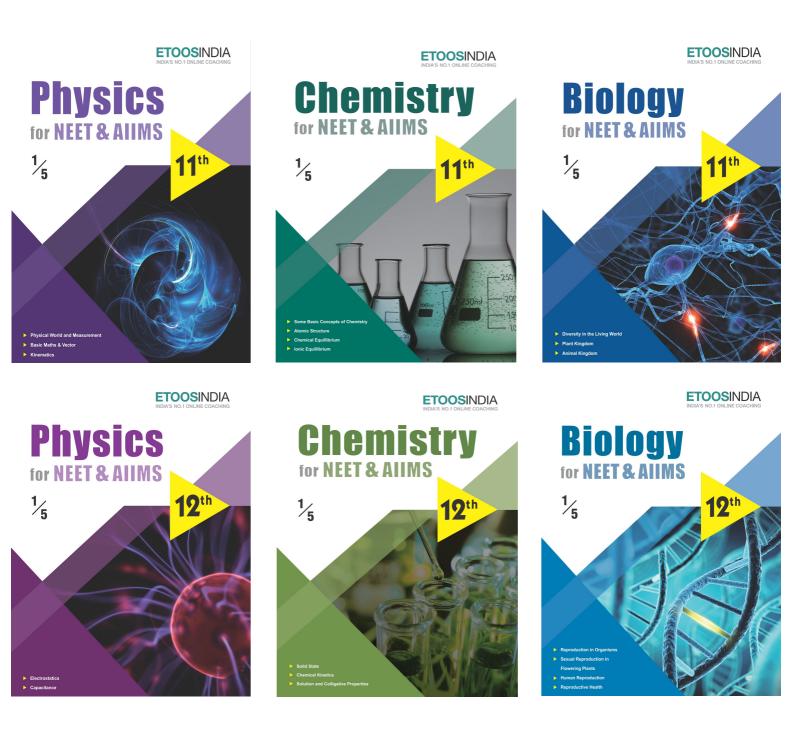
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### CHAPTER

## HALOALKANES AND HALOARENES

*The reactions of organic magnesium compounds are of two kinds - reactions of substitution and reactions of addition.* 

"VICTOR GRIGNARD"

### **INTRODUCTION**

ompounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as **halogen derivatives**.

There are three major classes of organohalogen compounds; alkyl halides, vinyl halides, and aryl halides.

An **alkyl halide** simply has a halogen atoms bonded to one of the sp<sup>3</sup> hybrid carbon atoms of an alkyl group. A **vinyl halide** or **Aryl halide** has a halogen atom bonded to one of the sp<sup>2</sup> hybrid carbon atoms or an aromatic ring. They are different from alkyl halides because their bonding and hybridization are different.

#### **CHEMISTRY FOR NEET & AIIMS**

Ex. 
$$CH_3 - C - CH_3$$
,  $CH_3 - C - CH_2 - CH_3$ ,  $CH_3 - C - CH_2$  ..... $CH_3$  etc. (All methyl ketones)  
 $CH_3 - C - COOH$ ,  $CH_3 - C - CHO$  Also show haloform reaction.  
(-) ve haloform reaction : Reaction in which haloforms are not formed with X<sub>2</sub> and alkali.  
 $CH_3 - C - \ddot{C}l$ ,  $CH_3 - C - \ddot{O}H$ ,  $CH_3 - C - \ddot{N}H_2$ ,  $CH_3$ ,  $CH_3 - C - \ddot{O} - CH_3$ . do not show haloform reaction.  
(iii) Preparation of pure CHCl<sub>3</sub> :  
 $CCl_3CHO_2H_2O \xrightarrow{NaOH} CHCl_3 + HCOONa + 2H_2O$   
Chloral hydrate (iv) Industrial Preparation :  
 $CH_3 - CH_3 - CH_3$ 

$$\begin{array}{c} CH_3CH_2 - OH \\ or \\ CH_3COCH_3 \end{array} \xrightarrow{aq. \ NaCl/electrolysis} CHCl_3 + HCOONa \\ & or \\ CH_3COONa \end{array}$$

**Physical Properties :** 

 $CHCl_3$  is colourless and sweet smelling liquid. it's B.P. is 61°C and it is insoluble in H<sub>2</sub>O and have density more than H<sub>2</sub>O. Chloroform is used as Anaesthetic.

