, S
- **15.** $A \rightarrow S$; $B \rightarrow S$; $C \rightarrow P$; $D \rightarrow S$

- 2. $A \rightarrow T$; $B \rightarrow S$; $C \rightarrow R$; $D \rightarrow Q$; $E \rightarrow P$
- 4. $A \rightarrow S ; B \rightarrow R ; C \rightarrow Q ; D \rightarrow P$
- 6. $A \rightarrow P ; B \rightarrow Q ; C \rightarrow R ; D \rightarrow S ; E \rightarrow T$
- 8. $A \rightarrow Q, B \rightarrow P, C \rightarrow S, D \rightarrow R$
- 10. $A \rightarrow S$, $B \rightarrow Q$, $C \rightarrow P$, $D \rightarrow R$
- **12.** $A \rightarrow P$; $B \rightarrow QR$; $C \rightarrow PR$; $D \rightarrow S$
- **14.** $A \rightarrow P$; $B \rightarrow R$; $C \rightarrow Q$; $D \rightarrow T$;

		_	_
S.No.	SN1	SN2	Both
1		✓	
2			✓
3			✓
4	✓		
<u>4</u> 5		\checkmark	
6		✓	
7			√
Ω	/		

EXERCISE - III

1. Butanol has capacity for inter molecular hydrogen bonding.

2. (i)
$$CH_3CH_2CHCI_2 \xrightarrow{\text{Boil} \atop \text{alkali} \atop -2\text{NaCl}} \left[CH_3 - CH_2 - CH \xrightarrow{\text{OH}} \xrightarrow{\text{OH}} \xrightarrow{\text{-H}_2\text{O}} CH_3 - CH_2 - CHO \text{ propanal} \right]$$
(Unstable)

- 3. (a) propyl chloride, (b) ortho
- 4. $CH_3 C = CH CH_3$ CH_3
- 5. Due to the presence of resonance in alkyl halide carbon halogen bond acquires the character of partial double bond and halogen is directly attached to sp² hybridised carbon so the halogen is not capable to leave as an leaving group.

6. The product obtained after the reaction contain equal amount of both d and *l*-isomers of 2-iodobutane and this racemic mixture does not show optical activity due to external compensation.

8.
$$\begin{array}{c} CH_3 & CH_3 CH_3 \\ CH_3 - C - CH - CH_3 \\ CH_3 CH_3 \end{array} \xrightarrow{\Delta} \begin{array}{c} CH_2SO_4 \\ CH_3 - C = C - CH_3 + H_2O \\ CH_3 CH_3 \end{array}$$
 (Major product)

Mechanism of above reaction is represented as follows:

$$CH_{3} \xrightarrow{C} CH \xrightarrow{C} CH \xrightarrow{C} CH_{3} \xrightarrow{H^{+}} CH_{3} \xrightarrow{C} CH \xrightarrow{C} CH \xrightarrow{C} CH_{3}$$

$$CH_{3} : OH \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3}$$

$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3$$

10. The oxirane ring is cleaved by the following mechanism :

11. In these two methods, method (ii) is the correct method for the formation of ether because in method (i), alkene is formed in place of ether.

(i)
$$(CH_3)_3 C - Br + Na - O - Me \longrightarrow CH_3 - C = CH_2 + NaBr + CH_3OH CH_3$$
iso-butene

(ii)
$$CH_3Br + Na\bar{O} - C(CH_3)_3 \longrightarrow H_3C - C - O - CH_3 + NaBr - CH_3$$

This reaction is called as Williamson's synthesis and it is based upon S_N 2-reaction mechanism.

