E	xercise # 1	Single Correct Choice Type Questions]
1.	Consider the chemical reaction, $2A(g) \longrightarrow B(g)+3C(g)$ The rate of this reaction can be expressed in terms correct relationship amongst rate expressions :	s of time derivatives of conc. of A(g) , B(g) or C(g). Identify the
	(A) Rate = $-\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt}$	(B) Rate = $\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}$
	(C) Rate = $-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}$	(D) Rate = $\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{1}{3} \frac{d[C]}{dt}$
2.	The differential rate law equation for the elementa	ry reaction A+2B $\xrightarrow{\kappa}$ 3C, is :
	$(\mathbf{A}) - \frac{d[\mathbf{A}]}{dt} = -\frac{d[\mathbf{B}]}{dt} = \frac{d[\mathbf{C}]}{dt} = k [\mathbf{A}] [\mathbf{B}]^2$	(B) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A]^2[B]$
	(C) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = k[A][B]^2$	(D) None of these
3.	The minimum energy for molecules to enter into a (A) Kinetic energy (C) Threshold energy	 chemical reaction is called. (B) Potential energy (D) Activation energy
4.	For an elementary process $2X + Y \rightarrow Z + W$, the (A) 2 (B) 1	molecularity is : (C) 3 (D) Unpredictable
5.	What is the order of a reaction which has a rate ex (A) 3/2 (B) 1/2	expression rate = k [A] ^{3/2} [B] ⁻¹ ? (C) 0 (D) None of these
6.	Following mechanism has been proposed for a re $2A+B \rightarrow D+E$ Step -1 $A+B \rightarrow C+D-(slow)$ Step -2 $A+C \rightarrow E-(fast)$ The rate law expression for the reaction is : (A) rate = K[A] ² [B] (C) rate = K[A] ²	action. (B) rate = K [A] [B] (D) rate = K[A][C]
7.	 Activation energy of a reaction is : (A) The energy released during the reaction (B) The energy evolved when activated complex is formed (C) Minimum amount of energy needed to overcome the potential barrier of reaction (D) The energy needed to form one mole of the product. 	
8.	 Catalyst increases the rate of reaction because : (A) it decreases ΔH (C) it decreases activation energy 	 (B) it increases ∆H (D) it increases activation energy
9.	Which of the following is not a Nucleophile ? (A) AICI ₃ (B) $(CH_3)_2$ NH	(C) C_2H_5OH (D) H_2O
10.	Which one of the following has maximum nucleop	philicity ?
	(A) CH_3S^{Θ} (B) $C_6H_5-\overset{\Theta}{O}$	(C) Et_3N (D) F^{Θ}



REACTION MECHANISM

11.	Which one of the following has minimum nucleoph (A) $(CH_3)_3$ CLi (B) NaNH ₂	ilicity ? (C) CH ₃ ONa	(D) NaOH		
12.	Which of the following is an electrophilic reagent ? (A) H_2O (B) OH^-	$(\mathbf{C}) \operatorname{NO}_2^+$	(D) None		
13.	Best leaving group is :				
	(A) F ⁻ (B) Cl ⁻	(C) Br⁻	(D) Γ		
14.	The correct order of leaving ability is :				
	(A) $\overset{\bullet}{O}$ H >H ₂ O (B) $\overset{\bullet}{O}$ H > $\overset{\bullet}{S}$ H		(D) $\stackrel{\Theta}{Cl} > \stackrel{\Theta}{I}$		
15.	 Substitution reactions involve : (A) Cleavage of a s-bond and formation of a new s-bond (B) Cleavage of two s-bond and formation of a new p -bond (C) Cleavage of a p-bond and formation of two new s -bond (D) None of these 				
16.	Which of the following reaction is a substitution re	eaction ?			
	(A) $CH_2 = CH_2 \xrightarrow{Ni/H_2} CH_3 - CH_3$	$ \begin{array}{c} \textbf{(B)} & \textbf{CH}_2 - \textbf{CH}_2 & \underline{\textbf{Zn}} \\ \textbf{Br} & \textbf{Br} \end{array} $	$CH_2 = CH_2 + ZnBr_2$		
	(C) $CH_3 - I + \stackrel{\Theta}{OH} \longrightarrow CH_3OH + \stackrel{\Theta}{I}$	(B) $\operatorname{CH}_2 - \operatorname{CH}_2 \xrightarrow{Zn}$ Br Br \xrightarrow{Pn} (D) $\operatorname{CH}_3 - \operatorname{CHO} \xrightarrow{\operatorname{KCN}}_{H^{\oplus}}$	H → CH₃ − C −OH CN		
17.	S _N 1 reactions occur through the formation of intern (A) Carbocation (B) Carbanion	nediate : (C) Free radical	(D) None of these		
18.	Which of the following is protic solvent ?(A) Acetone(B) Ethanol	(C) DMF	(D) Ether		
19.	Which of the following is aprotic solvent ? (A) DMSO (B) NH ₃	(C) H ₂ O	(D) CH ₃ COOH		
20.	Which solvent is non-polar solvent ? (A) CH ₃ -CO-CH ₃ (B) CH ₃ -SO-CH ₃	(C) CH ₃ COOH	(D) Cyclohexane		
21.	In an S _N 1 reaction, the configuration of the product undergoes :				
	(A) inversion (B) racemization	(C) retention	(D) difficult to predict		
22.	Which of the following alkyl halide is most reactive towards H_2O ?				
		(B) Ph–CH–Ph Cl			
	(A) OHC $- \bigcirc$ $- CH_2 - CI$ (C) Ph-C-Ph Cl	CI (D) H ₃ C-(O)-CH ₂ -	CI		

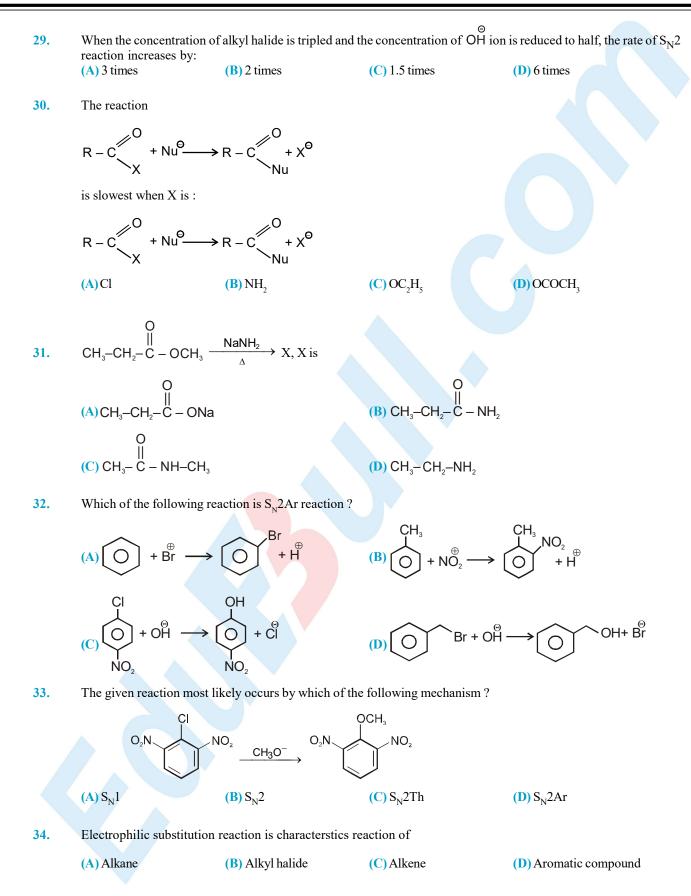


23.
$$CH_{1}-CH_{-}-CH_{-}-CH_{3} - CH_{2}-CH_{2} \rightarrow [X]$$

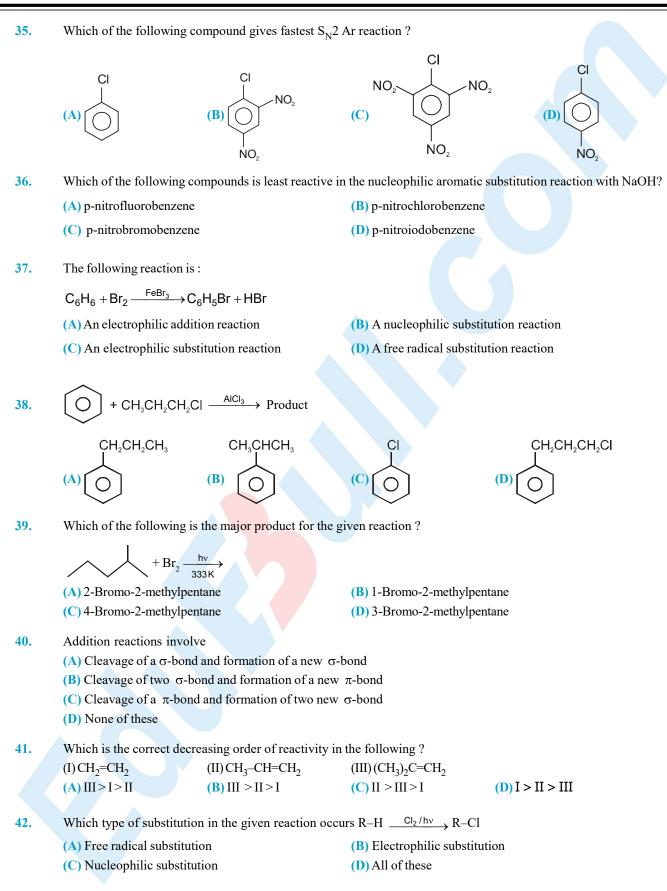
Identify X and the mechanism of the reaction.
(A) CH_{3}-CH_{2}-CH_{3}-CH_{2}-CI & S_{N}^{1}
(B) CH_{3}-CH_{-}-CH_{2}-CH_{3} & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(D) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(D) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(D) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{2}-BF & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{1}
(D) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{1}
(E) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(C) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(D) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(E) CH_{3}-CH-CH_{2}-CH_{3} & S_{N}^{2}
(E) CH_{3}-CH-CH_{2}-CH_{3} & (C) \\
(D) CH_{3}-CH-CH_{2}-CH_{3} & (C) \\
(D) CH_{3}-CH-CH_{2}-CH_{3} & (C) \\
(D) CH_{3}-C=C-CH_{2}-CH_{3} & (D) CH_{3}-C=C-CH_{2}-CH_{3} \\
(C) CH = C-CH_{2}-CH_{2} -CH_{3} & (D) CH_{3}-C=C-CH_{2}-CH_{3} \\
(C) CH = C-CH_{2}-CH_{2} -CH_{3} & (D) CH_{3}-C=C-CH_{2}-CH_{3} \\
(C) CH = C-CH_{2}-CH_{2} & (C) \\
(CH_{3}-CH & (B) \\
(C) \\
(C) \\
(C) \\
(C) \\
(D) \\
(C) \\
(D) \\
(D)



