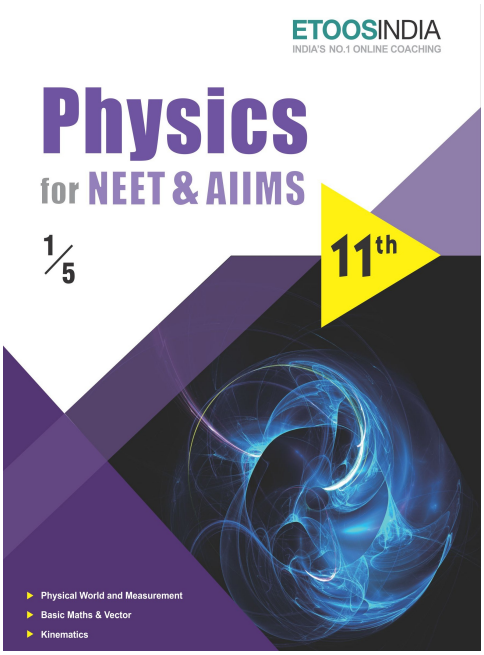
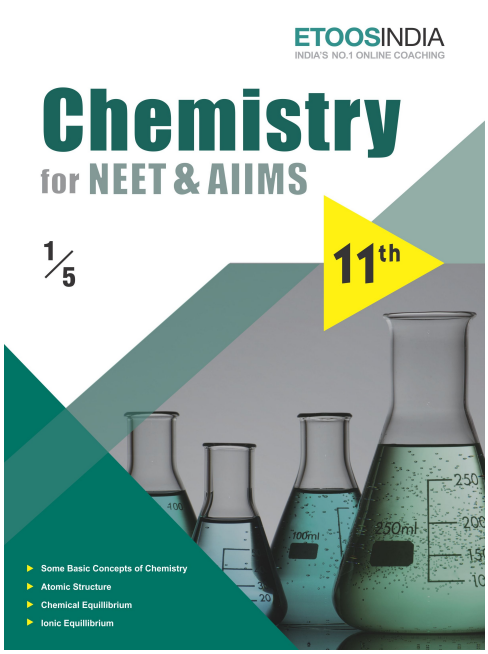
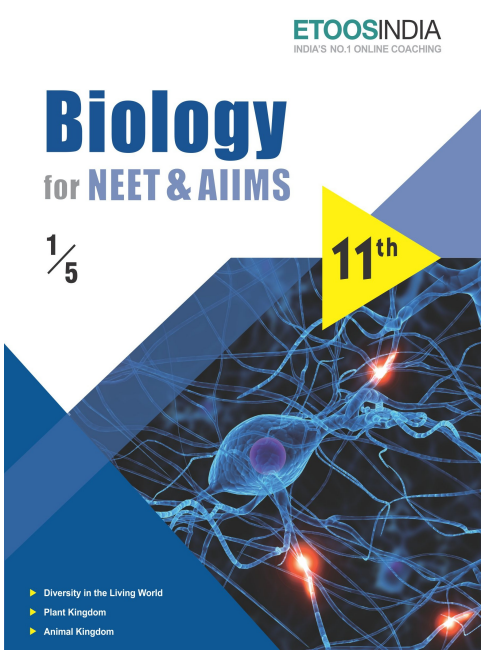
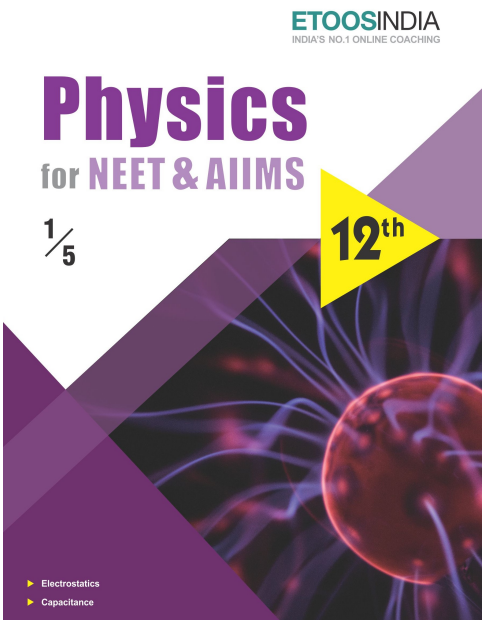
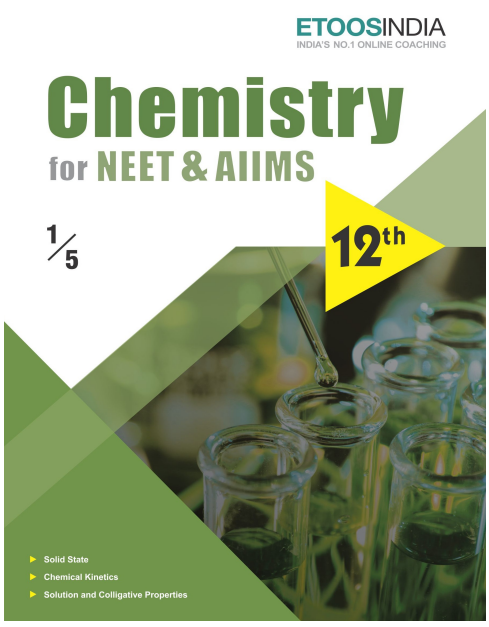
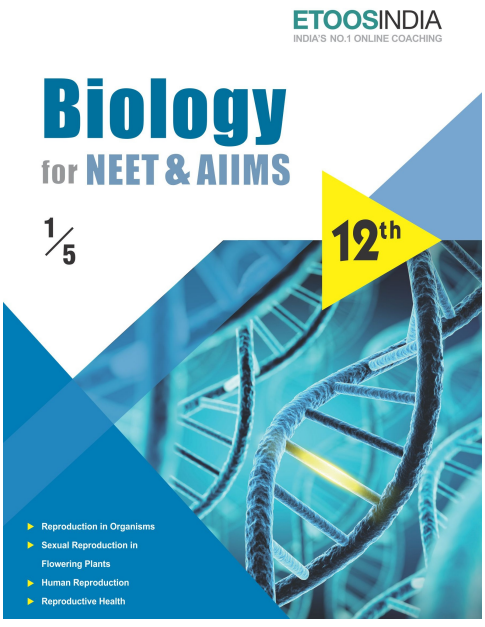












