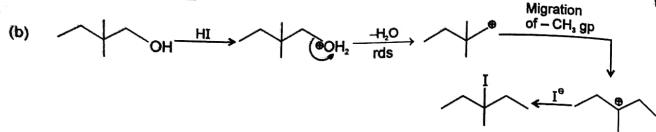
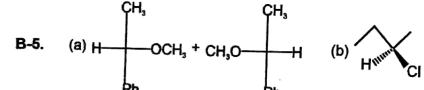
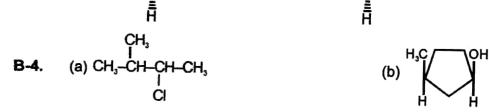
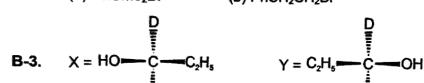


Organic Reaction Mechanisms-III



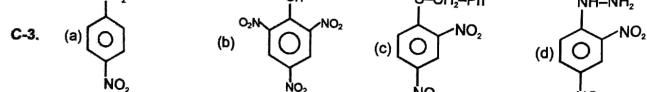
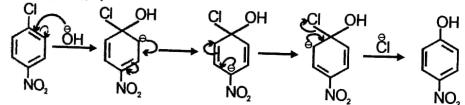
- B-1.** (a) $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 > \text{CH}_3\overset{\text{H}}{\underset{\text{Br}}{\text{C}}}(\text{CH}_2\text{CH}_2\text{CH}_3) > \text{H}_3\overset{\text{CH}_3}{\underset{\text{Br}}{\text{C}}}(\text{CH}_2\text{CH}_2\text{CH}_3)$
 1°-Bromopentane 2°-Bromopentane 3°-Bromo-2-methylbutane
 (b) $\text{CH}_3\overset{\text{CH}_3}{\underset{\text{Br}}{\text{CH}}}(\text{CH}_2\text{CH}_2\text{Br}) > \text{CH}_3\overset{\text{CH}_3}{\underset{\text{Br}}{\text{CH}}}(\text{CH}_2\text{CH}_2\text{Br}) > \text{H}_3\overset{\text{CH}_3}{\underset{\text{Br}}{\text{C}}}(\text{CH}_2\text{CH}_2\text{CH}_3)$
 1-Bromo-3-methylbutane 2-Bromo-3-methylbutane 2-برومو-2-ميثيلبنتان

- B-2.** (a) PhCMe_2Br (b) $\text{PhCH}_2\text{CH}_2\text{Br}$



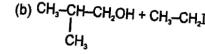
C-1. II > III > I

C-2. Mechanism →

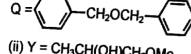


Organic Reaction Mechanisms-III

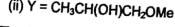
- D-1.** (a)  + CH_3I



- D-2.** $P = \text{C}_5\text{H}_9-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$



- D-3.** (i) $X = \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$



PART - II

- | | | | | |
|----------|----------|-----------|----------|----------|
| A-1. (A) | A-2. (B) | A-3. (B) | A-4. (A) | A-5. (D) |
| A-6. (B) | A-7. (B) | A-8. (C) | B-1. (B) | B-2. (B) |
| B-3. (A) | B-4. (D) | B-5. (B) | B-6. (B) | B-7. (B) |
| B-8. (D) | B-9. (A) | B-10. (B) | C-1. (C) | C-2. (C) |
| C-3. (D) | C-4. (B) | D-1. (A) | D-2. (B) | D-3. (C) |
| D-4. (C) | | | | |

PART - III

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

EXERCISE - 2

PART - I

- | | | | | |
|---------|---------|--------|--------|---------|
| 1. (B) | 2. (C) | 3. (B) | 4. (D) | 5. (D) |
| 6. (A) | 7. (A) | 8. (C) | 9. (B) | 10. (A) |
| 11. (A) | 12. (C) | | | |

PART - II

- | | | | |
|-----------------------|-------|-------|--------------------|
| 1. 3 | 2. 15 | 3. 3 | 4. 5 (Except (ii)) |
| 5. 4 (Except (i, iv)) | | 6. 22 | 7. 2 |

PART - III

- | | | | | |
|-----------|---------|---------|----------|----------|
| 1. (BC) | 2. (AB) | 3. (AC) | 4. (AB) | 5. (AB) |
| 6. (ABCD) | 7. (BC) | 8. (CD) | 9. (ABC) | 10. (AB) |