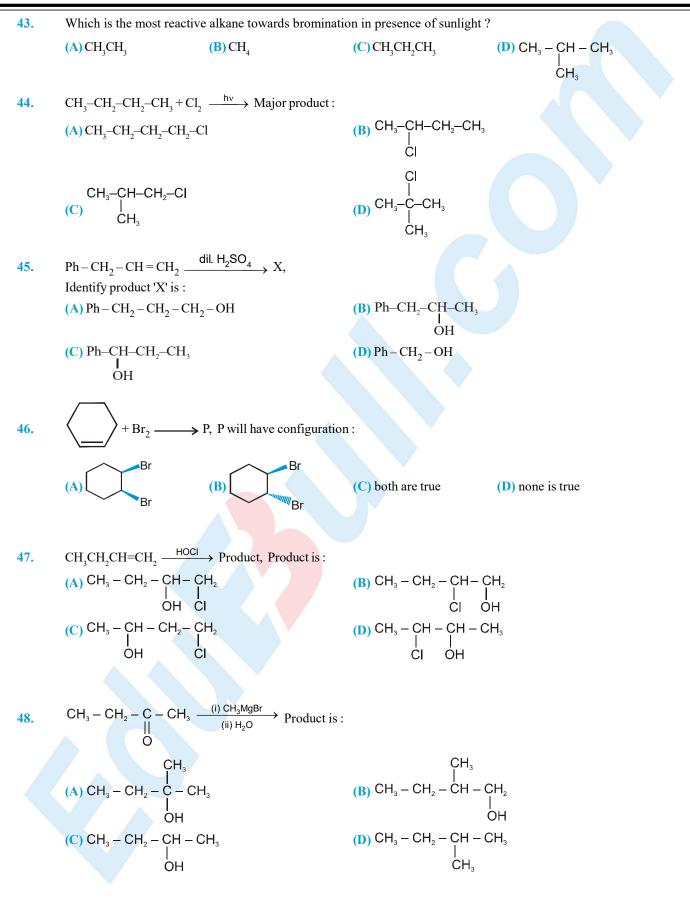
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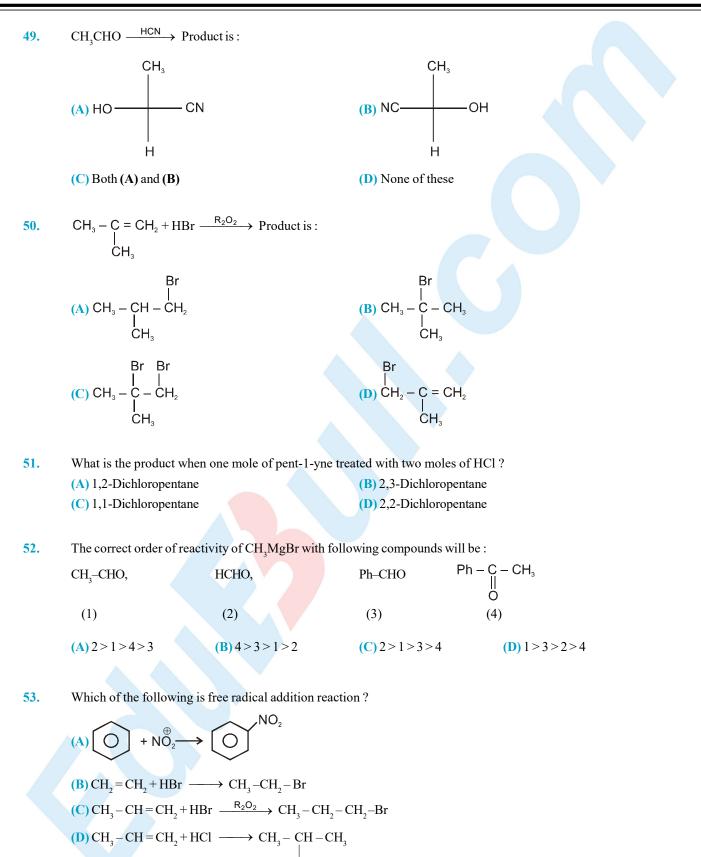














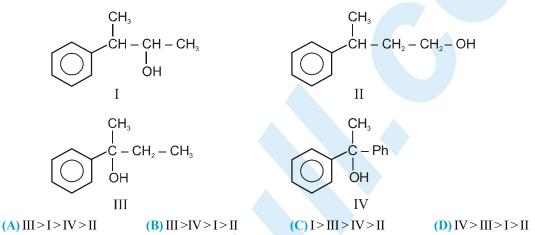
Cl

54. Which of the following reaction is an elimination reaction ?

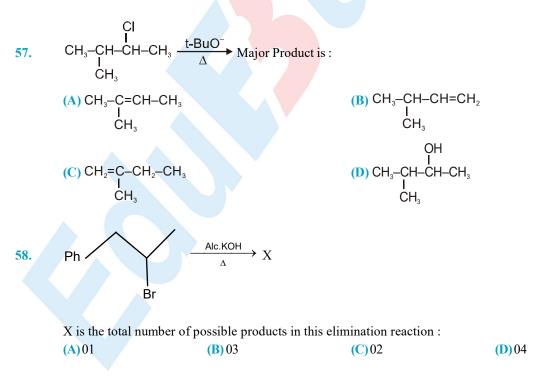
(A)
$$CH_3 - CH_2 - CH_2 - OH \xrightarrow{PCl_5} CH_3 - CH_2 - CH_2 - CI$$

(B) $CH_3 - CH = CH_2 \xrightarrow{HCl} CH_3 - CH - CH_3$
(C) $CH_3 - CH - CH_3 \xrightarrow{Alc.KOH} CH_3 - CH = CH_2$
(D) $CH_3 - CH - OH \xrightarrow{CH_3OH} CH_3 - CH = OCH_3$
O

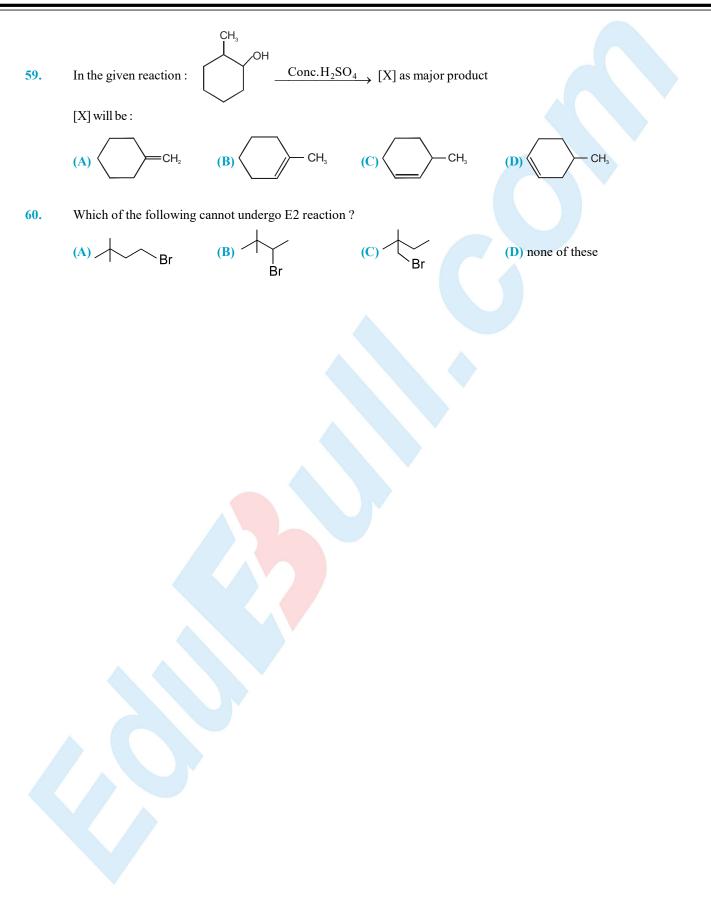
55. The relative rate of acid catalysed dehydration of following alcohols would be :



56.2-Chlorobutane on treatment with alcoholic KOH/Δ gives mainly
(A) 2-Butene(B) 1-Butene(C) 2-Butanol(D) 1-Butyne









Exercise # 2 Part # I > [Multiple Correct Choice Type Questions]

1. Observe the following reaction and tick correct option (s) $CH_{3} - CH - CH_{3} + CH_{3}ONa \xrightarrow{r_{1}} CH_{3} - CH - OCH_{3} \dots (I)$ $\begin{array}{c} \mathrm{CH}_3 - I + \mathsf{CH}_3 - \underset{I}{\mathsf{CH}_3} - \underset{C}{\mathsf{CH}_3} - \underset{I}{\mathsf{CH}_3} - \underset{I}{\mathsf{CH}_3} - \underset{I}{\mathsf{CH}_3} - \underset{I}{\mathsf{CH}_3} - \underset{I}{\mathsf{CH}_3} \end{array} \\ \end{array}$ (A) $r_1 < r_2$ (B) Transition state in reaction (I) is less stable then transition state in reaction (II) (C) Substrate of both the reactions are equally reactive to a particular nucleophile (D) r_1 and r_2 both are directly proportional to the concentration of nucleophile CH₃ONa $CH_3 - CH - CH_2 \xrightarrow{CH_3C \equiv C^{\Theta}} (X) \xrightarrow{CH_3I} (Y).$ Identify X & Y : 2. (A) $X = CH_3 - CH - CH_2 - C \equiv CCH_3$ $O - CH_3$ (B) $Y = CH_3 - CH_2 - CH - C \equiv CCH_3$ $O - CH_3$ (C) $Y = CH_3 - CH - CH_2 - C \equiv CCH_3$ (D) $X = CH_3 - CH - CH_2 - C \equiv CCH_3$ $0 - CH_3$ | 0⁰ H₂C H H $NO_2 \xrightarrow{H_2O} \text{product mixture } \xrightarrow{PCl_5}$ 3. MeO H Br D Fractional No of product 'm' (Total isomers) No. of Fractions 'n'. distillation (A) Value of m & n are 4,2 respectively. (B) Product mixture, and all fractions are optically active. (C) Value of m & n are 4,4 respectively. (D) Reaction of product mixture with PCl_5 is S_N^2 mechanism. 4. Which of the following reactions represent the major product. $CH_3CH_2O^-$ CH₃CH₂O[−] DMF DMSO H₃C − C − O[−] | | | CH₃ Br

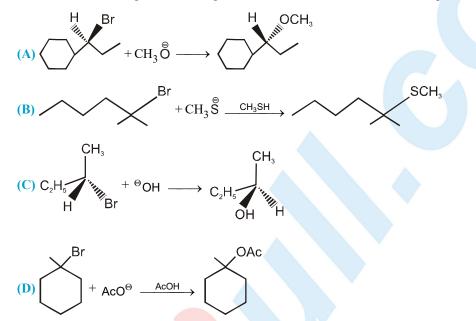


(**C**)

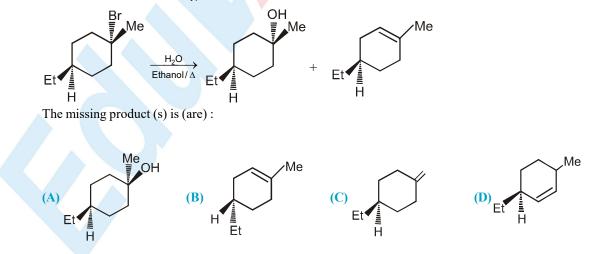
5. Which reaction results in the formation of a pair of enantiomers ?