**Chemical Properties :** 

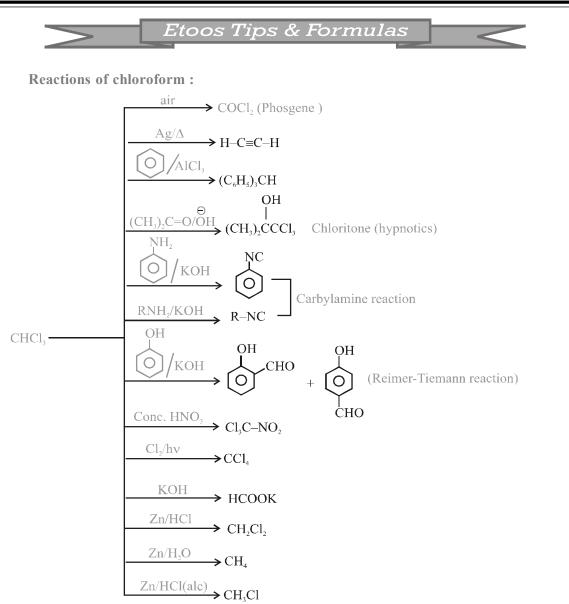
(i) Oxidation :  $CHCl_3 + [O] \xrightarrow{Air and light} COCl_2 + HCl$ 

Phosgene gas or Carbonyl Chloride

 $CHCl_3$  is stored in dark coloured bottles which are filled upto the brim to prevent oxidation of  $CHCl_3$  into  $COCl_2$  and 1% ethanol is also added to chloroform.

$$O = C \bigvee_{Cl}^{Cl} + 2HO - C_2H_3 \xrightarrow{-2HCl} O = C \bigvee_{OC_2H_5}^{OC_2H_5}$$
ETOOS KEY POINTS
  
Reagent Pure CHCl<sub>3</sub> Impure CHCl<sub>3</sub>(COCl<sub>2</sub>+HCl)
Blue litmus No Change turns into red
AgNO<sub>3</sub> No reaction White ppt of AgCl
Conc. H<sub>2</sub>SO<sub>4</sub> No reaction Yellow solution

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- Purity of chloroform (presence of phosgene) can be tested before use as anaesthetic by treating with aqueous solution of AgNO<sub>3</sub> because the presence of COCl, may cause cardiac failure.
- Chloroform is stored in dark colour bottle containing small amount of ethyl alcohol. (It converts phosgene into diethylcarbonate).

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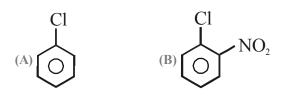
#### SOLVED EXAMPLE

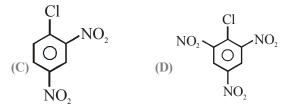
Sol.

- Ex. 1Which of the following is used as insecticide :<br/>(A) D.D.T.(B) Chloritone
  - (C) Chloropicrin (D) (A) and (C) both
- Sol. (D)
- Ex. 2 The product in the following reaction is :  $Ph-Cl+Fe/Br_2 \longrightarrow Product$ (A) o- bromo-chloro benzene (B) p- bromo-chloro benzene
  - (C) (A) and (B) both
  - (D) 2, 4, 6-tribromo chloro benzene
- **Sol.** (C) Since Cl group is deactivating and o/p directing group so only o– and p– products are formed.
- Ex. 3 The most reactive towards  $SN^1$  is : (A) PhCH<sub>2</sub>Cl (B) Ph-Cl (C) CH<sub>3</sub>CHCl(CH<sub>3</sub>) (D) p-NO<sub>2</sub>--Ph--CH<sub>2</sub>--Cl
- Sol. (A)  $S_{N^1}$  the intermediate carbocation is formed.