PART - IV

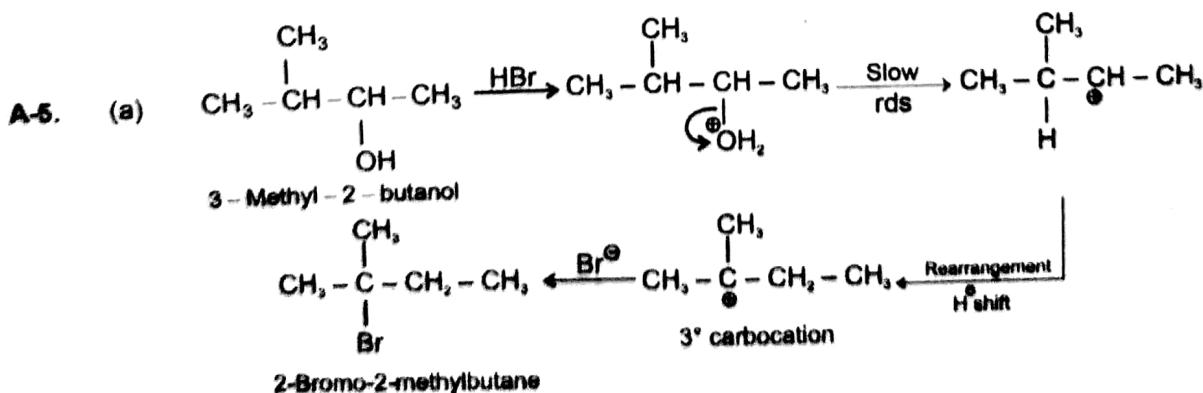
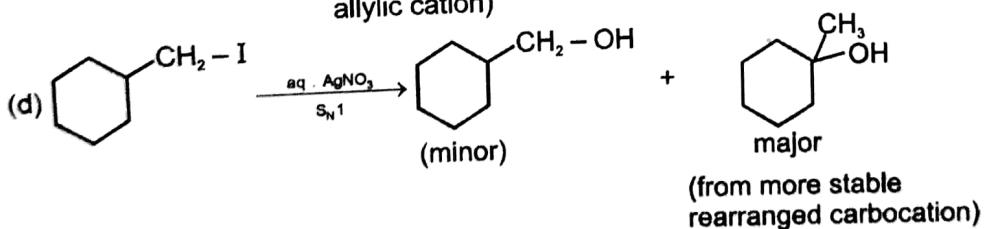
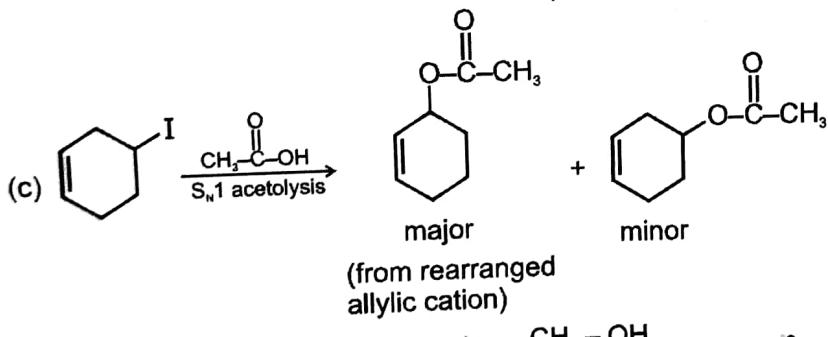
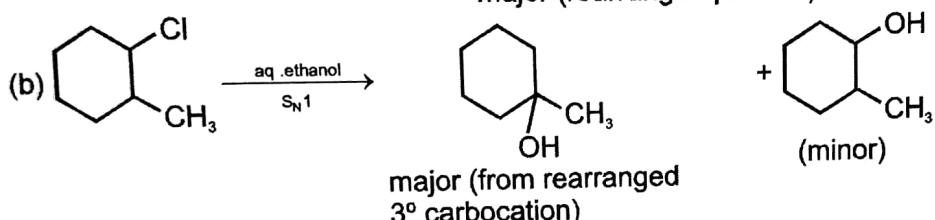
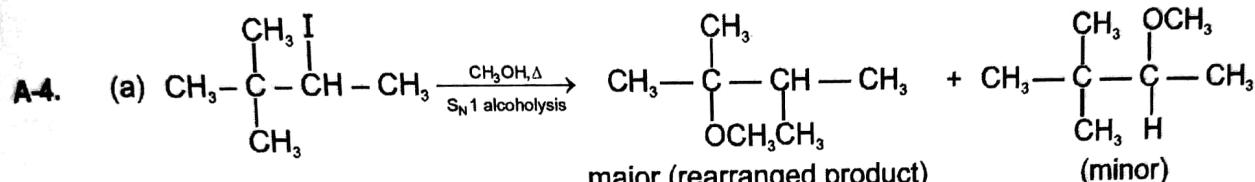
- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (B) | 2. (C) | 3. (B) | 4. (C) | 5. (B) |
| 6. (B) | 7. (D) | 8. (D) | | |

Answers**EXERCISE - 1****PART - I****A-1.** (a) 2-Bromopentane

(b) 2-Bromo-2-methylbutane

A-2. (a) Rate - doubled

(b) Rate – tripled

A-3. 3-Chlorocyclopropene form aromatic carbocation while 5-Chlorocyclopenta-1,3-diene form antiaromatic carbocation.

Organic Reaction Mechanisms-III

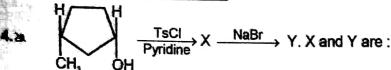
Comprehension # 3

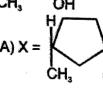
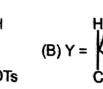
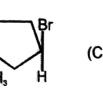
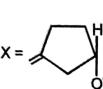
Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Column-1		Column-2		Column-3	
(I)	Ph-CH ₂ -CH ₂ -Br	(i)	NaOH/H ₂ O	(P)	* Ph-CH(OH)-CH ₃ (±)
(II)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{Br} \\ \\ \text{Ph} \end{array}$	(ii)	HI, H ₂ O/acetone	(Q)	$\begin{array}{c} \text{Me} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{Ph} \end{array}$
(III)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{Ph} \end{array}$	(iii)	NaOH/DMSO	(R)	Ph-CH ₂ -CH ₂ -OH
(IV)	Ph-CH ₂ -CH ₂ -OH	(iv)	SOCl ₂ /Pyridine, (NaOH/DMF)	(S)	$\begin{array}{c} \text{Me} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{Ph} \end{array}$

6. $\text{S}_{\text{N}}1 + \text{S}_{\text{N}}2$ mixed mechanism is observed in the reaction :
 (A) (I), (iii) (P) (B) (II) (i) (P) (C) (III) (iv) (Q) (D) (IV) (ii) (S)
7. Only $\text{S}_{\text{N}}1$ mechanism is observed in :
 (A) (I), (i) (R) (B) (II) (iii) (P) (C) (IV) (ii) (S) (D) (III) (ii) (P)
8. $\text{S}_{\text{N}}2$ mechanism is observed in :
 (A) (I), (iii) (R) (B) (IV) (iv) (R) (C) (II) (iii) (Q) (D) all

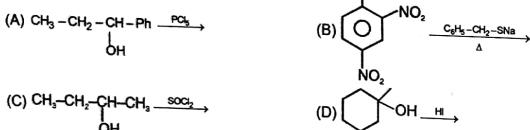
Organic Reaction Mechanisms-III



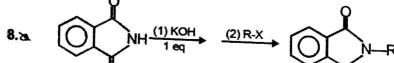
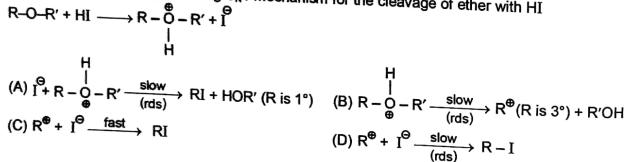
- (A) X =  (B) Y =  (C) X =  (D) Y = 

- 5.* Which of the following conditions are favourable for S_N2 mechanism in alkyl halides?
- Strong nucleophile
 - High conc. of nucleophile
 - 3° alkyl halide
 - Polar protic solvent

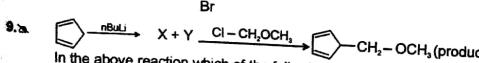
6. Which of the following reactions are nucleophilic substitution reaction?



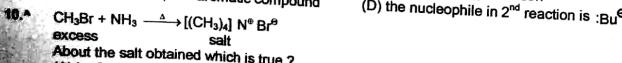
7. Identify correct steps representing S_N1 mechanism for the cleavage of ether with HI



- In which option correct rate for step-2 is given for the different R-X
- $\text{CH}_3-\text{CH}_2-\text{Br} < \text{CH}_3-\text{CH}-\text{CH}_3$
 - $\text{Ph}-\text{Cl} > \text{CH}_3-\text{Cl}$
 - $\text{Ph}-\text{CH}_2-\text{Br} > \text{Ph}-\text{CH}-\text{CH}_3$
 - $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Cl} > \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Cl}$



- In the above reaction which of the following are correct.
- Step-1 is an acid-base reaction
 - Step-2 is an S_N2 reaction
 - X = n-Butane; Y = aromatic compound
 - The nucleophile in 2nd reaction is $: \text{Bu}^\ominus$



About the salt obtained which is true?