6. Which of the following reaction will go faster if the concentration of the nucleophile is increased ?



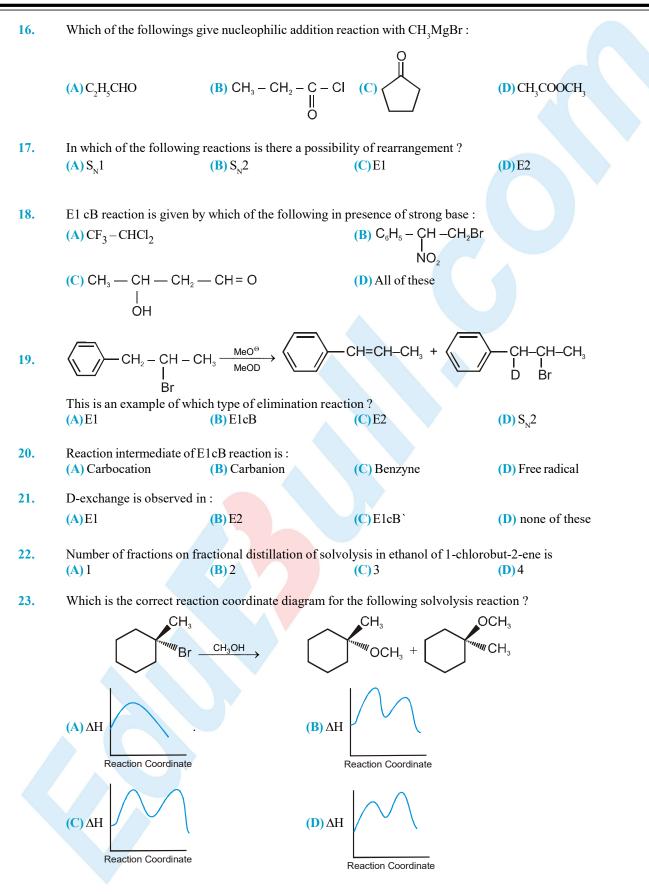
- 7. Which is/are correct about alkyl bromide having molecular formula C₅H₁₁Br
 (A) One isomeric alkyl bromide undergoes E1 elimination at the fastest rate
 (B) Only one is incapable of reacting by the E2 mechanism
 - (C) Only one isomer gives a single alkene on E2 elimination
 - (D) 2-Bromopentane gives the most complex mixture of alkenes on E2 elimination
- 8. Consider the following $E1/S_N$ 1 reaction :





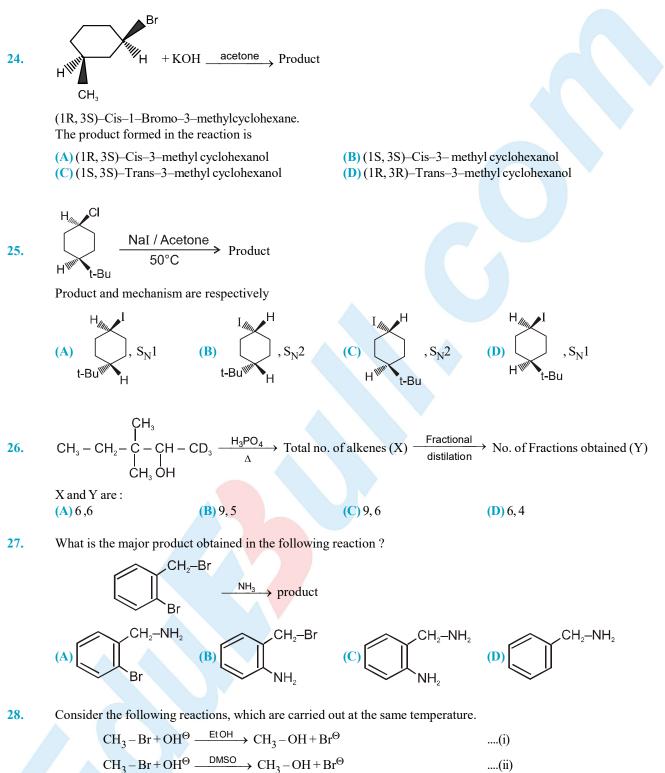
9. Account for the trend in relative rate observed for the formation of alcohol from the alkyl halide in H₂O / EtOH at 25°C. **Alkyl Halide Relative rate** (i) $CH_2 - Br$ 2140 $CH_3 - CH_2 - Br$ (ii) 171 4.99 (iii) $CH_3 - CH - Br$ CH₃ CH₂ $CH_3 - \overset{l}{C} - Br$ $\begin{matrix} I \\ CH_3 \end{matrix}$ (iv) 1010 Which of the following statements are true. (A) The first two alkyl halide react mainly by the S_N^2 pathway **(B)** The fourth alkyl halide react mainly by the S_N^{1} pathway (C) Water is a poor solvent for alkyl halide so EtOH is added in their solvation (D) Rate of last two can be explain by steric hindrance. 10. Electrophiles are (A) Electron deficent species (B) having atleast one pair of electron (D) having vacant p or d-orbital (C) Electron rich species 11. Which of the followings are nucleophile? **(B)** CN⁻ (C) OH-(A) BF, **(D)** NH₂ The correct nucleophilicity order is/are : 12. (A) $CH_3 O^{\Theta} > CH_3^{\Theta}$ **(B)** $CH_3S^{\Theta} > CH_3SH$ (C) $NH_3 > H_2O$ **(D)** $(CH_{3}CH_{2})_{3}N > (CH_{3}CH_{2})_{3}P$ The correct order/s of decreasing reactivity of the given compound towards hydrolysis under identical condition is/are: 13. (A) CH₂COCl>CH₂CONH, (B) CH, COCl>(CH, CO), O (C) CH,COOCH, > CH,COCl (D) (CH₂CO)₂O > CH₂CONH₂ Which of the followings give product O(A) $CH_3 - C - CI \xrightarrow{NaOH} CH_3 - C - OH$ (B) $CH_3 - CH_2 - CI \xrightarrow{NaOH} CH_3 - CH_2 - OH$ (B) $CH_3 - CH_2 - CI \xrightarrow{NaOH} CH_3 - CH_2 - OH$ (C) $CH_3 \xrightarrow{PCI_5} CH_3 - CH - CI$ (D) $CH_3 - CH - OH \xrightarrow{PCI_5} CH_3 - CH - CI$ 14. Which of the followings give product by S_{N2} Th mechanism? 15. Which of the following reactions is an electrophilic substitution ? О) + ⁰н -(A) $CH_2 - I + OH \longrightarrow CH_3OH + I$ NO. NO₂ **(D)**







REACTION MECHANISM



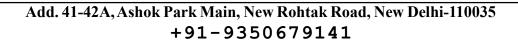
Which of the following statement is correct about these reactions.

(A) Both the reactions take place at the same rate

(B) The first reaction takes place faster than second reaction.

(C) The second reaction takes place faster than first reaction.

(D) Both the reactions take place by S_N^1 mechanism



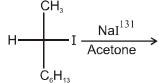
→ Rearranged Carbocation + AgBr

Rearranged carbocation is :

Br

$$(A) \stackrel{\oplus}{\longrightarrow} CH_3 \qquad (B) \stackrel{\oplus}{\longrightarrow} \qquad (C) \stackrel{\oplus}{\searrow}$$

30. Which statement is incorrect about the following reaction :



- (A) Only one product is formed
- (B) The product will have walden inversion
- (C) The reaction mixture will have optical rotation zero
- **(D)** The product is a mixture of $d + \bullet$ isomers

31. Which of the following statements are correct for the given alcohol?

$$R - OH \xrightarrow{X^{\Theta}} R - X + \overset{\Theta}{O}H$$

(A) Reaction will not take place because OH is poor leaving group; X is weak base and OH is strong base
(B) Reaction will not take place because OH is poor leaving group; X is strong base and OH is weak base.
(C) Reaction will not take place because OH is strong leaving group; X is strong base and OH is weak base.
(D) Reaction will not take place because OH is good leaving group; X is weak base and OH is strong base.

(D)

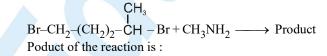
32.
$$CH_3 - I +$$
 (Reaction. I)

$$CH_3 - I + CH_3 - CH_2 - N - CH_2 - CH_3 \xrightarrow{\kappa_2} (Reaction.II)$$

 $CH_2 - CH_3$

Which of the following statement is correct. ?

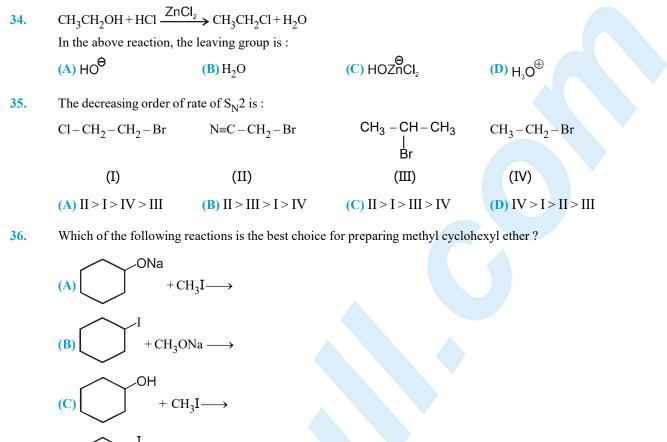
- (A) Rate of reaction in I is less than reaction II.
- (B) Rate of reaction in I is more than reaction II.
- (C) Rate of reaction is equal in both reaction.
- (D) Rate does not depend upon concentration of nucleophile.