 $C_6H_5$ — $CH_2Cl$ — $C_6H_5CH_2$  is maximum stable due to resonance.

Ex. 4 Which of the following undergoes Hydrolysis most easily :





Sol. (D) If there is more m-directing group then there will be more nuclephilic substitution reaction.

Ex. 5 The order of reactivity of following alcohols with halogen acids is .....

(i) 
$$CH_3CH_2 - CH_2 - OH$$
  
(ii)  $CH_3CH_2 - CH - OH$   
 $CH_3$ 

(iii) 
$$CH_3CH_2 - C - OH$$
  
 $CH_3$   
 $CH_3$ 

(B) Reaction between alcohols and halogen acid follows  $S_N^{-1}$  mechanism. In  $S_N^{-1}$  mechanism carbocations are formed as intermediates.

Let us consider the formation of carbocations with the given three alcohols

$$CH_3 - CH_2 - CH_2 - OH$$
  $CH_3 - CH_2 - CH$ 

In this case, 1° carbocation is formed. It is least stable. So, here  $S_N^2$  mechanism is followed. In this  $S_N^2$  mechanism a transitory state is observed in  $\alpha$ -carbon is linked with two nucleophiles.

$$\begin{array}{ccc} CH_3-CH_2-CH-OH \\ CH_3 \end{array} & \begin{array}{c} CH_3-CH_2-\overset{\bullet}{C}H+OH^- \\ CH_3 \end{array} \\ \begin{array}{c} 2^\circ \mbox{ carbocation (more stable than 1^\circ \mbox{ carbocation})} \\ CH_3-CH_2-\overset{\bullet}{C}-OH \\ CH_3 \end{array} & \begin{array}{c} CH_3 \\ H_3C-CH_2-\overset{\bullet}{C}+OH^- \\ CH_3 \\ 3^\circ \mbox{ carbocation (most stable)} \end{array} \end{array}$$

The raction proceeded with stable carbocatio. Higher the stability of carbocation, higher will be the possibilities of attack of  $X^-$  ion to the carbocation. As, the tertiary carbocation is most stable so the possibilities of attack of  $X^-$  ion are more prominent in case of tertiary carbocations. Thus, attack of  $X^-$  ion to carbocation is proceeded with tertiary carbocation as follows

$$\begin{array}{c} H_{3}C-CH_{2}-\overset{CH_{3}}{\overset{C}{\overset{G}{}}}+X \longrightarrow H_{3}C-CH_{2}-\overset{CH_{3}}{\overset{C}{\overset{C}{}}}-X \\ CH_{3} \\ \overset{3^{\circ} \text{ carbocation}}{\overset{G}{\overset{G}{}}} \end{array}$$

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#### **CHEMISTRY FOR NEET & AIIMS**