CHAPTER 15

REACTION MECHANISM

You mix a bunch of ingredients and once in a great while Chemistry happens.

"Bill Watterson"

INTRODUCTION

Reaction mechanism is the step by step sequence of elimentry reaction by which overall chemical change occurs. A chemical mechanism is the theoritical conjecture that tries to describe in detail what takes place at each stage of an overall chemical reaction. The detailed steps of a reaction are not observable in most cases. The conjectured mechanism is choosen because it is thermodynamically feasible and has experimental support in isolated intermediates or other quantitative and qualitative characteristics of the reaction. A complete mechanism must also explain the reason for the reactants and catalyst used, the stereochemistry observed in reactants and products, all products formed and the amount of each.

Types of Reactions

In organic chemistry the following types of reaction are more important,

(I) Substitution reaction

(II) Elimination reaction

(III) Addition reaction

(IV) Rearrangement reaction

(V) Isomerisation reactions

(I) Substitution Reaction:

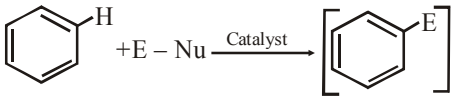
Reactions in which one atom or a group of substrate is replaced by other atom or group are called as substitution reactions.

(A) Electrophilic substitution reactions

(B) Nucleophilic substitution reactions

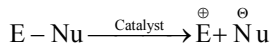
(C) Free radical substitution reactions

(A) Electrophilic substitution reactions[ESR] : Characteristic reaction of arenes is ESR

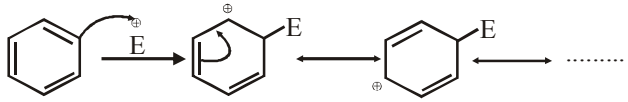


Mechanism :

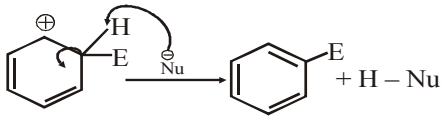
Formation of $\overset{\oplus}{E}$



Attack of $\overset{\oplus}{E}$

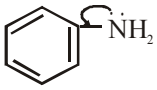


Abstraction of $\overset{\oplus}{H}$



Ex. Give reactivity order for electrophilic substitution reaction.