REACTION MECHANISM



(D)
$$+ CH_3OH \rightarrow$$

37. Which of the following chloride will exclusively give 2-Methyl but-2-ene on dehydrochlorination by a strong base?
(A) 2-Chloro-2-methyl butane
(B) 2-Chloro-3-methyl butane
(D) None of these

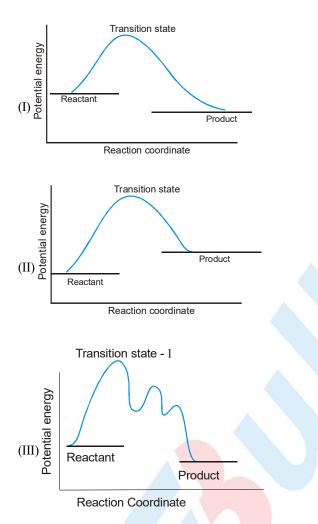
38.
$$OCH \xrightarrow{\text{CH}_2\text{OH}} A + SO_2 + HCl$$

The product A in the above reaction is





39. Following are the curves for nucleophilic substitution reaction.



The correct statement (s) is (are)

- (A) 'I' is potential energy diagram for S_N^2 reaction that takes place with a negative potential energy change.
- (B) 'II' is potential energy diagram for S_N^2 reaction with a positive potential energy change
- (C) 'III' shows potential energy diagram for S_N^1 reaction with large potential energy of activation for first (slowest) step (D) All of the above

40.
$$(CH_3)_3C-CH-CH_3 \xrightarrow{E1}_{E2}_{Y} X \text{ and } Y \text{ are respectively}$$

(A) $(CH_3)_2C=C(CH_3)_2 \text{ and } (CH_3)_3CCH=CH_2$
(B) $(CH_3)_3CCH=CH_2 \text{ and } (CH_3)_2C=C(CH_3)_2$
(C) $(CH_3)_2CH-C(CH_3)=CH_2 \text{ and } (CH_3)_2C=C(CH_3)_2$
(D) $(CH_3)_2C=C(CH_3)_2 \text{ and } (CH_3)_2CH-C(CH_3)=CH_2$

41.
$$(A) = (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
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(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(A) (CH_3)_3 C^{-O-CH_2-C_6H_5} can be prepared from Williamsons synthesis, using :
(B) C_6H_5 CH_2 Cl and (CH_3)_3 C^{-ONa} (C) (CH_3)_3 C^{-O-CH_2-C_1} can C_6H_5 ONa (C) (CH_3)_3 C^{-O$$

(D) All of these

Part # II

[Assertion & Reason Type Questions]

These questions contains, Statement-I (assertion) and Statement-II (reason).

- (A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I
- (B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I
- (C) Statement-I is True, Statement-II is False.
- (D) Statement-I is False, Statement-II is True.
- Statement-I: Primary benzylic halides are more reactive than primary alkyl halides towards S_{N¹} reaction.
 Statement-II: Reactivity depends upon the nature of the nucleophile and the solvent.
- Statement-I: Vinylic halides are reactive towards nucleophilic substitution reaction.
 Statement-II: Reactivity is due to the polarity of carbon-halogen bond.
- 3. Statement-I : Aryl halides undergo electrophilic substitution less readily than benzene. Statement-II : Aryl halide gives only meta product w.r.t. electrophilic substitution.
- 4. **Statement-I :** Iodination of akanes is carried out by heat in presence of readucing agent. **Statement-II :** Iodination of alkanes takepalce explosively.
- 5. Statement-I : Chloropropane has higher boiling point than chloroethane. Statement-II : Haloalkanes are polar molecules.



- 6. Statement-I : Polar solvent slows down S_N^{-1} reaction. Statement-II : CH_3 -Br is less reactive than CH_3Cl .
- Statement-I: Optically active 2-iodibutane on treatment with NaI in acetone undergoes racemisation.
 Statement-II: Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.
- Statement-I: Free radical chlorination of n-butane gives 72% of 2-chlorobutane and 28% of 1-chlorobutane though it has six primary and four secondary hydrogens.
 Statement-II: A secondary hydrogen is abstracted more easily than the primary hydrogen.
- 9. Statement-I: Boiling point of alkyl halide increases with increases in molecular weight. Statement-II: Boiling point of alkylhalides are in the order RI > RBr > RCI > RF.
- 10.Statement-I : Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.Statement-II : The reaction occurs by S_{s_1} mechanism.



Exerci	ise # 3 Part # I Matri	x Match	Type Questions]
. Match	n the column I with column II. Column-I (reaction)	Colu	mn-II (Mechanism)
(A)	$\begin{array}{ccc} CH_{3} & OH \\ Ph & C \\ (+) & H \end{array} + SOCl_{2} \end{array} \longrightarrow \begin{array}{ccc} CH_{3} & Cl \\ Ph & C \\ (+) & H \end{array}$	(p)	S _N 1
(B)	$\begin{array}{c} CH_{3} \\ Ph \\ (+) \end{array} \xrightarrow{OH} + SOCl_{2} \xrightarrow{Pyridine} \begin{array}{c} CH_{3} \\ H_{5}C_{6} \end{array} \xrightarrow{C} \end{array}$	Cl H	S _N 2
(C)	$CH_{3} \xrightarrow{CH} Br + OC_{2}H_{5}/EtOH \longrightarrow CH_{3}$	(r)	S _N i
(D)	$\begin{array}{c} CH_{3} \\ H_{5}C_{6} \end{array} \xrightarrow{C} H \\ H \end{array} \xrightarrow{H+HCl} \xrightarrow{CH_{3}} C \\ C_{6}H_{5} \end{array} \xrightarrow{Cl} H$	(8)	E ₂
. Match	n the column I with column II.		
	Column-I (Substrate)		Column-II e rate of solvolysis in 50% ous ethanol at 45°C)
(A)	≫~a	(p)	7700
(B)		(q)	1
(C)	H ₃ C H ₃ C	(r)	91
(D)	Ph	(s)	1,30,000
Part #]	II [Comprehension Type (Questions	s]

Comprehension #1

Nucleophilic substitution reactions generally expressed as

 $Nu^- + R - L \longrightarrow R - Nu + L^-$

Where $Nu^- \longrightarrow Nucleophile$; R—L \longrightarrow substrate; L \longrightarrow leaving group

The best leaving groups are those that become the most stable ions after they depart. Since most leaving groups leave as a negative ion, the best leaving groups are those ions that stabilize a negative charge most effectively. A good leaving group should be

(A) electron-withdrawing to polarize the carbon

(B) stable once it has left (not a strong base)

(C) polarisable- to maintain partial bonding with the carbon in the transition state (both S_N^1 and S_N^2). This bonding helps to stabilise the transition state and reduces the activation energy.



1. Among the following which is feasible ?

(A)
$$X^- + CH_3 - CH_2 - H \longrightarrow CH_3 - CH_2 - X + H^-$$

(B) $X^- + CH_3 - OH \longrightarrow CH_3 - X + \overline{O}H$
(C) $\overline{X^+} + H_3C - \bigcirc_{H}^{\oplus} + OH_3 - X + H_2O$
H

(D)
$$X^-$$
 + CH₃—CH₃—CH₃—X + \overline{C} H₃

- 2. Among the following which is false statement ?
 - (A) The weaker the base after the group departs, the better the leaving group
 - (B) A reactive leaving group would raise the energy of the product, driving the equilibrium towards the reactants
 - (C) Relative leaving group ability may vary with change of solvent
 - (D) Better leaving group only increases S_N^2 rate, not S_N^1 .

3.
$$CH_3Br$$
 CH_3F CH_3OH $CH_3OSO_2CF_3$
(I) (II) (III) (IV)

The correct order of decreasing reactivity of the above compounds towards CH_3O^- in an S_N^- reaction is :

- (A) I > IV > II > III (B) IV > I > II > III (C) IV > I > III > III (D) IV > II > I > III
- 4. $\begin{array}{ccc} Cl^- & CH_3O^- & CH_3S^- & \Gamma\\ (l) & (l) & (l) & (l) \end{array}$

The correct order of increasing leaving group capability of above anoins (A) III < IV < II < I(B) II < III < I < IV(C) II < IV < III < I(D) I < III < II < IV

Comprehension #2

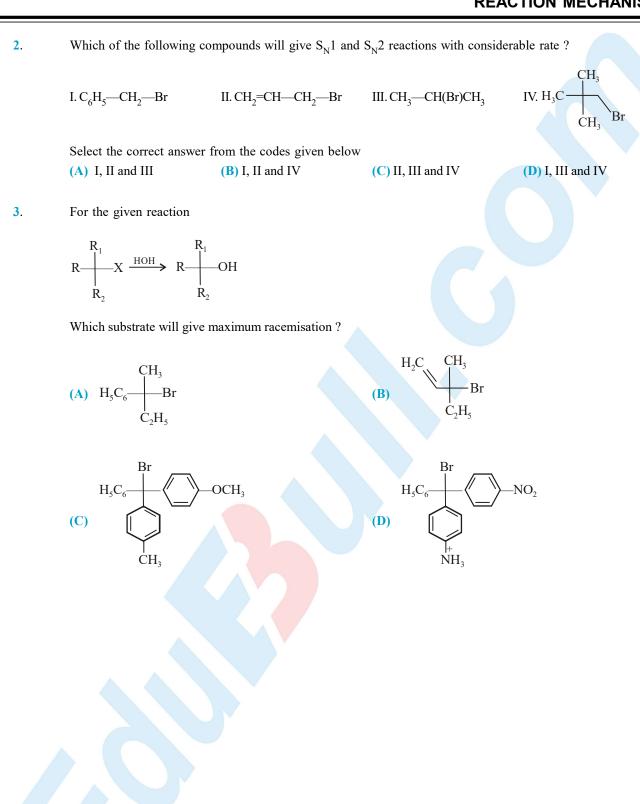
Nucleophilic aliphatic substitution reaction is mainly of two types : $S_N 1$ and $S_N 2$. The $S_N 1$ mechanism is a two step process. Reaction velocity of $S_N 1$ reaction depends only on the concentration of the substrate. Since product formation takes place by the formation of carbocation, optically active substrate gives (+) and (-) forms of the product. In most of the cases the product usually consits of 5-20% inverted product and 80-95% racemised species. The more stable the carbocation, the greater is the proportion of racemisation. In solvolysis reaction, the more nucleophilic the solvent, the greater is the proportion of inversion.