- by S_N2 mechanism.
- by S_N1 mechanism.
- NH_3 is nucleophile.
- 4 equivalent of NH_3 is used during reaction.

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ADV ORM III 22

Organic Reaction Mechanisms-III

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

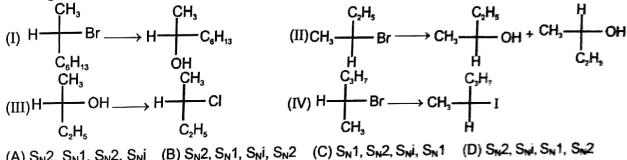
One of the most interesting and useful aspects of stereochemistry is the study of what happens to optically active molecules when they react. The product isolated from the reaction of the chiral material can tell us a great deal about the reaction mechanism. We observe

S_N2 → Inversion of configuration

S_N1 → Racemisation

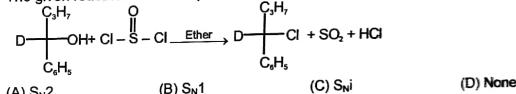
S_Ni → Retention of configuration

1. In the given reactions, the reaction mechanism respectively is :



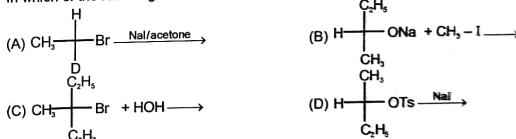
- (A) S_N2, S_N1, S_N2, S_Ni (B) S_N2, S_N1, S_Ni, S_N2 (C) S_N1, S_N2, S_Ni, S_N1 (D) S_N2, S_Ni, S_N1, S_N2

2. The given reaction is an example of which type of mechanism ?



- (A) S_N2 (B) S_N1 (C) S_Ni (D) None

3. In which of the following reaction retention of configuration is observed ?

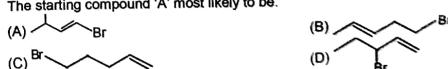


Comprehension # 2

An organic compound 'A' has molecular formula $\text{C}_2\text{H}_6\text{Br}$. It decolorises brown colour of bromine water but does not rotate plane polarised light. 'A' on treatment with HBr/ROOR forms $\text{C}_2\text{H}_5\text{Br}_2$ which on further

treatment with $\text{NaOH}(\text{aq})$ gives the cyclic ether 

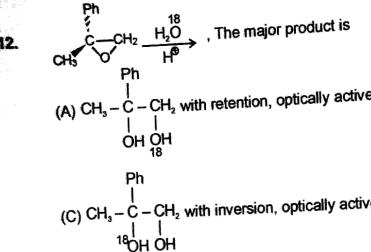
4. The starting compound 'A' most likely to be.



5. Compound 'A' on treatment with HBr will produce

- (A) An achiral dibromide (B) A racemic mixture
(C) A single pure enantiomer (D) A meso dibromide

Organic Reaction Mechanisms-III

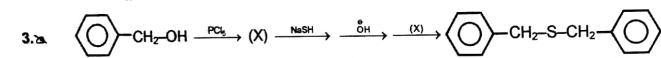


PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. The most reactive chlorine towards H_2O is :

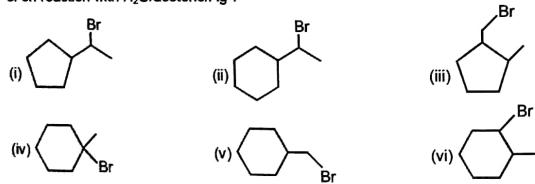


2. When the concentration of alkyl halide is tripled and the concentration of OH^- ion is reduced to half, the rate of $\text{S}_{\text{n}}2$ reaction increases by X times. Report your answer as $10X$.

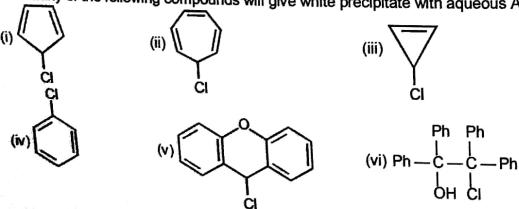


The number of times where $\text{S}_{\text{n}}2$ reaction taken place in above reaction sequence is

4. Among the 6, how many cyclic isomers of molecular formula $\text{C}_7\text{H}_13\text{Br}$ can form 1-methylcyclohexane-1-ol on reaction with $\text{H}_2\text{O}/\text{acetone}/\text{Ag}^+$.

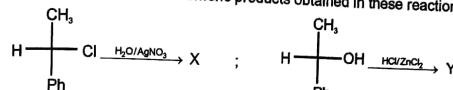


5. How many of the following compounds will give white precipitate with aqueous AgNO_3 .

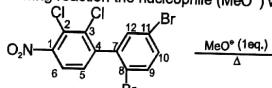


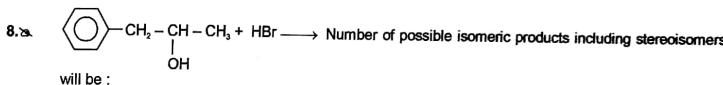
Organic Reaction Mechanisms-III

6. Find the total number of isomeric products obtained in these reactions. Report your answer as X/Y :



7. In the following reaction the nucleophile (MeO^-) will displace which of the halogen atom most readily.



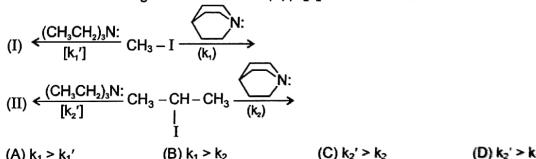
8. 

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

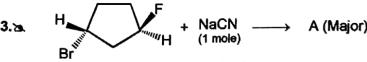
1. Which of the following order is/are correct for the solvolysis in 50% aqueous ethanol at 44.6°C .