(i)



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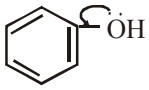
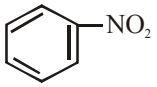


Less EN of nitrogen so more + M so more e^- density So more reactive

Less + M of – OH due to more EN

(ii)



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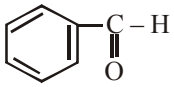
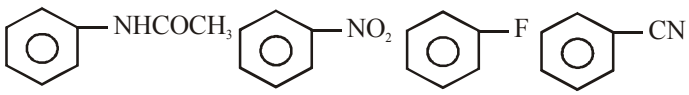


More – M of – NO_2 & more –I so e^- density decrease (more) so less reactive

less – M of – CHO & less –I so e^- density decreases (less) so more reactive.

(iii)



+M –M (more) –I –M (less)

ESR order I > III > IV > II

Etoos Tips & Formulas

1. Rate determining step

The slowest step of the mechanism known as rate determining step of the reaction.Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction and generally using rate determine step (R.D.S).

An organic reaction can be represented as

$$\textbf{Reactant (substrate) + Reagent} \xrightarrow{\text{solvent}} \textbf{Product}$$

Homolytic bond dissociation

Ex. $A–B \longrightarrow A^{\circ} + B^{\circ}$

Hetrolytic bond dissociation

Ex. $A–B \longrightarrow A^{\oplus} + B^{\ominus}$

2. Types of Reagents

A reagent generates three type of attacking species. Which are nucleophile, electrophile and radical.

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

(a) Electrophiles : Electrophiles are electron deficient species.

Ex. $\overset{\oplus}{H}$ $\overset{\oplus}{Cl}$,$\overset{\oplus}{Br}$,$\overset{\oplus}{NO_2}$, $\overset{\oplus}{CH_3}$ (positively charged species), PCl_5, SO_2, SO_3 BH_3(species with vacant orbital at central atom, carbenes) etc.

(b) Nucleophiles : It is the electron rich species having atleast one unshared pair of electron. It can be neutral or negativetely charged it is always a lewis base.

Ex. CN^-, OH^-, Br^- , I^- , NH_3 , H_2O etc.

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

Ex. $\dot{C}H_3$ $C_2H_5^{\bullet}$, $C_2H_5O^{\bullet}$, $CH_3COO^{\bullet}$, $X^{\bullet}$ etc.

3. Nucleophilicity

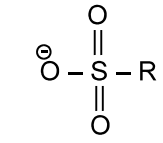
The tendency to give e^- pair to an electron deficient carbon atom is defined as nucleophilicity.

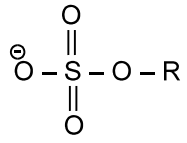
Leaving group Ability/Nucleofugality

(a) Order of leaving ability of halide ion

$\overset{\ominus}{I} > \overset{\ominus}{Br} > \overset{\ominus}{Cl} > \overset{\ominus}{F}$

(b) Other good leaving groups are


Alkanesulphonate ion


Alkyl sulphate ion

SOLVED EXAMPLE

Ex.1 In the case homologous series of alkanes, which one of the following statements is incorrect

(A) The members of the series are isomers of each other

(B) The members of the series have similar chemical properties

(C) The members of the series have the general formula C_nH_{2n+2}, where n is an integer

(D) The difference between any two successive members of the series corresponds to 14 unit of relative atomic mass

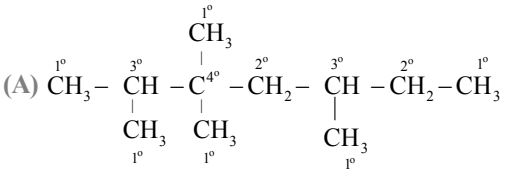
Sol. **(A)** The difference between any two successive members of the homologous series $-CH_2-$ i.e., the molecular weight of every two adjacent members differ by 14. $(CH_2 = 12+2 = 14)$

Ex.2 How many primary, secondary, tertiary and quaternary carbons are present in the following hydrocarbon

$CH_3-CH(CH_3)-C(CH_3)_2-CH_2-CH(CH_3)-CH_2-CH_3$

	Primary	Secondary	Tertiary	Quaternary
(A)	6	2	2	1
(B)	2	6	3	0
(C)	2	4	3	2
(D)	2	2	4	3

Sol. **(A)**



$1^o \Rightarrow$ Primary 6, $2^o \Rightarrow$ Secondary 2

$3^o \Rightarrow$ Tertiary 2, $4^o \Rightarrow$ Quanternary1

Ex.3 The octane number of a sample of petrol is 40. It means that its knocking property is equal to the mixture of

(A) 40% n-heptane + 60% iso-octane **(B)** 40% petrol + 60% iso-octane

(C) 60% n-heptane + 40% iso-octane **(D)** 60% petrol + 40% iso-octane

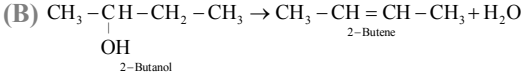
Sol. **(C)** Octane number of fuel is the percentage of iso- octane in mixture.