- 1.
- Which one of the following compound will give S_N^1 reaction predominantly ?

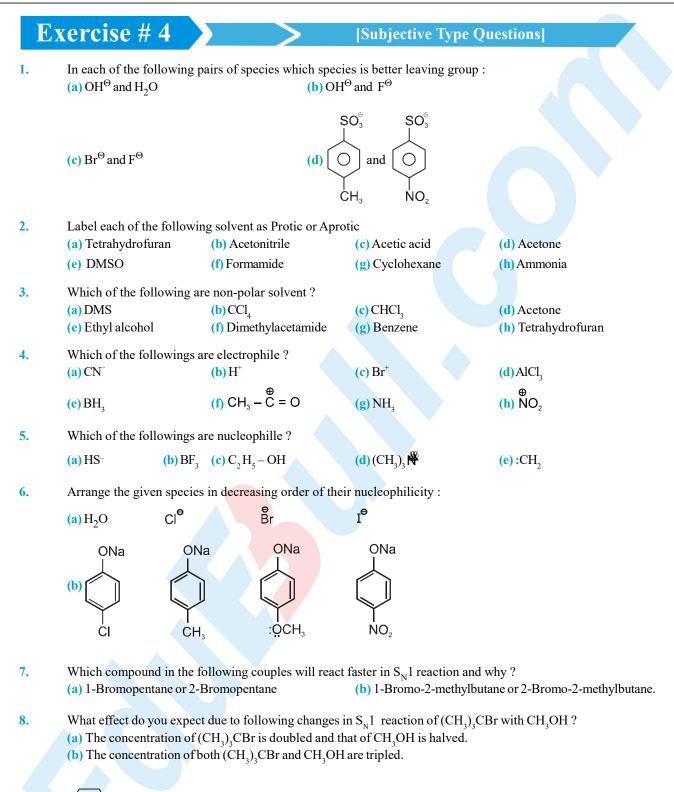
(B) H₃C - $(A)H_5C_6$ —Br (C) H₂C – Br (D) All of these



REACTION MECHANISM







9. $(\bigcirc -CH_2 - CH - CH_3 + HBr \longrightarrow A+B)$ | OH

A and B are two structural isomeric products of this reaction. Identify each. Which is predominant?

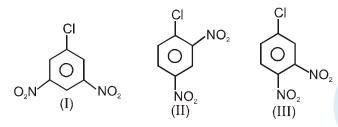


- **10.** Explain the order of the rate of esterification of the following acid with MeOH : CH₃COOH>MeCH₂COOH>Me₂CHCOOH>Me₃CCOOH
- 11. What will be the major product of the following reaction ?

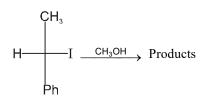
(a)
$$CH_3-C-CI+CH_3OH \longrightarrow$$

(b)
$$CH_3 - C - OC_2H_5 + H_2O \longrightarrow$$

12. Write the correct reactivity order with NaOH for the following compounds.



13. Write the product of the following reaction with proper stereochemistry.



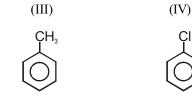
- Arrange the compounds of each set in order of reactivity towards S_N2 displacement.
 (a) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
 (b) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
- 15. What will be the major product of the following reaction ?

(a)
$$CH_3 \xrightarrow{\text{CH}_3} CH_-CH_-CH_3 \xrightarrow{\text{PCI}_5} (b) \xrightarrow{\text{H}_3C} H \xrightarrow{\text{NaOH}} DMSO$$

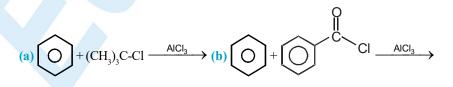
ЭNа

16. Arrange the following in decreasing order of their reactivity with an electrophile.





17. Complete the following reactions :



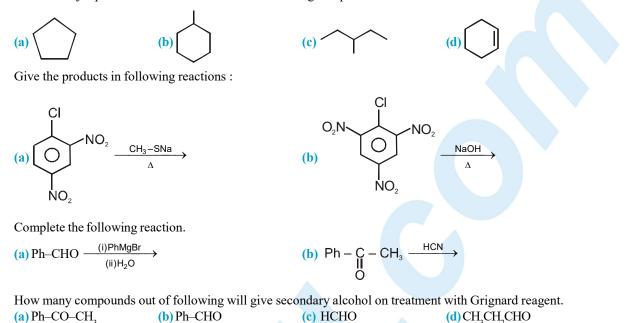


19.

20.

21.

18. Give the major product of monobromination of following compounds.



22. Give products of reaction when 2-Methylbut-2-ene react with HBr in presence and absence of peroxide.

23.
$$(H_2CH_3) \xrightarrow{Cl_2} X \text{ (major product)} + Y \text{ (minor product)}$$

Give structure of X & Y.

24. What will be order of reactivity of following compounds towards ionic addition of HBr ?

$$CH_{3} - CH = CH - CH_{3}$$

$$I$$

$$CH_{3} - CH = CH - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3}$$

$$CH_{3} - CH_{3} - CH_{3}$$

$$H_{1} - C = CH - CH_{3}$$

$$H_{2} - CH_{3} - CH_{3}$$

$$H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

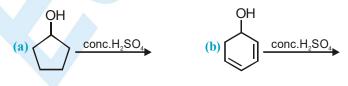
$$H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

$$H_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

$$H_{3} - CH_{3} - CH$$

- 25. Give the product formed when But-1-yne reacts with two moles of Br₂.
- 26. Give the product formed when But-1-yne reacts with two moles of HBr in prensence of peroxide.
- 27. Arrange the following alcohol in increasing order of reactivity towards acid catalyzed dehydration.

28. What would be the major product in the following reaction ?





29. What would be the major product in the following reaction?

$$F$$
 H_3 H A

30. Give major product and classifiy the mechanism in the following reactions.

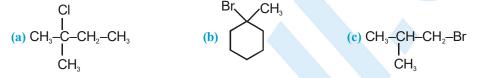
(a)
$$CH_3-CH-CH_2 - CH_3 \xrightarrow{\text{alc.KOH}} \Delta$$

Br
(c) $CH_3-CH-CH_2 - C-Ph \xrightarrow{\text{Conc. NaOH}} \Delta$
(b) $CH_3-CH-CH_2 - Ph \xrightarrow{\text{Cons. H}_2SO_4} \Delta$
OH

31. Arrange the following alkyl halide in increasing order of reactivity towards alcoholic KOH.

$$(I) CH_{3}-CH-CH_{3} (II) CH_{3}-C-CH_{2}CH_{3} (III) CH_{3}-C-C-CH_{2}CH_{3} (III) CH_{3}-C-C-CH_{3} (III) CH_{3}-C-C-C$$

32. What is the major product of dehydrohalogenation when following compounds are treated with alcoholic KOH.



- 33. 'X' is a smallest optically active alkanol. On dehydration it can form Y number of alkenes (including stereoisomers). On reaction with Lucas reagent it forms Z number of alkyl halides (including stereoisomers). Identify the numbers Y and Z.
- 34. 3, 3-Dimethylbutan-2-ol loses a mole of water in the presence of concentrated sulphuric acid to give tetramethylethylene as a major product. Suggest a suitable mechanism.
- 35. Predict the major products (including stereochemistry) when R-2-Butanol reacts with the following reagents.

- **36**.
- 37. The order of nucleophilicity in a period does not depend on nature of solvent whether it is protic or aprotic but the order of nucleophilicity in a group is different in polar protic and polar aprotic solvent. Explain.
- 38. Write the product of the following reaction :

(a)
$$CH_2OH$$

 $TsCI$, CH_3CH_2SNa
(b) $CH_3-CH_2-CH_2-CH_2-Br$, $CH_3-C=C-Na$
Me
(c) HO , HI , $TsCI$, NH_3/Δ
Et



39. (a) Optically active 2-Bromobutane undergoes recemization on treatment with a solution of KBr. Give a mechanism for this racemization.

(b) In contrast, optically active 2-Butanol does not recemize on treatment with a solution of KOH. Explain why a reaction like that in part (a) does not occur.

(c) Optically active 2-Butanol racemizes in dilute acid. Propose a mechanism for this racemization.

40. Identify the reactants / products in following reactions :

(a)
$$CH_2 - O - CH_2$$
 \rightarrow + conc HI \rightarrow (P+Q)
Dibenzyl ether

(b)
$$\bigcirc CH_2 - O - \bigcirc CH_2 - O - (X + Y)$$

(c) W
$$\xrightarrow{\text{HI (conc.)}}_{\text{excess}} \longrightarrow^{\text{I}}_{\text{+}} \text{CH}_{3}\text{I}$$

(d)
$$Z \xrightarrow{\text{HI (conc.)}} (CH_3)_2 CHI + CH_3 CH_2 CH_2 I$$

41. When ethyl bromide is added to potassium t-butoxide, the product is ethyl t-butyl ether.

$$\begin{array}{c} \mathsf{CH}_3\mathsf{CH}_2-\mathsf{Br} \\ \text{ethyl bromide} \end{array} + \begin{array}{c} (\mathsf{CH}_3)_3\mathsf{C}-\mathsf{OK} \\ \text{potassium t-butoxide} \end{array} \longrightarrow \begin{array}{c} (\mathsf{CH}_3)_3\mathsf{C}-\mathsf{O}-\mathsf{CH}_2\mathsf{CH}_3 \\ \text{ethyl t-butyl either} \end{array}$$

(a) What happens to the reaction rate if the concentration of ethyl bromide is doubled?

(b) What happens to the rate if the concentration of potassium t-butoxide is tripled and the concentration of ethyl bromide is doubled?

(c) What happens, if the temperature is raised?

- 42. When (R)-2-bromobutane is heated with water, the S_N^1 substitution proceeds twice as fast as the S_N^2 . Calculate the approximate enantiomeric excess and the specific rotation expected for the product. The specific rotation of (R)-2 butanol is -13.5° .
- 43. In 80% ethanol at 55°C Isopropyl bromide react with hydroxide according to the following kinetic equation. where the rate is expressed as moles per litre per second.

rate = 4.7×10^{-5} (RX) (OH⁻) + 0.24×10^{-5} (RX)

What percentage of isopropyl bromide react with S_N1 mechanism when [OH⁻] conc is 5 molar

44. The alkene (X) produced by solvolysis of 3-chloro-3-methylpentane, is more in quantity than the alkene (Y) produced by solvolysis of 3-chloro-3-ethylpentane. Explain and also write the structure of X and Y.