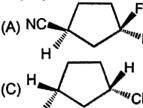
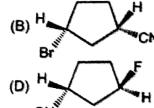
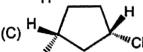
- (A) $\text{CH}_3 - \text{Cl} < \text{CH}_2 = \text{CH} - \text{Cl} < \text{CH}_2 = \text{CH}_2 - \text{Cl}$
- (B) $\text{CH}_2 = \text{CH}_2 - \text{Cl} < \text{CH}_2 = \text{CH} - \text{Cl} < \text{Ph} - \text{CH}_2 - \text{Cl}$
- (C) $\text{CH}_2 = \text{CH}_2 - \text{Cl} < \text{CH}_2 = \text{CH} - \text{Cl} < \text{CH}_3 - \text{Cl}$
- (D) $\text{CH}_2 = \text{CH}_2 - \text{Cl} < \text{CH}_3 - \text{Cl} < \text{CH}_2 = \text{CH} - \text{Cl}$

2. Observe the following reaction I and II. k_1, k_1', k_2, k_2' are rate constants. Select the correct option(s).



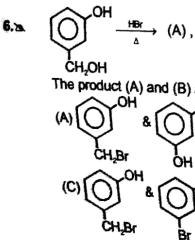
- (A) $k_1 > k_1'$ (B) $k_1 > k_2$ (C) $k_2' > k_2$ (D) $k_2' > k_1$

3. 

- (A) 
- (B) 
- (C) 
- (D) 

Organic Reaction Mechanisms-III

3. In an S_N1 reaction of alkyl halide on chiral centres there is :
 (A) 100 % racemization
 (B) inversion more than retention leading to partial racemization
 (C) 100 % retention
 (D) 100 % inversion
4. Following are the curves for nucleophilic substitution reaction.
-
- The correct statement is :
 (A) 'I' is potential energy diagram for S_N2 reaction that takes place with a negative potential energy change.
 (B) 'II' is potential energy diagram for S_N2 reaction with a positive potential energy change
 (C) 'III' shows potential energy diagram for S_N1 reaction with large energy of activation for first (slowest) step
 (D) All of the above
5. Aryl halides are less reactive towards nucleophilic substitution reactions as compared to alkyl halides due to
 (A) The formation of less stable carbanion
 (B) Longer carbon-halogen bond
 (C) The inductive effect
 (D) sp^2 -hybridized carbon attached to the halogen

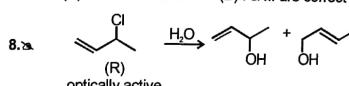


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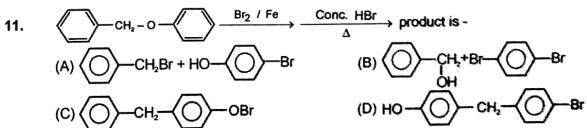
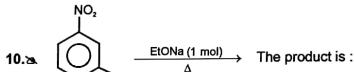
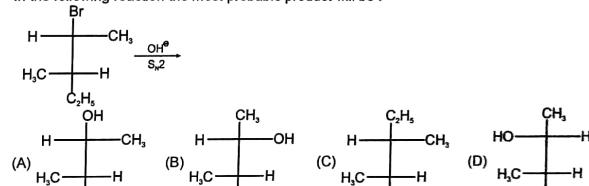
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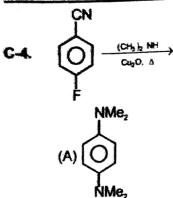
Organic Reaction Mechanisms-III

7. S_N1 reaction undergoes through a carbocation intermediate as follows :
 $R-X \text{ (aq.)} \xrightleftharpoons[\text{Slow}]{\text{R}^*(\text{aq.}) + X^-(\text{aq.})} \xrightarrow[\text{fast}]{H_2O} ROH(\text{aq.}) + H^+(\text{aq.})$
 [R = t-Bu, iso-Pr, Et, Me] (X = Cl, Br, I)
- The correct statements are
 I. The decreasing order of rate of S_N1 reaction is t-BuX > iso-PrX > EtX > MeX
 II. The decreasing order of ionisation energy is MeX > EtX > iso-PrX > t-BuX
 III. The decreasing order of energy of activation is t-BuX > iso-PrX > EtX > MeX
 (A) I & II are correct (B) I & III are correct (C) II and III are correct (D) I, II & III are correct

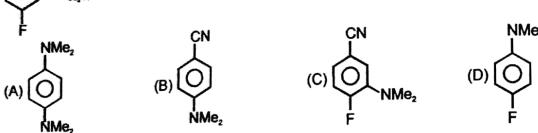


9. In the following reaction the most probable product will be :



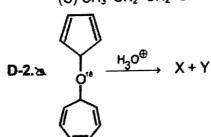


The product is :

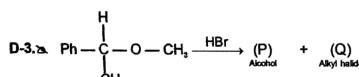
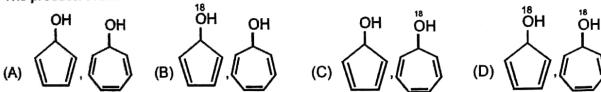


Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

- D-1. In the given reaction, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow[\Delta]{\text{HCl}} [\text{X}] + [\text{Y}]$
 What will be :
 (A) $\text{CH}_3\text{CH}_2\text{OH}$ & $\text{CH}_3\text{CH}_2\text{Cl}$ (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ & $\text{CH}_3\text{CH}_2\text{OH}$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ & $\text{CH}_2=\text{CH}_2$ (D) $\text{CH}_3\text{CH}=\text{CH}_2$ & $\text{CH}_2=\text{CH}_2$

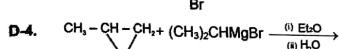


The products X and Y are



(P) & (Q) respectively is :

- (A) $\text{Ph}-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{OH}, \text{CH}_3\text{Br}$ (B) $\text{Ph}-\text{CH}_2\text{OH}, \text{CH}_3\text{CH}_2\text{Br}$
 (C) $\text{CH}_3\text{OH}, \text{Ph}-\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$ (D) $\text{CH}_3\text{OH}, \text{Ph}-\text{CH}_2\text{CH}_2\text{Br}$



What will be the product :

- (A) $\text{CH}_3-(\text{CH}_2)_4-\text{CH}_2\text{OH}$ (B) $\text{CH}_3-\text{CH}=\text{CH}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_3$
 (C) $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{OH}}{\text{CH}}}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}_3$ (D) $\text{CH}_3-\text{CH}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}(\text{CH}_3)_2}{\text{CH}}}_3$

PART - III : MATCH THE COLUMN

1. Match List-I (Alkyl chloride) with List-II (Rates of solvolysis) and select the correct answer using the code given below the lists :

	List-I	List-II
(P)		(1) 1
(Q)		(2) 0.07
(R)		(3) 7700
(S)		(4) 91

Codes :

- (A) P-2 ; Q-1 ; R-4 ; S-3 (B) P-2 ; Q-1 ; R-3 ; S-4

- (C) P-1 ; Q-2 ; R-3 ; S-4 (D) P-1 ; Q-2 ; R-4 ; S-3

2. Match the column-I with column-II :

Column-I	Column-II
Substrate	Stereochemistry of product
(A)	(p) Retention
(B)	(q) Racemisation
(C)	(r) Inversion
(D)	(s) Intermediate is carbocation

Exercise-2

PART - I : ONLY ONE OPTION CORRECT TYPE

1. Arrange the following compounds in order of decreasing reactivity towards $\text{S}_{\text{N}}1$ reaction.



- (A) ii > iii > i (B) i > ii > iii (C) iii < ii < i (D) i > iii > ii

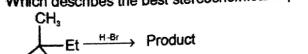
2. The decreasing order of rate of $\text{S}_{\text{N}}2$ reaction for given compounds is :

- (I) CH_3Cl (II) $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{C}}}-\text{CH}_2\text{Cl}$ (III) $\text{CH}_3-\overset{\text{O}}{\underset{\text{C}}{\text{CH}}}-\text{CH}_2\text{Cl}$ (IV) $\text{CH}_3-\text{CH}_2\text{Cl}$

- (A) IV > III > II > I (B) II > III > I > IV (C) II > I > IV > III (D) none

Organic Reaction Mechanisms-III

B-8.a Which describes the best stereochemical aspects of the following reaction?