]	Exercise # 1	SINGLE OBJ	IECTIV	VE NEET LEVEL
1. 2.	How many structural isomers are compound with molecular formula (A) 2 (B) 5 (C) 7 (D) 9 In $CH_3CH_2Br$ , % of $Br$ is (A) 80 (B)		11.	The following reaction is known as $C_2H_5OH + SOCl_2 \xrightarrow{Pyridine} C_2H_5Cl + SO_2 + HCl$ (A) Kharasch effect (B) Darzen's procedure (C) Williamson's synthesis (D) Hunsdiecker synthesis reaction
3.	(C) 70 (D) Gem- dibromide is (A) $CH_3CH(Br)OH(Br)CH_3$ (B) $CH_3CBr_2CH_3$ (C) $CH_2(Br)CH_2CH_2$	7	12.	<ul> <li>What is the main product of the reaction between 2-methyl propene with <i>HBr</i></li> <li>(A) 1-bromo butane</li> <li>(B) 1-bromo-2 methyl propane</li> <li>(C) 2-bromo butane</li> <li>(D) 2-bromo-2 methyl propane</li> </ul>
4.	( <b>b</b> ) $CH_2BrCH_2Br$ Ethylidene dibromide is ( <b>A</b> ) $CH_3 - CH_2 - Br$ ( <b>B</b> ) $Br - CH_2 - CH_2 - Br$ ( <b>C</b> ) $CH_3 - CHBr_2$ ( <b>D</b> ) $CH_2 = CBr_2$		13.	Halogenation of alkanes is (A) A reductive process (B) An oxidative process (C) An isothermal process (D) An indothermal process $\stackrel{+}{N} \equiv NBF_4$
5.	Benzylidene chloride is (A) $C_6H_5CH_2Cl$ (B) $C_6H_6$ (C) $C_6H_4ClCH_2Cl$ (D) $C_6H_6$	H <sub>5</sub> CHCl <sub>2</sub> H <sub>5</sub> CCl <sub>3</sub>	14.	
6.		o outyl chloride utyl chloride		In the above process product <i>A</i> is (A) Fluorobenzene (B) Benzene (C) 1, 4-difluorobenzene
7.		logen derivatives of (B) Methane (D) Benzene	15.	( <b>D</b> ) 1, 3-difluorobenzene Silver acetate + $Br_2 \xrightarrow{CS_2}$ . The main product of this reaction is
8.	<ul> <li>Benzene hexachloride is</li> <li>(A) 1, 2, 3, 4, 5, 6-hexachlorocyclohexane</li> <li>(B) 1, 1, 1, 6, 6, 6-hexachlorocyclohexane</li> <li>(C) 1, 6-phenyl-1, 6-chlorohexane</li> <li>(D) 1, 1-phenyl-6, 6-chlorohexane</li> </ul>			(A) $CH_3 - Br$ (B) $CH_3COI$ (C) $CH_3COOH$ (D) None of these
9.	Number of $\pi$ – bonds present in <i>B</i> , hexachloride) are (A) 6 (B) Zero (C) 3 (D) 12		16.	Diazonium salts + $Cu_2Cl_2$ + $HCl \rightarrow \bigcirc$ ,
10.	The general formula for alkyl halid (A) $C_n H_{2n+1} X$ (B) $C_n H_n$ (C) $C_n H_{n+1} X$ (D) $C_n H_n$	$H_{2n+2}X$		<ul> <li>the reaction is known as</li> <li>(A) Chlorination</li> <li>(B) Sandmeyer's reaction</li> <li>(C) Perkin reaction</li> <li>(D) Substitution reaction</li> </ul>