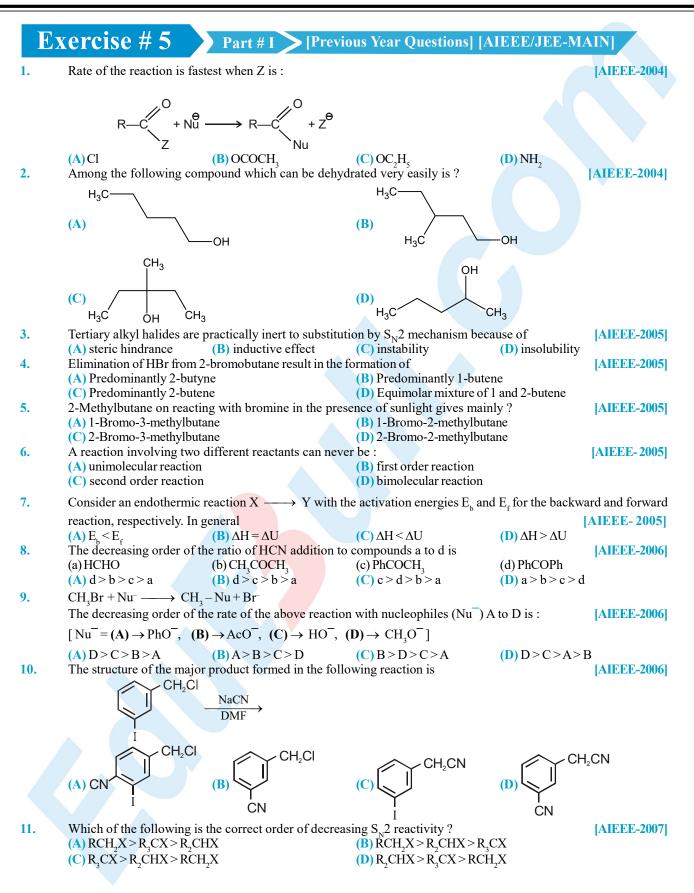
45. Which reacts faster

(a) Ph CH ₂ Br	and	Ph CMe ₂ Br $(H_2O - C_2H_5OH)$
(b) $PhCH_{2} - CH_{2}Br$	and	Ph CMe, Br (NaI – Acetone)
(c) $Ph CH_2 - CH_2 - Cl$	and	$PhCMe_2Br$ (KOH+ C_2H_5OH)

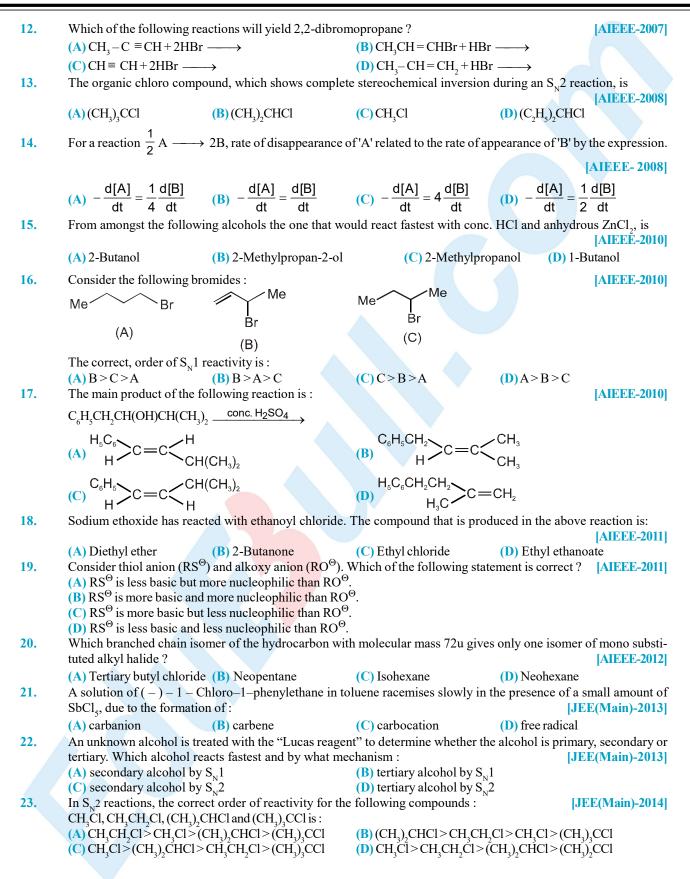
46. What is the effect of increasing solvent polarity over the reactions

47.
(a)
$$CH_3 - Cl + NH_3 \longrightarrow CH_3 NH_3 Cl^{\Theta}$$
 (b) $Me_3 \overset{\oplus}{S} + OH^{\Theta} \longrightarrow Me - OH + Me_2S$
 $H \to H^{\Theta} + KNH_2 \longrightarrow Product$, Identify the product.



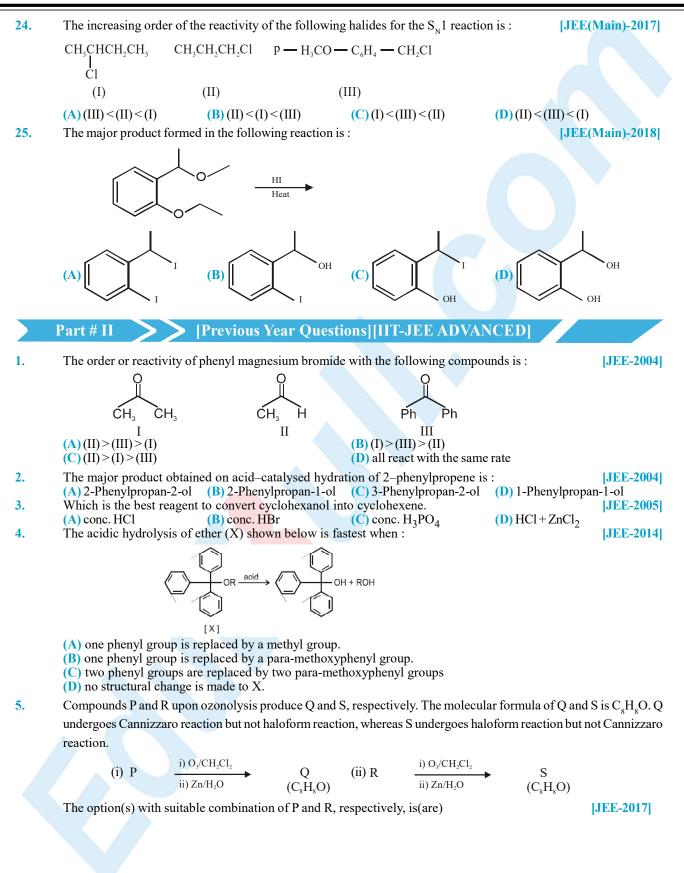




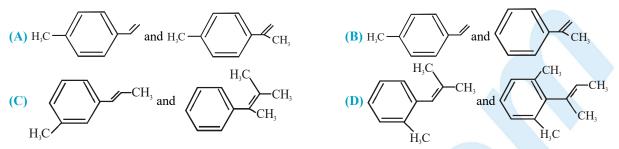




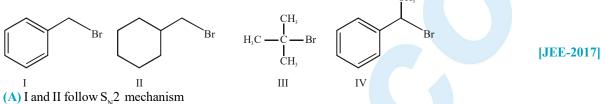
REACTION MECHANISM







6. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reactions is(are)



- (B) Compound IV undergoes inversion of configuration
- (C) The order of reactivity for I, III and IV is : IV > I > III
- **(D)** I and III follow S_N1 mechanism

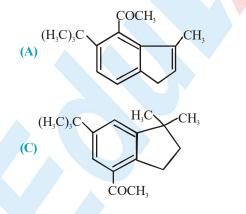
Paragraph for Q. 7 & Q. 8

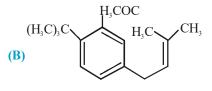
The reaction of compound P with CH_3MgBr (excess) in $(C_2H_5)_2O$ followed by addition of H_2O gives Q. The compound Q on treatment with H_2SO_4 at 0°C gives R. The reaction of R with CH_3COCl in the presence of anhydrous AlCl₃ in CH_2Cl_2 followed by treatment with H_2O produces compound S. [Et in compound P is ethyl group]

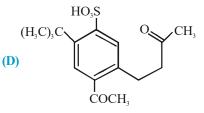


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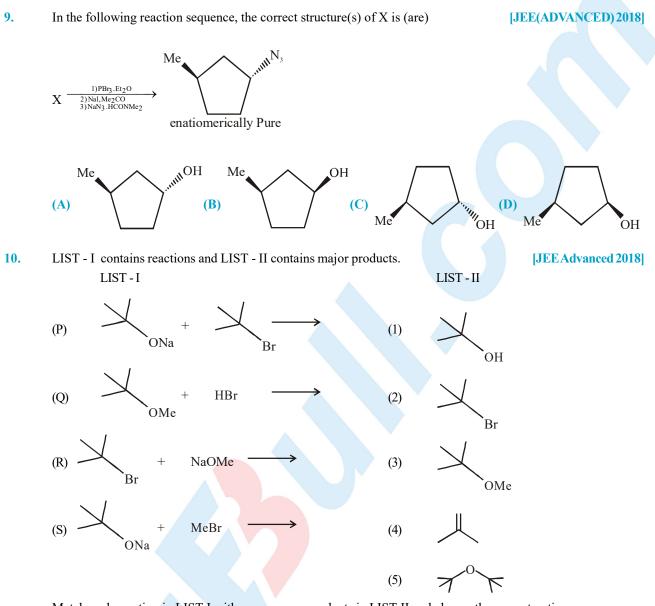
- 7. The reactions, Q to R and R to S are
 - (A) Friedel-Crafts alkylation and Friedel-Crafts acylation
 - (B) Dehydration and Friedel-Crafts acylation
 - (C) Friedel-Crafts alkylation, dehydration and Friedel-Crafts acylation
 - (D) Aromatic sulfonation and Friedel-Crafts acylation
- 8. The product S is