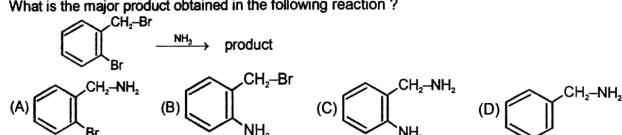
- (A) Inversion of configuration occurs at the carbon undergoing substitution.
 (B) Retention of configuration occurs at the carbon undergoing substitution.
 (C) Racemization occurs at the carbon undergoing substitution.
 (D) The carbon undergoing substitution is not stereogenic.

Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

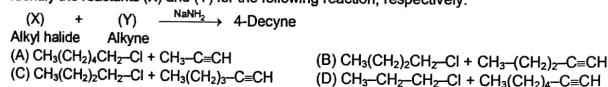
B-1. S_N2 mechanism proceeds through intervention of :
 (A) Carbonium ion (B) Transition state (C) Free radical (D) Carbanion

B-2.a In S_N2 reaction if we doubled the concentration of reactant and nucleophile the rate of S_N2 reaction increases by :
 (A) 2 times (B) 4 times (C) 8 times (D) No change

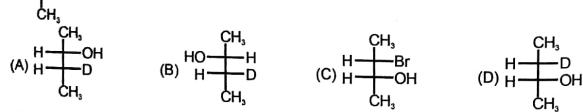
B-3.a What is the major product obtained in the following reaction?



B-4.a Identify the reactants (X) and (Y) for the following reaction, respectively.



B-5.a $H-\overset{\text{Br}}{|}\text{---} \overset{\text{H}}{|}\text{---} \overset{\text{D}}{|}\text{---} \overset{\text{H}}{|}\text{---} \overset{\text{CH}_3}{|}\text{---} \xrightarrow{\text{NaOH, DMSO}}$ Product, Product is :



B-6. $CH_3(CH_2)_2CH_2OH \xrightarrow{HBr}$ X,
 1-butanol

Identify X and the type of 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) $CH_3-CH_2-CH_2-CH_3$ & S_N1 (D) $CH_3-CH_2-CH_2-CH_3$ & S_N2

B-7. $H-\overset{\text{CH}_3}{|}\text{---} \overset{\text{OH}}{|}\text{---} \xrightarrow{PCl_5}$ X ; (X) is

- (D-2-Butanol)
 (A) S-2-Chlorobutane
 (C) Mixture of R and S, 2-Chlorobutane

- (B) R-2-Chlorobutane
 (D) 1-Chlorobutane

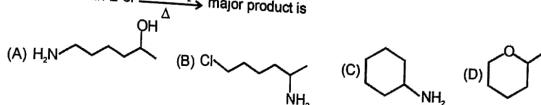
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ADV ORM III-1

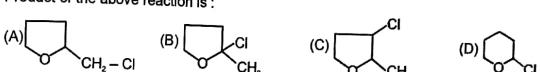
Organic Reaction Mechanisms-III

B-8.a 6-Chlorohexan-2-ol $\xrightarrow[\Delta]{NaNH_2}$ major product is

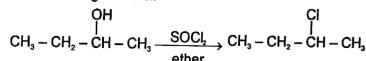


B-9. $\text{C}_3\text{H}_7\text{OCH}_2\text{CH}_3 \xrightarrow[\Delta]{SOCl_2}$ Product

Product of the above reaction is :



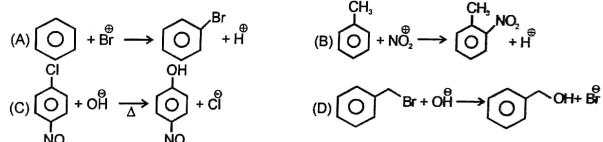
B-10. Consider the following reaction.



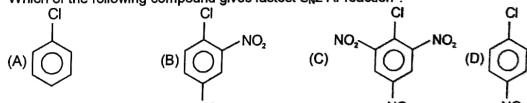
In the above reaction which phenomenon will take place :
 (A) Inversion (B) Retention (C) Racemisation (D) Isomerisation

Section (C) : Bimolecular aromatic nucleophilic substitution reaction (S_N2Ar)

C-1. Which of the following reaction is S_N2Ar reaction ?



C-2.a Which of the following compound gives fastest S_N2Ar reaction ?



C-3.a $\text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{RONa/\Delta}$ OR

Above reaction has maximum rate when :
 (A) Y = -I (B) Y = -Br (C) Y = -Cl (D) Y = -F

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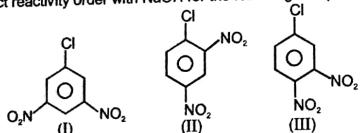
Organic Reaction Mechanisms-III

B-5. a. Write the product of the following reaction with proper stereochemistry.

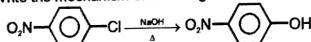


Section (C) : Bimolecular aromatic nucleophilic substitution reaction ($S_N2 Ar$)

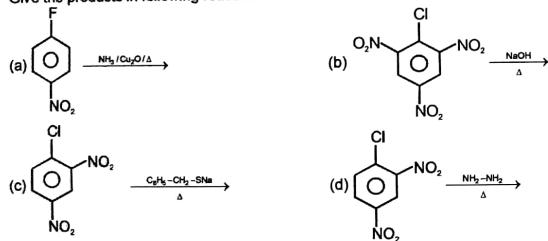
C-1. a. Write the correct reactivity order with NaOH for the following compounds.



C-2. Write the mechanism of following reaction :

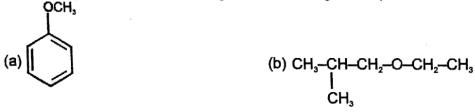


C-3. a. Give the products in following reactions :

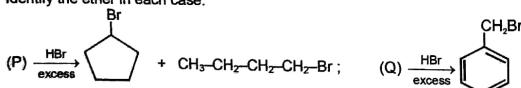


Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

D-1. a. Predict the product of the following reactions using one equivalent of HI.