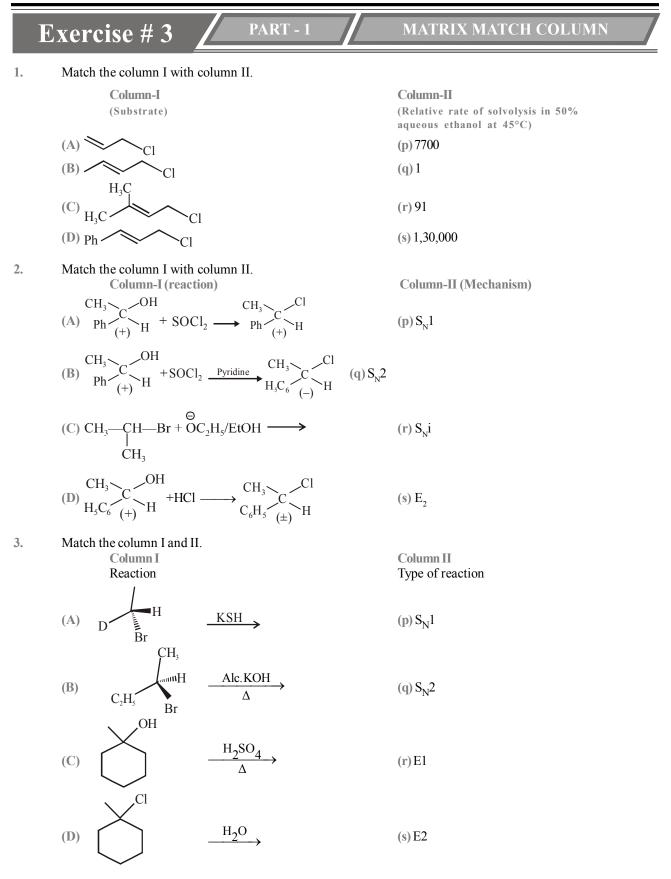
#### **HALOALKANES & HALOARENES**

#### **SINGLE OBJECTIVE** AIIMS LEVEI Exercise # 2 8. Which one of the following compounds most readily 1. Consider the following reaction sequence, undergoes substitution by $S_N 2$ mechanism ? $CH_{3}C \equiv CH \xrightarrow[HgSO_{4}]{aq.H_{2}SO_{4}} A \xrightarrow[Heat]{PCl_{5}} B.$ (A) $H_3C$ (B) $H_3C$ The products (A) and (B) are, respectively, (A) CH,COCH, and CH,CCl,CH, (B) CH, CH, CHO and CH, CH, CHCl, (C) CH, CHOHCH, and CH, CHClCH, $(C) H_3C \longrightarrow Cl \qquad (D) \xrightarrow{H_3C} CH_3$ (D) CH, CH, CH, OH and CH, CH, CH, Cl Which of the following has highest dipole moment: 2. (B) CH,F (A) CH,Cl (D) CH,I (C) CH, Br 9. Sec. Butyl chloride undergo alkaline hydrolysis in the polar solvent by 3. In $S_{N^1}$ the first step involves the formation of (A) $S_{N^2}$ (B) $S_{Nl}$ (A) free radical (B) carbanion (C) $S_{N^1}$ and $S_{N^2}$ (D) none of these (C) carbocation (D) final product 10. The products of reaction of alcoholic silver nitrite The product formed in the reaction 4. with ethyl bromide are $\underset{\text{H}_{\text{III}}}{\text{H}_{\text{III}}} \xrightarrow{\text{OH}} + \text{SOCl}_2 \rightarrow \text{is-}$ (A) Ethane (B) Ethene (C) Ethyl alcohol (D) Nitro ethane 11. The reaction $,CH,Br + OH^- \longrightarrow CH,OH + Br^-$ $(A) \overset{Cl}{\longrightarrow} H \qquad (B) \overset{Cl}{\longrightarrow} H$ obeys the mechanism (A) $S_{N^{l}}$ **(B)** $S_{N^2}$ (D) E, $(\mathbb{C})E_1$ 12. Ethylidene chloride can be prepared by the reaction of HCl and (A) Ethane (B) Ethylene The reaction $HO HO + SOCl_2$ (C) Acetylene (D) Ethylene glycol 5. Grignard reagent can be prepared by 13. $H^{\text{M}} = SO_2 + O_2 + O_1$ (A) $CH_3$ — $CH_2$ — $Cl + Mg \xrightarrow{dry}{ether}$ (B) $CH_3 \longrightarrow CH \longrightarrow CH_2 + Mg \xrightarrow{dry}_{ether} Hg \xrightarrow{dry}_{ether}$ proceeds by the mechanism **(B)** $S_{N^2}$ (A) $S_{N^{l}}$ CH<sub>2</sub> (C) CH<sub>3</sub> -C $-OH + Mg \xrightarrow{dry}{ether}$ (D) $S_{E^2}$ (C) S, i CH<sub>2</sub> 1, 3- Dibromopropane reacts with metallic zinc to 6. (D) All of them form (A) propene (B) cyclopropane 14. Most stable carbocation formed from (CH<sub>2</sub>)<sub>2</sub>C–Br, (C) propane (D) hexane $(C_6H_5)_3$ CBr, $(C_6H_5)_2$ CHBr and $C_6H_5$ CH<sub>2</sub>Br would be (A)C,H, CH, 7. To form alkane isonitrile, alkyl halide is reacted with: (B) (CH,), <sup>⊕</sup><sub>C</sub> (A) KCN (B) AgCN $(\mathbb{C})(\mathbb{C}_{6}\mathbb{H}_{5}), \overset{\oplus}{\mathbb{C}}$ (**D**) (**C**,**H**,), <sup>⊕</sup>CH (C) HCN (D) NH<sub>4</sub>CN