Ex.4 Formation of 2-butene as major product by dehydration of 2-butanol is according to

(A) Markownikoff rule **(B)** Saytzeff rule

(C) Peroxide effect **(D)** Anti-Markownikoff rule

Sol. **(B)**

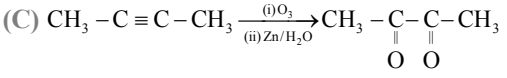


According to this rule H atom goes from that β- carbon which is less hydrogenated.

Ex.5 $CH_3C \equiv CCH_3 \xrightarrow[(ii)H_2O/Zn]{(i)\ X} CH_3-\underset{O}{\overset{|}{C}}-\underset{O}{\overset{|}{C}}-CH_3$ X in the above reaction is

(A) HNO_3 **(B)** O_2 **(C)** O_3 **(D)** $KMnO_4$

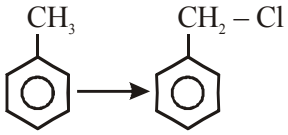
Sol. **(C)**



Exercise # 1 SINGLE OBJECTIVE NEET LEVEL

1. To which of the following four types does this reaction belong $B^- + R - A \rightarrow B - R + A^-$
(A) Unimolecular electrophilic substitution
(B) Bimolecular electrophilic substitution
(C) Unimolecular nucleophilic substitution
(D) Bimolecular nucleophilic substitution

2. An alkyl halide may be converted into an alcohol by
(A) Elimination
(B) Addition
(C) Substitution
(D) Dehydrohalogenation

3. 

The above reaction proceeds through
(A) Nucleophilic substitution
(B) Electrophilic substitution
(C) Free radical substitution
(D) More than one of the above processes

4. Geometry of reaction intermediate in SN^1 reaction is
(A) Tetrahedral
(B) Planar
(C) Triangular bipyramidal
(D) None of these

5. $$H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br + KOH(Aq.) \rightarrow H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH + KBr$$
above reaction is
(A) SN^1 (B) SN^2
(C) E_1 (D) Both (A) and (B)

6. In electrophilic substitution reaction nitrobenzene is
(A) Meta-directing
(B) Ortho-directing
(C) Para-directing
(D) Not reactive and does not undergo any substitution
(E) Non-selective

7. The most common type of reaction in aromatic compounds is
(A) Elimination reaction
(B) Addition reaction
(C) Electrophilic substitution reaction
(D) Rearrangement reaction

8. The function of $AlCl_3$ in Friedel-Craft's reaction is
(A) To absorb HCl
(B) To absorb water
(C) To produce nucleophile
(D) To produce electrophile

9. Which of the following can't be used in Friedal Craft's reactions
(A) $FeCl_3$ (B) $FeBr_2$
(C) $AlCl_3$ (D) NaCl

10. The nitration of a compound is due to the
(A) NO_2 (B) NO_3
(C) NO (D) NO_2^+

11. Dehydrohalogenation of an alkyl halide is a/an
(A) Nucleophilic substitution reaction
(B) Elimination reaction
(C) Both nucleophilic substitution and elimination reaction
(D) Rearrangement

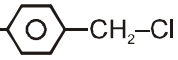
12. Addition of HCl to vinyl chloride gives 1, 1-dichloroethane because of
(A) Mesomeric effect of Cl
(B) Inductive effect of Cl
(C) Restricted rotation around double bond
(D) None of these

13. Formation of ethylene from acetylene is an example of
(A) Elimination reaction
(B) Substitution reaction
(C) Addition reaction
(D) Condensation reaction

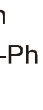
14. Conversion of CH_4 to CH_3Cl is an example of which of the following reaction
(A) Electrophilic substitution
(B) Free radical addition
(C) Nucleophilic substitution
(D) Free radical substituion

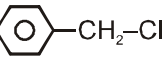
Exercise # 2 SINGLE OBJECTIVE AIIMS LEVEL

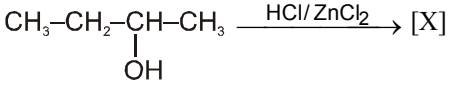
1. Which of the following alkyl halide is most reactive towards H_2O ?

(A) 

(B) 

(C) 

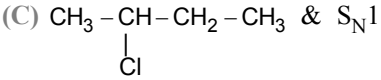
(D) 

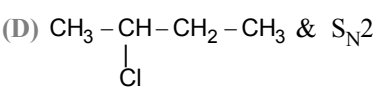
2. 