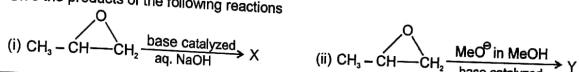


D-2. Few dialkyl ethers & cyclic ethers were allowed to react with excess of HBr with the following results. Identify the ether in each case.



Organic Reaction Mechanisms-III

D-3. a. Give the products of the following reactions



PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

A-1. a. S_N1 reaction occurs through the formation of intermediate :

- (A) Carbocation (B) Carbanion (C) Free radical (D) Carbene

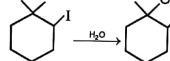
A-2. a. In an S_N1 reaction, the configuration of the product undergoes :

- (A) inversion (B) racemization (C) retention (D) difficult to predict

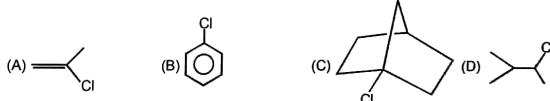
A-3. a. When the concentration of alkyl halide is doubled and the amount of H_2O taken as solvent is reduced to half, the rate of S_N1 reaction increases by:

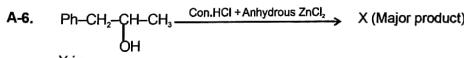
- (A) 3 times (B) 2 times (C) 1.5 times (D) 6 times

A-4. a. Which of the following is not expected to be intermediate of the following reaction ?

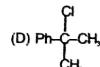


A-5. Which of the following compound can show S_N1 reaction :

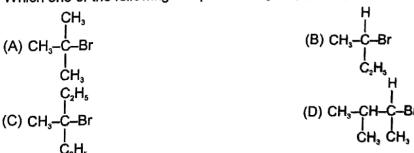


A-6. 

X is :

- (A)  (B)  (C)  (D) 

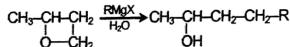
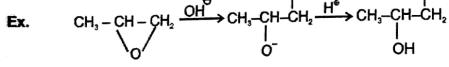
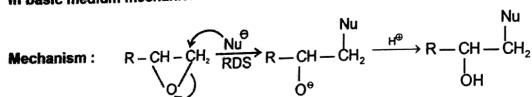
A-7. a. Which one of the following compound will give (d) and (e) form in S_N1 reaction (as major product)



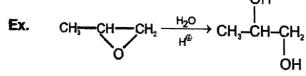
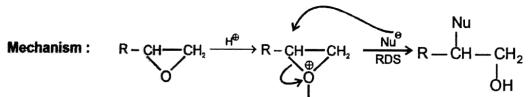
(3) Nucleophilic substitution reaction of Epoxide :

Epoxides are much more reactive than ether because of angle strain in three membered ring therefore epoxides readily undergo nucleophilic substitution reaction.

In basic medium mechanism is S_N2 . Nucleophile attacks on less hindered carbon.



In acidic medium mechanism is S_N1 type. Nucleophile attacks on more substituted carbon.



Exercise-1

PART - I : SUBJECTIVE QUESTIONS

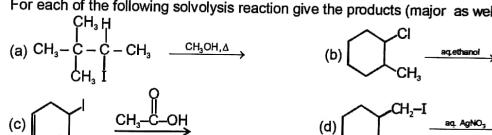
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

- A-1. Which compound in the following couples will react faster in S_N1 reaction and why ?
 (a) 1-Bromopentane or 2-Bromopentane
 (b) 1-Bromo-2-methylbutane or 2-Bromo-2-methylbutane.

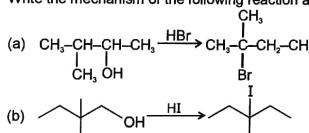
- A-2. What effect do you expect due to following changes in S_N1 reaction of $(\text{CH}_3)_3\text{CBr}$ with CH_3OH ?
 (a) The concentration of $(\text{CH}_3)_3\text{CBr}$ is doubled and that of CH_3OH is halved.
 (b) The concentration of both $(\text{CH}_3)_3\text{CBr}$ and CH_3OH are tripled.

- A-3. Why 3-Chlorocyclopropene is solvolyzed in methanol at much higher rate than 5-Chlorocyclopenta-1,3-diene?

- A-4. For each of the following solvolysis reaction give the products (major as well as minor)



- A-5. Write the mechanism of the following reaction and mention the rate determining step.

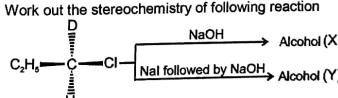
Section (B) : Bimolecular nucleophilic substitution reaction (S_N2 & S_Ni)

- B-1. Arrange the compounds of each set in order of decreasing 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

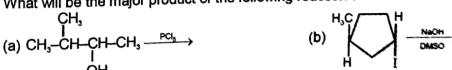
- B-2. Which reacts faster

- (a) PhCH_2Br or PhCM_2Br ($\text{H}_2\text{O} / \text{C}_2\text{H}_5\text{OH}$)
 (b) $\text{PhCH}_2\text{CH}_2\text{Br}$ or PhCM_2Br ($\text{NaI} / \text{Acetone}$)

- B-3. Work out the stereochemistry of following reaction

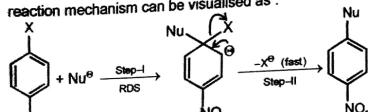


- B-4. What will be the major product of the following reaction?

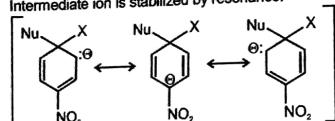


Section (C) : Bimolecular aromatic nucleophilic substitution reaction ($S_N2 Ar$)

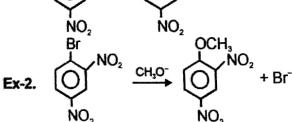
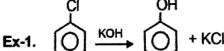
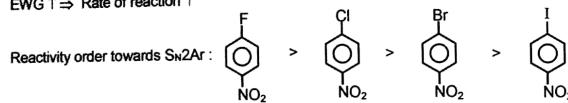
This is the characteristic reaction of arylhalides with ortho or para electron withdrawing substituent. The reaction mechanism can be visualised as :



Intermediate ion is stabilized by resonance.