12. Due to formation of more stable 3°-carbonium ion with t-butanol that 1°-carbonium ion in n-butanol.

$$\begin{array}{c} \text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} \text{OH} \xrightarrow{H^{+} - \text{H}_{2} \text{O}} \\ & \text{n-butanol} \end{array}$$

- 13. (a) Cis and trans forms of stibene $C_6H_5CH=CHC_6H_5$; (b) $CH_3 > CHI + CH_3I$
- 14. (i) $CH_3 C = CH CH_3$ 15. Ethyne
- **16.** (i) Methane does not react with chlorine in the dark because chlorine atoms are required for this reaction and chlorine atoms are obtained only in the presence of light.
 - (ii) It is in accordance with Markownikoff's rule which predicts the stability of secondary carbonium ion over primary carbonium ion.
- 17. sp³

 CH₂ $H_2 \mapsto [H_2O + O] \xrightarrow{KMnO_4} CH_2OH$ CH₂

 CH₂OH

$$2KMnO4 + 3 \begin{vmatrix} CH2 & CH2OH \\ + 4H2O \longrightarrow 3 \begin{vmatrix} CH2OH \\ - CH2OH \end{vmatrix} + MnO2 + 2KOH$$

20. $\begin{array}{c} (C_5H_8) \xrightarrow{H_2} C_5H_{12} \\ \text{compound F} \\ \hline \\ Ozonolysis \\ \text{formaldehyde} \end{array} + H_3C - C - CHO \\ \hline \\ 0 \\ 2\text{-ketopropanal} \\ \end{array}$

Hence, compound E must be diene.
$$CH_2 = C - CH = CH_2$$
 Compound $F = CH_3 - CH - CH_2 - CH_3$ CH_3 CH_3

- **21.** (A) (B)
- 22. Resonance is present in 1, 3-butadiene that's why every bond acquire the character of partial double bond.
- 23. higher electronegativity of sp carbon
- 24. (X) CH_3 , (Y) $CH_3 C (CH_2)_4 CH = O$
- **25.** 5 **26.** 8 **27.** 9 **28** 5 **29.** 5

PART-II: GRINARD REAGENT

EXERCISE - I

(CH₃)₃CMgCl on reaction with D₂O produces 1.

[IIT 1996]

- (A) (CH₂)₂CD
- (B) (CH₂)₂COD
- $(C)(CD)_{2}CD$
- (D) (CD)₃COD

Which of the following will react with water: 2.

[IIT 1998]

- (B) Cl₃CCHO
- (C) CCI₄
- (D) CICH₂CH₂CI
- Identify the correct order of boiling point of the following compounds: 3.

[IIT 2002]

- CH₂CH₂CH₂CHO

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

 $Ph - C \equiv C - CH_3 \xrightarrow{Hg^{2+}/H^+} A$ 4.

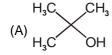
[IIT 2003]

A is



5. In the reaction, [IIT 2003]

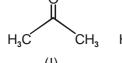
Ethyl ester $\xrightarrow{CH_3MgBr}$ P, the poduct P will be



(B)
$$C_2H_5$$
 OH

- The order of reactivity of phenyl magnesium bromide with the following compounds is 6.

[IIT 2004]



- (II)

(III)

(A)(II) > (III) > (I)

(B)(I) > (III) > (II)

(C)(II) > (I) > (III)

- (D) All react with the same rate
- 7. Phenyl magnesium bromide reacting with t-Butyl alcohol gives

[JEE 2005]

- (A) Ph OH

Paragraph for Question Nos. 8 and 9

An acyclic hydrocarbon \mathbf{P} , having molecular formula C_6H_{10} , gave acetone as the only organic product through the following sequence of reaction, in which **Q** is an intermediate organic compound.