Identify X and the mechanism of the reaction.

(A) $CH_3-CH_2-CH_2-CH_2-Cl$ & S_N1

(B) $CH_3-CH_2-CH_2-CH_2-Cl$ & S_N2

(C) 

(D) 

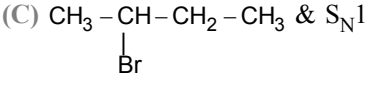
3. $CH_3(CH_2)_2CH_2OH \xrightarrow{HBr} X,$

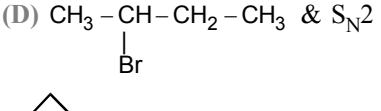
1 - butanol

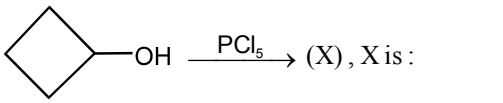
Identify X and the mechanism of the reaction

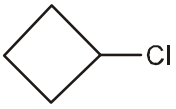
(A) $CH_3-CH_2-CH_2-CH_2-Br$ & S_N1

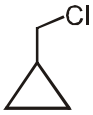
(B) $CH_3-CH_2-CH_2-CH_2-Br$ & S_N2

(C) 

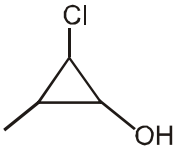
(D) 

4. 

(A) 

(B) 

(C) 

(D) 

5. What is the final product of reaction.

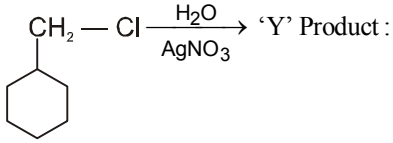
$CH_3-C\equiv CH \xrightarrow{Na} \xrightarrow{CH_3-CH_2-I}$ Product

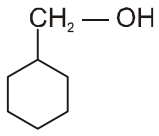
(A) $CH_2=CH-CH_2-CH_3$

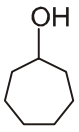
(B) $CH_3-CH_2-C\equiv C-CH_2-CH_3$

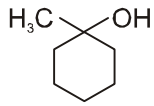
(C) $CH\equiv C-CH_2-CH_2-CH_3$

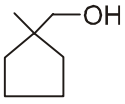
(D) $CH_3-C\equiv C-CH_2-CH_3$

6. 

(A) 

(B) 

(C) 

(D) 

7. S_N2 mechanism proceeds through intervention of :

(A) Carbonium ion **(B)** Transition state

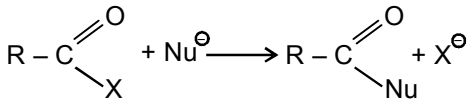
(C) Free radical **(D)** Carbanion

8. When the concentration of alkyl halide is tripled and the concentration of $\overset{\ominus}{O}H$ ion is reduced to half, the rate of S_N2 reaction increases by:

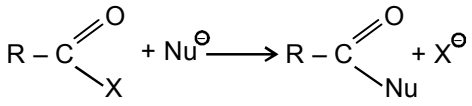
(A) 3 times **(B)** 2 times

(C) 1.5 times **(D)** 6 times

9. The reaction



is slowest when X is :

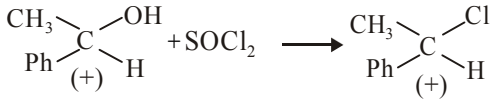
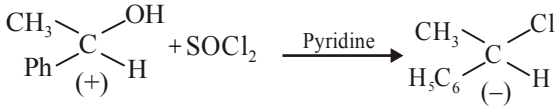
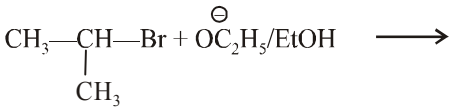
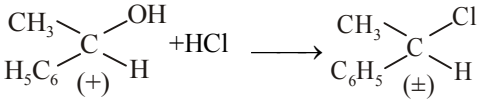


(A) Cl **(B)** NH_2

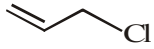
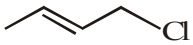
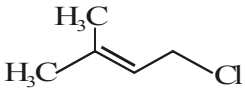
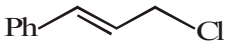
(C) OC_2H_5 **(D)** $OCOCH_3$

Exercise # 3 PART - 1 MATRIX MATCH COLUMN

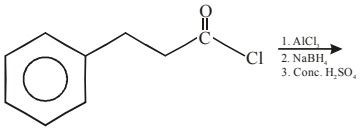
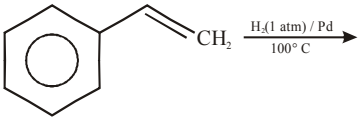
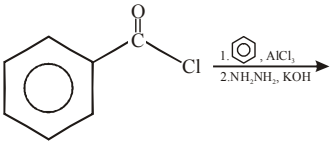
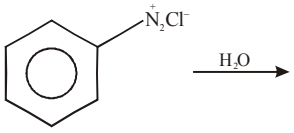
1. Match the column I with column II.