EWG ↑ ⇒ Rate of reaction ↑



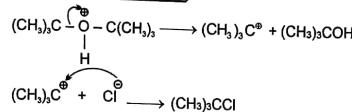
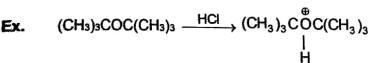
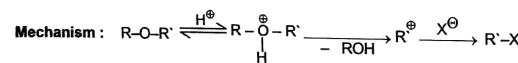
Section (D) : Nucleophilic substitution reaction of Ethers & Epoxides

(1) S_N1 Reaction of Ethers

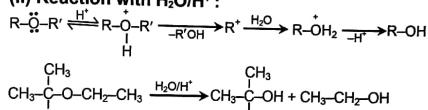
(i) Reaction with HX :

Ethers are unreactive towards most bases, but they can react under acidic conditions. A protonated ether can undergo substitution or elimination with the expulsion of an alcohol. Ethers react with conc. HBr and HI because these reagents are sufficiently acidic to protonate the ether, while bromide iodide are good nucleophiles for the substitution.

If R or R' is 3° then mechanism will be S_N1 otherwise S_N2 .



(ii) Reaction with H_2O/H^+ :

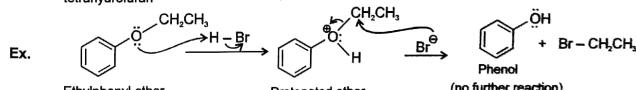
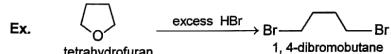
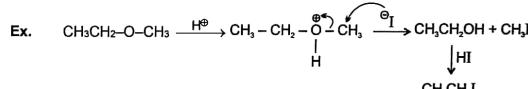
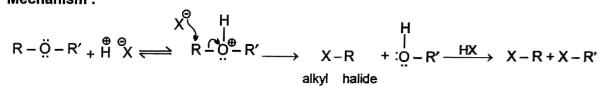


(2) S_N2 Reaction of Ethers

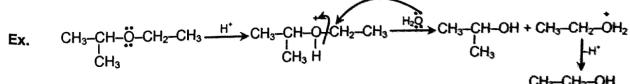
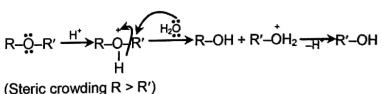
(i) Reaction with HX :

A protonated ether can undergo substitution reaction. Ether react with conc. HBr and HI because these reagents are sufficiently acidic to protonate the ether. If R or R' is 3° then mechanism will be S_N1 otherwise S_N2 .

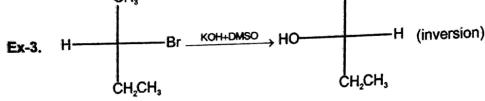
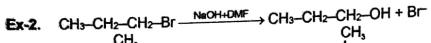
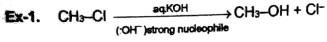
Mechanism :



(ii) Reaction with H_2O/H^+ :

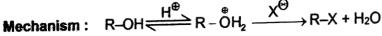


Organic Reaction Mechanisms-III



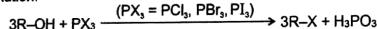
(2) S_N2 Reaction of Alcohol :

(i) Reaction with HX : The protonated β unbranched primary alcohol is well suited for the S_N2 reaction.

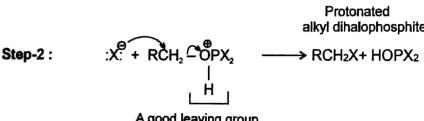
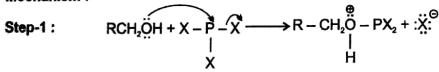


(ii) Reaction with phosphorus trihalides

Several phosphorus halides are useful for converting alcohols to alkyl halides. PBr_3 , PCl_3 , & PCl_5 work well and are commercially available. Phosphorus halides produce good yields of most primary and secondary alkyl halides, but none works well with tertiary alcohols. The two phosphorus halides used most often are PBr_3 and the P_4/I_2 combination.



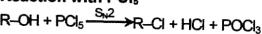
Mechanism :



Remarks

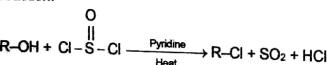
The mechanism for the reaction involves attack of the alcohol group on the phosphorus atom, displacing a halide ion and forming a protonated alkyl dihalophosphite. In second step a halide ion acts as nucleophile to displace HOPX_2 , a good leaving group due to the electronegative atoms bonded to the phosphorus.

(iii) Reaction with PCl_5



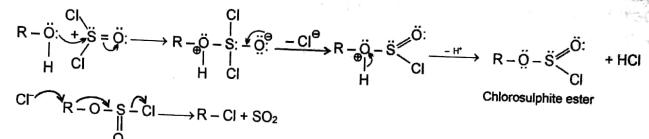
(iv) Reaction with thionyl chloride in presence of pyridine

Thionyl chloride (SOCl_2) is often the best reagent for converting an alcohol to an alkyl chloride. The by products (gaseous SO_2 and HCl) leave the reaction mixture and ensure that there can be no reverse reaction.

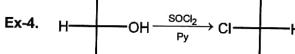
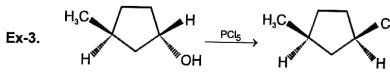
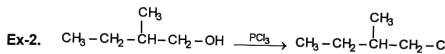
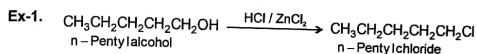


Organic Reaction Mechanisms-III

Mechanism :



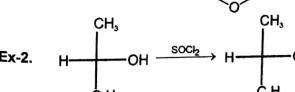
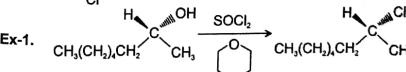
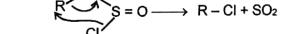
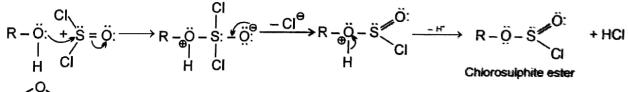
In the first step, the nonbonding electrons of the hydroxyl oxygen atom attack the electrophilic sulphur atom of thionyl chloride. A chloride ion is expelled a proton and gives test of chloro sulphite ester. Second step is an S_N2 mechanism.