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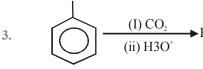
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#### **HALOALKANES & HALOARENES**

### Exercise # 4 PART - 1 6.

- 1. An organic compound A ( $C_4H_0Cl$ ) on reaction with Na/diethly gives a hydrocarbon which on monochlorination gives only one chlora derivative, [CBSE AIPMT 2001] then A is (A) t-butyl chloride (B) s-butyl chloride (C) iso-butyl chioride (D) n-butyl chloride
- 2. Reactivity order of halides for dehydrohalogenation is [CBSE AIPMT 2002] (A) R - F > R - CI > R - Br > R - I(B) R - I > R - Br > R - Cl > R - F $(\mathbb{C})$  R—I>RCI>R—Br>R—F (D) R - F > R - I > R - Br > R - CI

MgBr



#### In the above reaction product 'P' is

[CBSE AIPMT 2002]





 $CH_2CH_2CI \xrightarrow{NaCN} X \xrightarrow{Ni/H_2} Y \xrightarrow{Aceticanhydride} Z$ 4. In above reaction sequence, Z is [CBSE AIPMT 2002] (A) CH, CH, CH, NHCOCH, (B) CH, CH, CH, NH, (C) CH, CH, CH, CONHCH, (D) CH, CH, CH, CONHCOCH,

5. When phenol is treated with CHCl, and NaOH, the product formed is [CBSE AIPMT 2000] (A) benzaldehyde (B) salicylaldehyde (C) salicylic acid (D) benzoic acid

#### PREVIOUS YEAR (NEET/AIPMT)

When CH<sub>2</sub>CH<sub>2</sub>CHCl<sub>2</sub> is treated with NaNH<sub>2</sub>, the product formed is [CBSE AIPMT 2002]

(A)  $CH_3 - CH = CH_2$  $(\mathbf{B}) \operatorname{CH}_3 - \operatorname{C} = \operatorname{Ch}_2$ (C)  $CH_3 - CH_2CH \swarrow NH_2$ 

(D) CH<sub>3</sub>CH<sub>2</sub>CH 
$$< \binom{Cl}{NH_2}$$

- 7. Which of the following is responsible for depletion of the ozone layer in the upper strate of the atmosphere? [CBSE AIPMT 2004]
  - (A) Polyhalogens (B) Ferrocenes
  - (C) Fullerenes (D) Freons