Column-I (reaction)	Column-II (Mechanism)
(A) 	(p) S_N1
(B) 	(q) S_N2
(C) 	(r) S_Ni
(D) 	(s) E_2

2. Match the column I with column II.

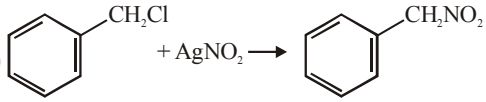
Column-I (Substrate)	Column-II (Relative rate of solvolysis in 50% aqueous ethanol at 45°C)
(A) 	(p) 7700
(B) 	(q) 1
(C) 	(r) 91
(D) 	(s) 1,30,000

3. Match the entries listed in Column I with appropriate entries listed in Column II.

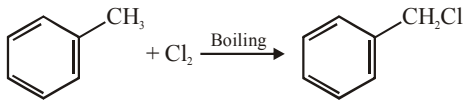
Column-I	Column-II
(A) 	(p) Electrophilic sustitution
(B) 	(q) A hydrocarbon is the final product
(C) 	(r) Aromaticity is destroyed
(D) 	(s) Nucleophilic substitution

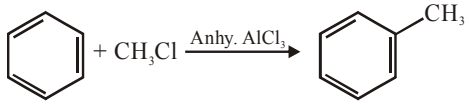
Exercise # 4 PART - 1 PREVIOUS YEAR (NEET/AIPMT)

1. Which one of the following is a free radical substitution reaction? [CBSE AIPMT 2003]

(A) 

(B) $CH_3CHO + HCN \longrightarrow CH_3CH(OH)CN$

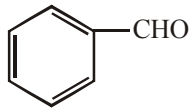
(C) 

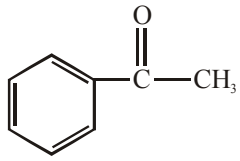
(D) 

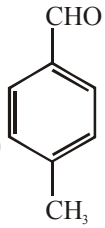
2. Which of the following reactions is an example of nucleophilic substitution reaction? [CBSE AIPMT 2009]

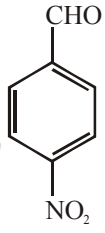
(A) $RX + KOH \rightarrow ROH + KX$
(B) $2\,RX + 2NA \rightarrow R - R + 2NaX$
(C) $RX + H_2 \rightarrow RH + HX$
(D) $RX + Mg \rightarrow RMgX$

3. Which one is most reactive towards nucleophilic addition reaction? [CBSE AIPMT 2014]

(A) 

(B) 

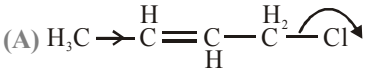
(C) 

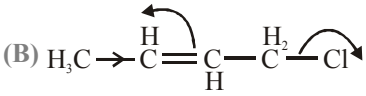
(D) 

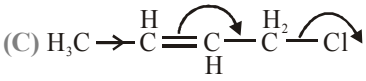
4. Which of the following organic compounds has same hybridisation as its combustion (CO_2) product? [CBSE AIPMT 2014]

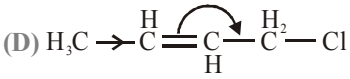
(A) Ethane (B) Ethyne
(C) Ethene (D) Ethanol

5. Which of the following is the most correct electron displacement for a nucleophilic reaction to take place? [CBSE AIPMT 2015]

(A) 

(B) 

(C) 

(D) 

6. In an S_N1 reaction on chiral centres there is [CBSE AIPMT 2015]

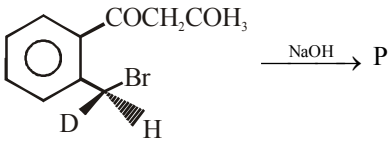
(A) 100 % racemisation
(B) inversion more than retention leading to partial racemisation
(C) 100% retention
(D) 100% inversion

7. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is [NEET 2016, Phase I]