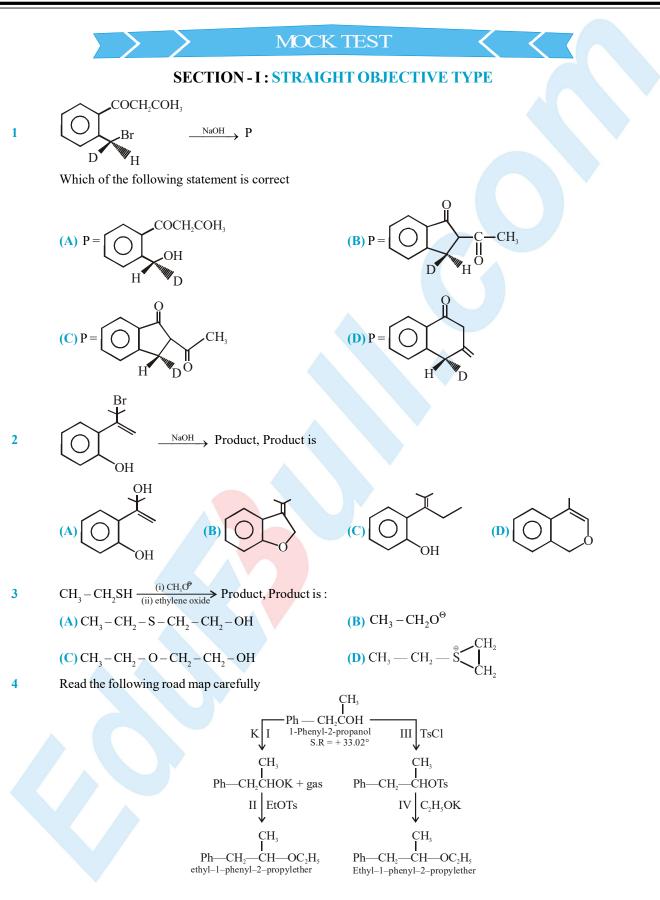




Match each reaction in LIST-I with one or more products in LIST-II and choose the correct option.

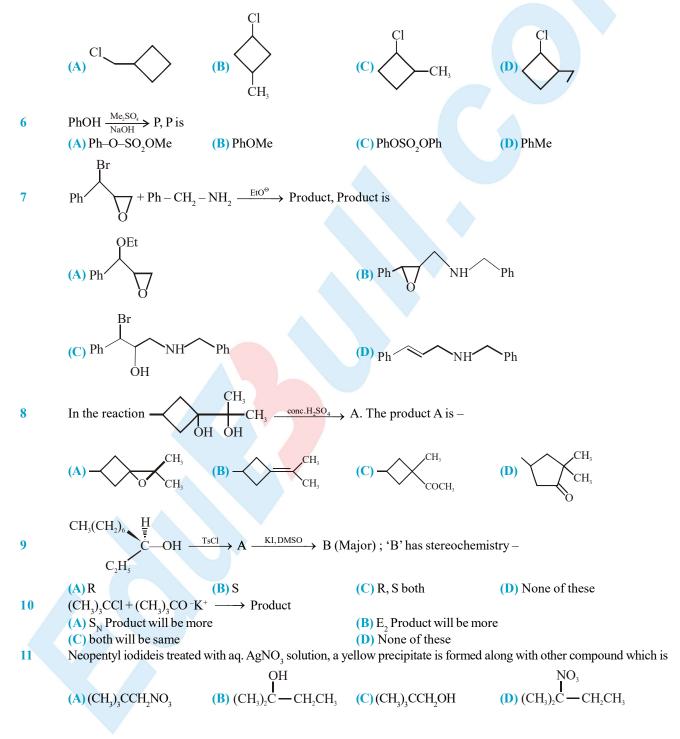
- (A) $P \rightarrow 1, 5; Q \rightarrow 2; R \rightarrow 3; S \rightarrow 4$
- **(B)** $P \rightarrow 1, 4; Q \rightarrow 2, 4; R \rightarrow 4; S \rightarrow 3$
- (C) $P \rightarrow 1, 4; Q \rightarrow 1, 2; R \rightarrow 3, 4; S \rightarrow 4$
- **(D)** $P \rightarrow 4, 5; Q \rightarrow 4; R \rightarrow 4; S \rightarrow 3, 4$





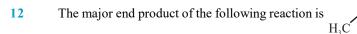


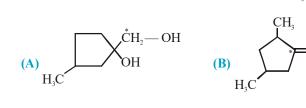
- (A) Both the ethers obtained by the two routes have opposite but equal optical rotation.
- (B) One of the either is obtained as a recemic mixture.
- (C) Step II & III both are S_N^2 reaction and both have inversion
- (D) Step II has inversion but step III has retention.
- 5 A compound A has the molecular formula C_5HgCl . It does not react with bromine in carbon tetrachloride. On treatment with strong base it produces a single compound B. B has a molecular formula C_5H_8 and reacts with bromine in carbon tetrachloride. Ozonolysis of B produces a compound C which has a molecular formula $C_5H_8O_2$. Which of the following structures is that of A?





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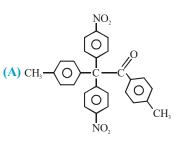


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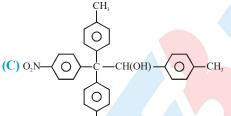
14

CH



ОН ОН

NO₂ NO₂



NO

(A) HOCH, CH, CH, CH, CHO + CH, CHO

The products of hydrolysis of

 \bigcirc –CH₃ (**D**) None of these

 $\xrightarrow{H_3O^{\oplus}}$, is

 $\xrightarrow{H^+}$ A; Product 'A' is

,^{*}H₂Cl

ΟН

(C) H₂

(B) NO,-

aq.AgNO3

CH₃

Ο

0

ĊΗ,

0

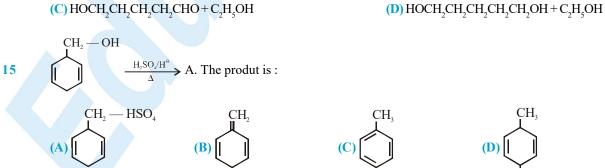
(D)

CH,

NO

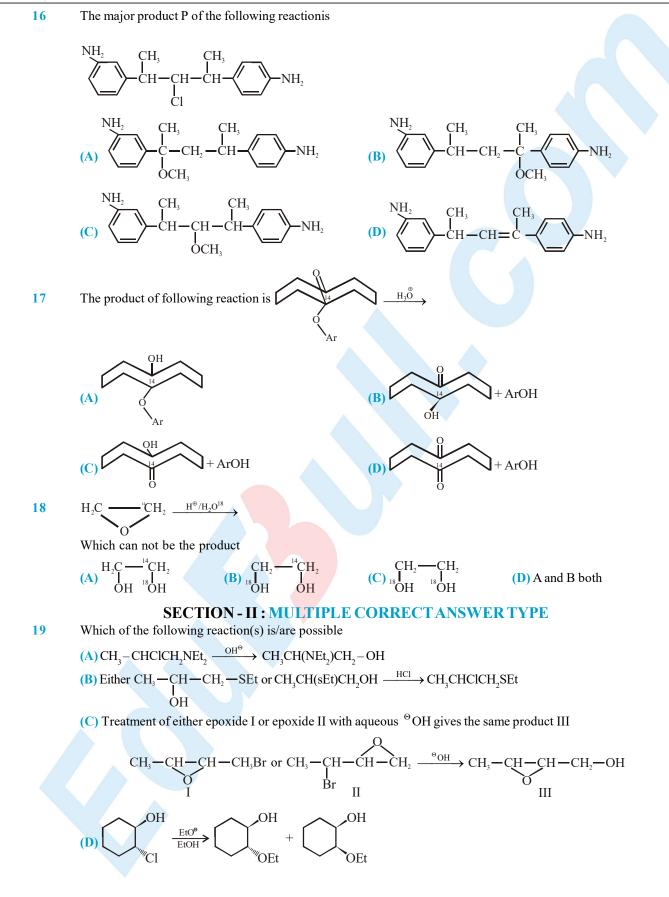
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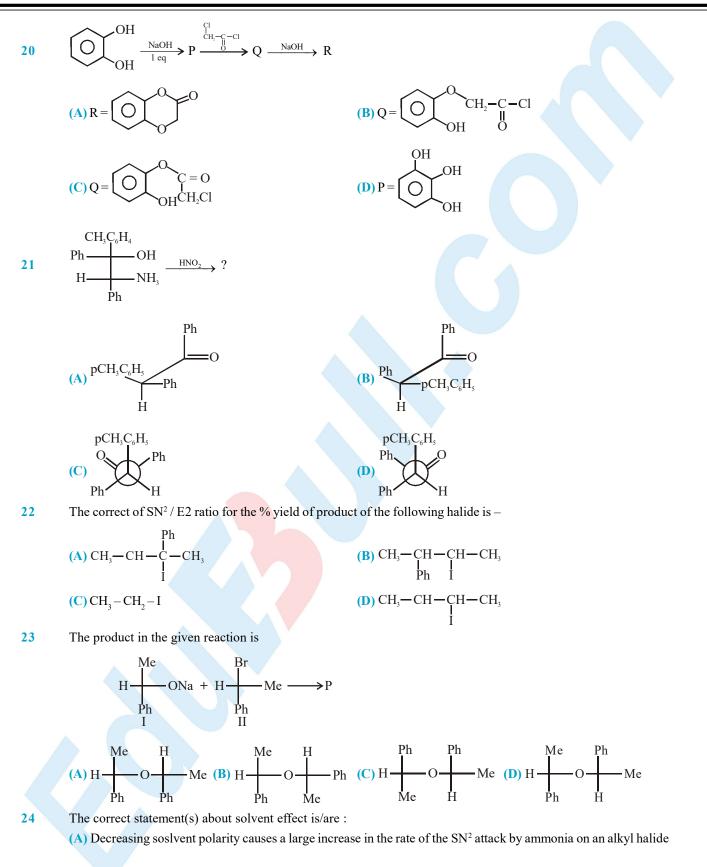


 $-C_{2}H_{5}$









$$RX + \dot{N}H_3 \longrightarrow R\dot{N}H_3 + \ddot{X}$$

(B) Increasing solvent polarity causes a large causes a large decrease in the rate of the SN² attack by hydroxide ion on trimethylsulfonium ion.

$$\begin{array}{rcl} \overset{\Theta}{\mathrm{HO}} & + & \left(\mathrm{CH}_{3}\right)_{3} \\ & & & \\$$

(C) Increasing solvent polarity causes a small decrease in the rate of the SN^2 attack by trimethylamins on trimethylsulfornium ion.

$$(CH_3)_3 \ddot{N} + (CH_3)_3 \overset{\oplus}{S} \longrightarrow CH_3 \overset{\oplus}{N} (CH_3)_3 + (CH_3)_2 S$$

SECTION - III : ASSERTION AND REASON TYPE

Read the following question and choose the correct answer

(A) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

- (B) Statement-2 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1.
- (C) Statement-1 is True, Statement-2 is Fasle
- (D) Statement-1 is False, Statement-2 is True.