8. The structure of compound P is:

(A)
$$CH_3CH_2CH_2CH_2 - C \equiv C - H$$

(B)
$$H_3CCH_2 - C \equiv C - CH_2CH_3$$

$$H_3C$$
(C) $H - C - C \equiv C - CH_3$
 H_3C

$$\begin{array}{c} H_3C \\ (D) \ H_3C - C - C \equiv C - H \end{array}$$

9. The structure of the compound **Q** is:

$$\begin{array}{c} H_3C \\ (A) \\ H - C - C - CH_2CH_3 \\ H_3C \\ \end{array}$$

$$\begin{array}{c} \text{H}_{3}\text{C} & \text{OH} \\ \text{(C)} & \text{H} - \text{C} - \text{CH}_{2}\text{CHCH}_{3} \\ \text{H}_{3}\text{C} & \end{array}$$

10. The major product in the following reaction is [IIT Advance - 2014]

$$CI$$
 CH_3
 $CH_3MgBr, dry ether, 0°C$
 CH_3
 $CH_3MgBr, dry ether, 0°C$

In the following reactions

$$C_8H_6 \xrightarrow{\text{Pd-BaSO}_4} C_8H_8 \xrightarrow{\text{i. B}_2H_6} X$$

$$\downarrow H_2O$$

$$\downarrow H_2SO_4, H_2SO_4$$

$$C_8H_8O \xrightarrow{\text{i. EtMgBr, H}_2O} Y$$
ii. H⁺, heat

11. Compound X is

12. The major compound Y is

13. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are)

[IIT-JEE Advanced 2015]

(A)
$$H_3C$$
 CH_3

(B) H_2C
 H_2C
 H_3

(C) H_2C
 H_3

(D) H_2C
 H_3

EXERCISE - II

- 1. Write the structural formula of the main organic product formed when ethyl acetate is treated with double the molar quantity of methyl magnesium bromide and the reaction mixture is poured into water. **[IIT 1981]**
- 2. State the conditions under which the following preparation is carried out. "Aniline from benzene"

[JEE 1983]

- 3. Arrange the following in order of their increasing reactivity towards HCN / RMgX [IIT 1985] CH_3CHO , CH_3COCH_3 , HCHO, $C_2H_5COCH_3$
- 4. Identify the major product in the following reactions:

[IIT 1993]

$$C_6H_5COOH + CH_3MgI \rightarrow ? + ?$$

5. Predict the major product in the following reaction :

[IIT 1994]

$$\text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{CH}_3 \xrightarrow{\text{(i) CH}_3\text{MgBr (excess)}}$$

6. The total number of carboxylic acid groups in the product **P** is

[JEE ADVANCE: 2013]

$$\begin{array}{c|c}
 & 1. \ H_3O^+, \Delta \\
\hline
 & 2. \ O_3 \\
 & 3. \ H_2O_2
\end{array}$$
(P)

ANSWER KEY

EXERCISE -

- 1. Α 2. В 3. В Α 5. 6. С 7. В
- С 12. 8. D В 10. D 11. D 13. BD

EXERCISE - II

1. Esters when treated with Gringard reagents followed by hydrolysis form ketones. Ketones react further with excess Grignard reagent followed by hydrolysis to form tertiary alcohols.

$$CH_3 - C - OCH_2CH_3 \xrightarrow{(1) CH_3MgBr} H_3C - C - CH_3$$
Ethyl acetate

$$CH_3 - C - CH_3 \xrightarrow{(1) CH_3MgBr} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

$$CH_3 - C - CH_3 \xrightarrow{(2) H^+/H_2O} H_3C - C - OH$$

3. Steric hindrance at carbonyl carbon determine the reactivity towards nucleophilic addition reaction. Greater the steric hindrance, smaller the reactivity.

$$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$$

- $C_6H_5COOH + CH_3MgI \rightarrow CH_4 + C_6H_5COOMgBr$ 4.
- $C_6H_5 CH_2 C OCH_3 \xrightarrow{(1) CH_3MgBr} C_6H_5 CH_2 C CH_3$ 5.

$$C_6H_5 - CH_2 - C - CH_3 \xrightarrow{(1) CH_3MgBr} C_6H_5 - CH_2 - C - CH_3 \xrightarrow{(2) H^{+}/H_2O} C_6H_5 - CH_2 - C - CH_3$$

6. 2