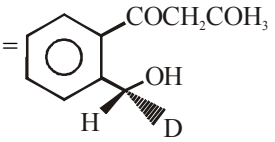
(A) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration
(B) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
(C) a carbonyl compound with a hydrogen atom on its alphs-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
(D) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol

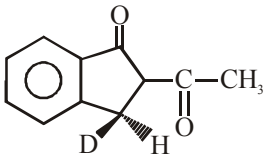
MOCK TEST

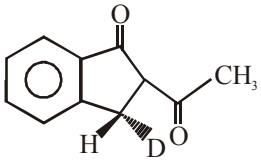
STRAIGTH OBJECTIVE TYPE

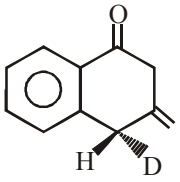
1. 

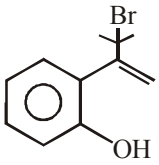
Which of the following statement is correct

(A) P = 

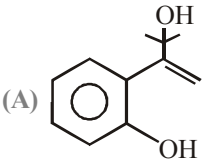
(B) P = 

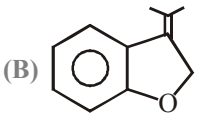
(C) P = 

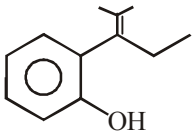
(D) P = 

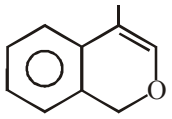
2. 

$\xrightarrow{NaOH}$ Product, Product is

(A) 

(B) 

(C) 

(D) 

3. $CH_3 - CH_2SH \xrightarrow[(ii)\ \text{ethylene oxide}]{(i)\ CH_3O^{\ominus}}$ Product, Product is :

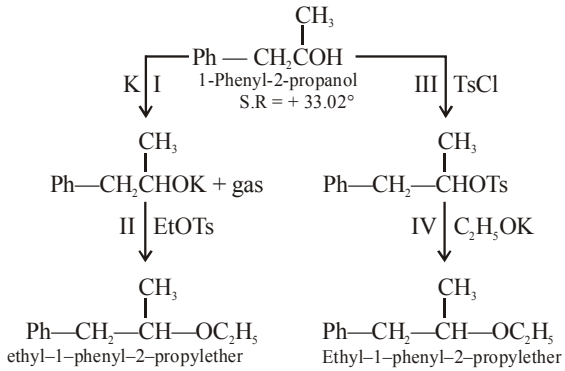
(A) $CH_3 - CH_2 - S - CH_2 - CH_2 - OH$

(B) $CH_3 - CH_2O^{\ominus}$

(C) $CH_3 - CH_2 - O - CH_2 - CH_2 - OH$

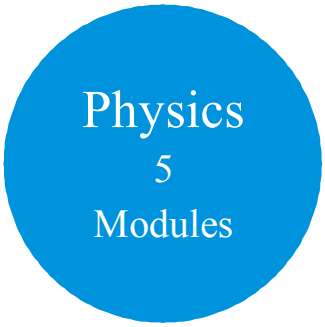
(D) $CH_3 - CH_2 - \overset{\oplus}{S}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$

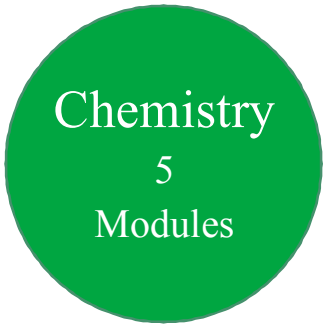
4. Read the following road map carefully

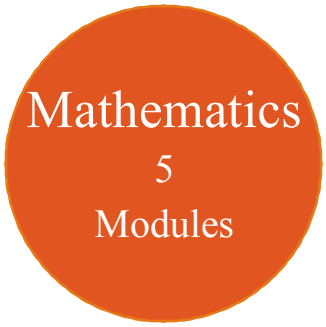


(A) Both the ethers obtained by the two routes have opposite but equal optical rotation.
(B) One of the either is obtained as a recemic mixture.
(C) Step II & III both are S_N2 reaction and both have inversion
(D) Step II has inversion but step III has retention.