25 Statement-1:
$$(CH_3)_3CCH \xrightarrow{H_3SO_4} (CH_3)_3CCH = CH_2 + CH_3 \xrightarrow{CH_3} C = C \xrightarrow{CH_3} + CH_2 = C \xrightarrow{CH_3} CH_3 + CH_$$

Statement-2 : It follows Hofmann's elimination by E2.

26 Statement-1 :
$$CH_3 \rightarrow CH_3 \rightarrow CH_3 \rightarrow CH_3 \rightarrow Ph$$

Statemen-2 : Elimination follows E_1 mechanism.

27 Statement-1: Ethers are prepared from alcohols acid medium through S_N1 or S_N2 mechanisms depending upon nature of alcohol.

Statement - 2 : ROH + H⁺ $f = R - \overset{+}{O}H_2$

$$R - O: \xrightarrow{+} R - OH_2 \iff R - OH_2 + H_2O \longrightarrow ROR + H_3O^+$$

$$R-OH+H^{+} f ROH_{2} \xleftarrow{\text{slow}} R^{+} + H_{2}O$$

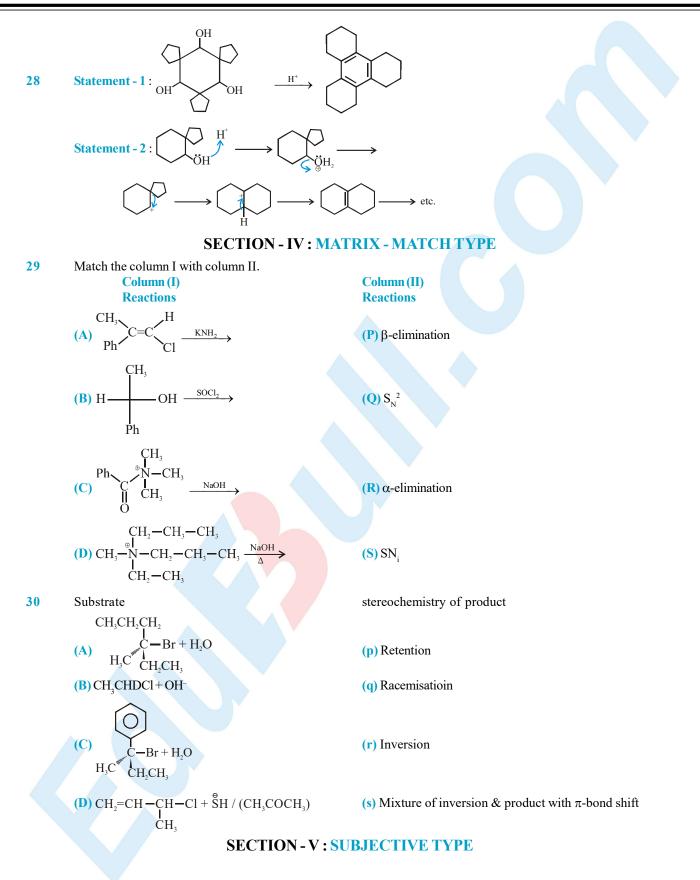
$$R+\ddot{O} - R \rightarrow R - O^{+} - R \xrightarrow{H_{2}O} ROR + H_{3}O$$

$$H$$

$$H$$

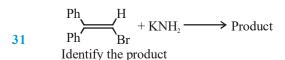
$$H$$



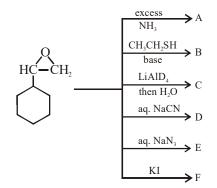




REACTION MECHANISM



32 Give products



SECTION - VI : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension

A hydrocarbon (X) of the formula C_6H_{12} does not react with bromine water but reacts with bromine in presence of light, forming compound (Y). Compound (Y) on treatment with Alc. KOH gives compound [Z] which on ozonolysis gives (T) of the formula $C_6H_{10}O_2$. Compound (T) reduces Tollens reagent and gives compound (W). (W) gives iodoform test and produce compound (U) which when heated with P_2O_5 forms a cyclic anhydride (V).

33 Compound V is

$$(A) \xrightarrow{O}_{H_{3}} \xrightarrow{O}_{C} - CH_{2} - CH_{2} - CH = O$$

$$(B) \xrightarrow{O}_{C} (C) CH_{3} - C - CH_{2} - CH_{2} - CH = O$$

$$(D) CHO - CH = CH - CHO$$

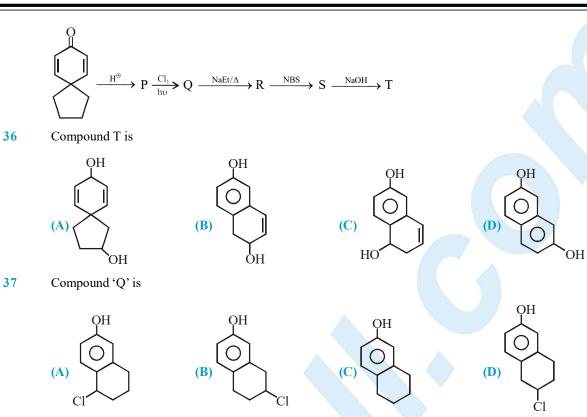
$$(D) CHO - CH = CH - CHO$$

$$(A) COOH - (CH_{2})_{2} - COOH$$

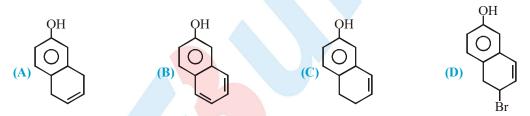
$$(B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (B) \xrightarrow{O}_{COOH} (C) \xrightarrow{O}_{COOH} (C) \xrightarrow{O}_{COOH} (C) \xrightarrow{O}_{COOH} (C) \xrightarrow{O}_{C} - CH_{3} (C) \xrightarrow{O}_{C} - CH_{3} (C) \xrightarrow{O}_{C} - CH_{3} (D) \xrightarrow{O}_{C} - CH_{$$



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38 When treating 'S' with strong base, product obtained is



Comprehension

Two optically active isomeric alcohols X and Y (M.F. = $C_9H_{12}O$) on oxidation with KMnO₄ give benzoic acid. X gives positive iodoform test but Y does not X looses optical activity on oxidation with CrO_3/H^+ but Y does not.

39 'Y' can be

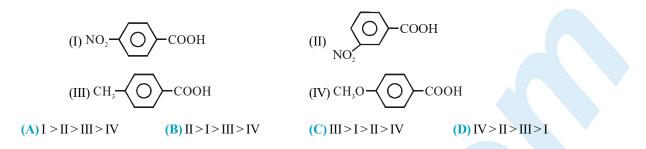


40

The rate of reaction of 'X' with the following acids will be in the following order is



REACTION MECHANISM



41 The possible product(s) on reaction of 'X' with NaBr + H_2SO_4 (along with appropaite mechanism) will be (A) PhCH₂-CH-CH₃ by S_N^2 mechanism Br (B) PhCH₂-CH-CH₃ S_N^1 mechanism Br

(C) Ph -CH-CH₂CH₃by S_N^{-1} mechanism Br (D) Ph -CH-CH₂CH₃by S_N^{-2} mechanism Br



ANSWER KEY

EXERCISE - 1

 1. C
 2. C
 3. C
 4. C
 5. B
 6. B
 7. C
 8. C
 9. A
 10. D
 11. D
 12. C
 13. D

 14. C
 15. A
 16. C
 17. A
 18. B
 19. A
 20. D
 21. B
 22. C
 23. C
 24. D
 25. A
 26. D

 27. C
 28. B
 29. C
 30. B
 31. B
 32. C
 33. D
 34. D
 35. C
 36. D
 37. C
 38. B
 39. A

 40. A
 41. B
 42. A
 43. D
 44. B
 45. C
 46. B
 47. A
 48. A
 49. C
 50. A
 51. D
 52. C

 53. C
 54. C
 55. D
 56. A
 57. B
 58. B
 59. B
 60. C

EXERCISE - 2 : PART # I

 1. A, B
 2. C, D
 3. B, C, D
 4. A, B, D
 5. B, D
 6. A, C
 7. A, B, D
 8. A, B, C

 9. A, B, C
 10. A, D
 11. B, C, D
 12. B, C
 13. A, B, D
 14. A, C
 15. C, D
 16. A, C
 17. A, C

 18. D
 19. B
 20. B
 21. C
 22. C
 23. B
 24. C
 25. C
 26. C
 27. A
 28. C
 29. B
 30. D

 31. A
 32. B
 33. C
 34. C
 35. A
 36. A
 37. D
 38. A
 39. D
 40. A
 41. B
 42. B

PART # II

1. B 2. D 3. C 4. D 5. B 6. C 7. A 8. A 9. B 10. A

EXERCISE - 3 : PART # I

1. $A \rightarrow (r), B \rightarrow (q), C \rightarrow (s), D \rightarrow (p)$ 2. $A \rightarrow (q), B \rightarrow (r), C \rightarrow (s), D \rightarrow (p)$

PART # II

Comprehension #1: 1. C 2. D 3. B 4. B Comprehension #2: 1. A 2. A 3. C

EXERCISE - 5 : PART # I

 1. A
 2. C
 3. A
 4. C
 5. D
 6. A
 7. A
 8. D
 9. D
 10. C
 11. B
 12. A
 13. C

 14. A
 15. B
 16. A
 17. A
 18. D
 19. A
 20. B
 21. C
 22. B
 23. D
 24. B
 25. D

PART # II

1. C 2. A 3. C 4. C 5. B,C 6. A,B,C,D 7. B 8. C 9. B 10. B

MOCK TEST

 1
 C
 2
 B
 3
 A
 4
 A
 5
 B
 6
 B
 7
 B
 8
 D
 9
 A
 10
 C
 11
 B
 12
 D
 13
 B

 14
 C
 15
 C
 16
 B
 17
 C
 18
 C
 19
 A,B,C,D
 20
 A,C,D
 21
 A,C
 22
 A
 23
 A
 24
 (B,C)

 25
 D
 26
 A
 27
 A
 28
 A
 33
 B
 34
 C
 35
 A
 36
 B
 37
 A
 38
 B
 39
 C
 40
 A
 41
 C