8. Chloropicrin is obtained by the reaction of [CBSE AIPMT 2004]

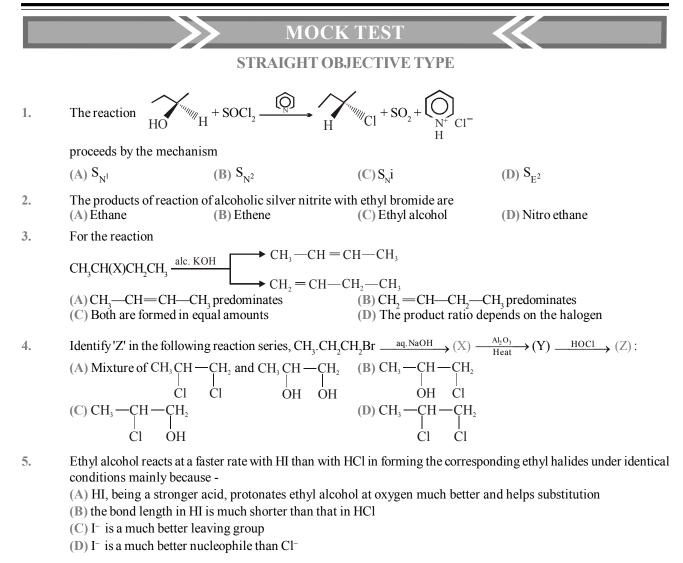
- (A) steam on carbon tetrachloride
- (B) nitric acid on chlorobenzene
- (C) chlorine on picric acid
- (D) nitric acid on chloroform
- 9. Which of the following undergoes nucleophilic substitution exclusivery by  $S_N 1$  mechanism
  - [CBSE AIPMT 2005] (B) Ethyl chloride (A) Benzyl chloride (C) Chlorobenzene (D) Isoproply chloride
  - In a  $S_N 2$  substitution reaction of the type [CBSE AIPMT 2008]

 $R - Br - Cl \rightarrow R - Cl + Br \rightarrow$ Which one of the following has the highest relative rate?  $(A) CH_3 - CH_2 - CH_2 Br$  $(\mathbf{B}) \operatorname{CH}_{3} - \operatorname{CH}_{2} - \operatorname{CH}_{2} \operatorname{Br}$ CH<sub>2</sub> CH<sub>3</sub> 

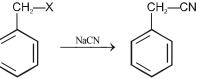
$$\begin{array}{c} C \\ H_3 \\ \end{array}$$

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#### **CHEMISTRY FOR NEET & AIIMS**



6.

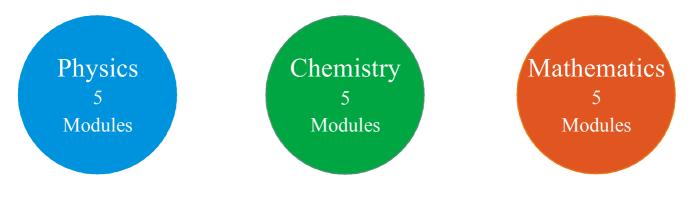


In the given reaction rate is fastest, when (X) is :

(A)-OH  
(B)-NH<sub>2</sub>
(C)-
$$\overset{O}{=}$$
-OCH<sub>3</sub>
(D)-O- $\overset{O}{=}$ -CH<sub>3</sub>  
(D)-O

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# 11<sup>th</sup> Class Modules Chapter Details



#### PHYSICS

#### CHEMISTRY

#### **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

#### BIOLOGY

#### 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

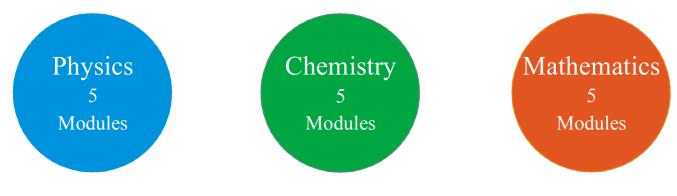
- 1. Photosynthesis in Higher Plants
- 2. Respiration in Plants
- 3. Plant Growth and Development
- 4. Digestion & Absorption
- 5. Breathing & Exchange of Gases

#### Module-5

- Body Fluids & Its Circulation
   Excretory Products & Their Elimination
- **3.** Locomotion & Its Movement
- 4. Neural Control & Coordination
- **5.** Chemical Coordination and Integration

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# 12<sup>th</sup> 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
- Alcohol, Phenol & Ether
   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

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