11th Class Modules Chapter Details

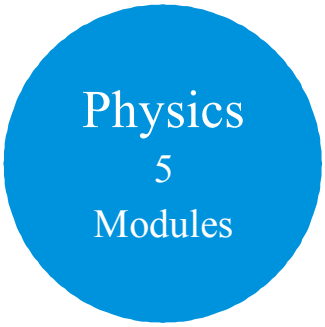


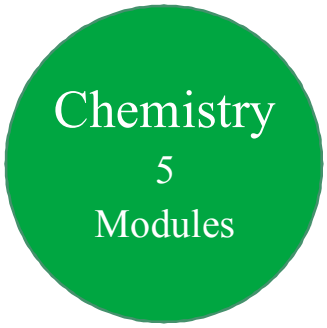


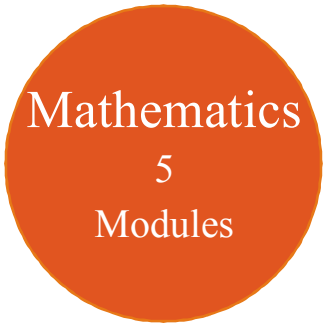


PHYSICS	CHEMISTRY	BIOLOGY
Module-1 1. Physical World & Measurements 2. Basic Maths & Vector 3. Kinematics **Module-2** 1. Law of Motion & Friction 2. Work, Energy & Power **Module-3** 1. Motion of system of particles & Rigid Body 2. Gravitation **Module-4** 1. Mechanical Properties of Matter 2. Thermal Properties of Matter **Module-5** 1. Oscillations 2. Waves	**Module-1(PC)** 1. Some Basic Conceps of Chemistry 2. Atomic Structure 3. Chemical Equilibrium 4. Ionic Equilibrium **Module-2(PC)** 1. Thermodynamics & Thermochemistry 2. Redox Reaction 3. States Of Matter (Gaseous & Liquid) **Module-3(IC)** 1. Periodic Table 2. Chemical Bonding 3. Hydrogen & Its Compounds 4. S-Block **Module-4(OC)** 1. Nomenclature of Organic Compounds 2. Isomerism 3. General Organic Chemistry **Module-5(OC)** 1. Reaction Mechanism 2. Hydrocarbon 3. Aromatic Hydrocarbon 4. Environmental Chemistry & Analysis Of Organic Compounds	**Module-1** 1. Diversity in the Living World 2. Plant Kingdom 3. Animal Kingdom **Module-2** 1. Morphology in Flowering Plants 2. Anatomy of Flowering Plants 3. Structural Organization in Animals **Module-3** 1. Cell: The Unit of Life 2. Biomolecules 3. Cell Cycle & Cell Division 4. Transport in Plants 5. Mineral Nutrition **Module-4** 1. Photosynthesis in Higher Plants 2. Respiration in Plants 3. Plant Growth and Development 4. Digestion & Absorption 5. Breathing & Exchange of Gases **Module-5** 1. Body Fluids & Its Circulation 2. Excretory Products & Their Elimination 3. Locomotion & Its Movement 4. Neural Control & Coordination 5. Chemical Coordination and Integration

12th Class Modules Chapter Details







PHYSICS

Module-1

1. Electrostatics
2. Capacitance

Module-2

1. Current Electricity
2. Magnetic Effect of Current and Magnetism

Module-3

1. Electromagnetic Induction
2. Alternating Current

Module-4

1. Geometrical Optics
2. Wave Optics

Module-5

1. Modern Physics
2. Nuclear Physics
3. Solids & Semiconductor Devices
4. Electromagnetic Waves

CHEMISTRY

Module-1(PC)

1. Solid State
2. Chemical Kinetics
3. Solutions and Colligative Properties

Module-2(PC)

1. Electrochemistry
2. Surface Chemistry

Module-3(IC)

1. P-Block Elements
2. Transition Elements (d & f block)
3. Co-ordination Compound
4. Metallurgy

Module-4(OC)

1. HaloAlkanes & HaloArenes
2. Alcohol, Phenol & Ether
3. Aldehyde, Ketone & Carboxylic Acid

Module-5(OC)

1. Nitrogen & Its Derivatives
2. Biomolecules & Polymers
3. Chemistry in Everyday Life

BIOLOGY

Module-1

1. Reproduction in Organisms
2. Sexual Reproduction in Flowering Plants
3. Human Reproduction
4. Reproductive Health

Module-2

1. Principles of Inheritance and Variation
2. Molecular Basis of Inheritance
3. Evolution

Module-3

1. Human Health and Disease
2. Strategies for Enhancement in Food Production
3. Microbes in Human Welfare

Module-4

1. Biotechnology: Principles and Processes
2. Biotechnology and Its Applications
3. Organisms and Populations

Module-5

1. Ecosystem
2. Biodiversity and Conservation
3. Environmental Issues