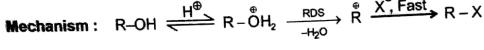
(3) $S_{\text{N}i}$ Reaction :

In $S_{\text{N}i}$ mechanism an internal nucleophile attacks from the same side of leaving group, means retention of configuration. It is an $S_{\text{N}i}$ mechanism, where i means internal
 $\text{ROH} + \text{SOCl}_2 \longrightarrow \text{RCl} + \text{SO}_2 \uparrow + \text{HCl} \uparrow$

Mechanism :

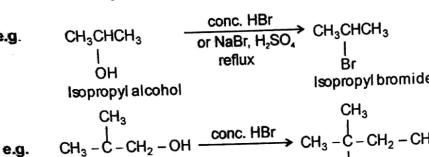


Organic Reaction Mechanisms-III



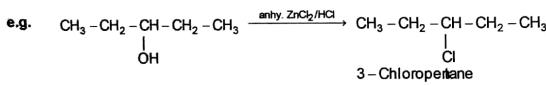
Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : 3° > 2° > 1°



Lucas Reagent

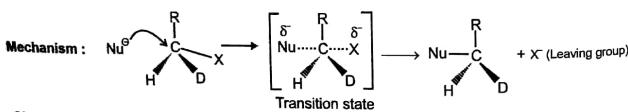
- A mixture of concentrated hydrochloric acid and anhydrous zinc chloride is called the Lucas reagent.
- Whether an alcohol is primary, secondary or tertiary is identified by the Lucas test, which is based upon the difference in reactivity of the three classes of alcohol towards hydrogen halides.
- Alcohol (of not more than six carbons in their molecule) are soluble in the Lucas reagent. The corresponding alkyl chlorides are insoluble.
- Formation of a chloride from an alcohol is indicated by the cloudiness that appears when the chloride separates from the solution hence, the time required for cloudiness to appear is a measure of the reactivity of the alcohol.
- A tertiary alcohol reacts immediately with the Lucas reagent, a secondary alcohol reacts within five minutes and a primary alcohol does not react appreciably at room temperature.



Section (B) : Bimolecular nucleophilic substitution reaction (S_N2)

Nucleophilic substitution in which incoming group replaces leaving group in one step only.

(1) S_N2 Reaction of Alkyl halide :



Characteristic of S_N2

- It is bimolecular, one step concerted process
- It is second order reaction because in the rds both species are involved

3. Kinetics of the reaction : rate \propto [alkyl halide] [nucleophile]

rate = $k[\text{alkyl halide}] [\text{nucleophile}]$

If the concentration of alkyl halide in the reaction mixture is doubled, the rate of the nucleophilic substitution reaction is double. If the concentration of nucleophile is doubled the rate of reaction is also double. If the concentration of both are doubled then the rate of the reaction quadruples.

Organic Reaction Mechanisms-III

4. Energetics of the reaction :

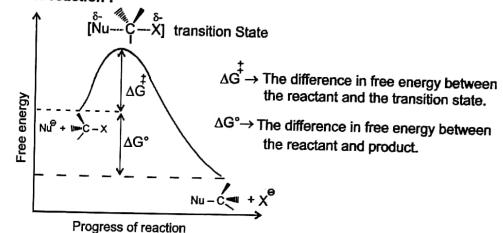


Figure : A free energy diagrams for S_N2 reaction

5. No intermediates are formed in the S_N2 reaction, the reaction proceed through the formation of an unstable arrangement of atoms or groups called transition state.

6. The stereochemistry of S_N2 reaction : As we seen earlier, in an S_N2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as Walden inversion.



7. Factor's affecting the rate of S_N2 reaction : Number of factors affect the relative rate of S_N2 reaction, the most important factors are

(i) Effect of the structure of the substrate :

S_N2 reactivity CH₃ > 1° > 2° > 3° (unreactive)

The important reason behind this order of reactivity is a steric effect. Very large and bulky groups can often hinder the formation of the required transition state and crowding raises the energy of the transition state and slow down the rate of reaction.

Table : Relative rate of reaction of alkyl halides by S_N2 mechanism.

Substituent	Compound	Relative rate
Methyl	CH ₃ X	30
1°	(CH ₃) ₂ CHX	1
2°	(CH ₃) ₂ CH ₂ X	0.02
Neopentyl	(CH ₃) ₃ CCH ₂ X	0.00001
3°	(CH ₃) ₃ CX	~ 0

(ii) Concentration and reactivity of the nucleophile :

– As nucleophilicity of nucleophile increases rate of S_N2 increases.

– Anionic nucleophiles mostly give S_N2 reaction

– A stronger nucleophile attacks upon α-carbon with faster rate than the rate of departing of leaving group.

(iii) The effect of the solvent : Polar aprotic solvent have crowded positive centre, so they do not solvate the anion appreciably therefore the rate of S_N2 reactions increased when they are carried out in polar aprotic solvent.

(iv) The nature of the leaving group : Weaker bases are good leaving groups. A good leaving group always stabilise the transition state and lowers its free energy of activation and there by increases the rate of the reaction. Order of leaving ability of halide ion F⁻ < Cl⁻ < Br⁻ < I⁻

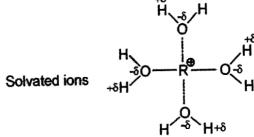
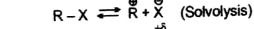
Reagents for alkyl halide are : OH⁻, SH⁻, I⁻, CN⁻, NH₃ (strong anionic nucleophiles)

Organic Reaction Mechanisms-III

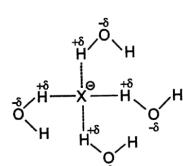
Reactivity of S_N1 \propto stability of carbocation.

S_N1 reactivity : $3^\circ > 2^\circ > 1^\circ > \text{CH}_3-X$

- (i) Concentration and reactivity of the nucleophile \rightarrow The rate of S_N1 reaction is unaffected by the concentration and nature of the nucleophile.
 Weak and neutral nucleophile favours S_N1 reaction.
 Mostly solvents (protic) itself functions as nucleophiles in S_N1 reaction, so S_N1 reaction is termed as solvolysis reaction.
 water \rightarrow hydrolysis : $\text{C}_2\text{H}_5\text{OH} \rightarrow$ ethanolysis
 $\text{CH}_3\text{COOH} \rightarrow$ acetolysis : $\text{NH}_3 \rightarrow$ ammonolysis
- (iii) Effect of the solvent : (ionising ability of the solvent)
 The use of a polar protic solvent will greatly increase the rate of ionisation of an alkyl halide in any S_N1 reaction because it solvates cations and anions so effectively and stabilises the transition state leading to the intermediate carbocation and halide ion, thus the energy of activation is lower.



Solvolytic



Solvated ions

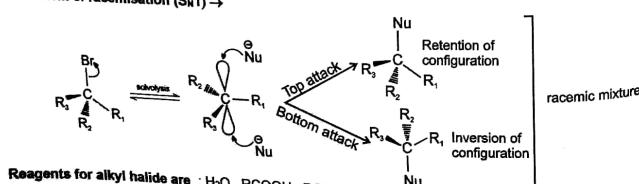
Table - : Dielectric constants (ϵ) and ionisation rate of t-Butylchloride in few common solvents

Solvent	ϵ	Relative rate
H_2O	80	8000
CH_3OH	33	1000
$\text{C}_2\text{H}_5\text{OH}$	24	200
$(\text{CH}_3)_2\text{CO}$	21	1
$\text{CH}_3\text{CO}_2\text{H}$	6	-

(iv) The nature of the leaving group \rightarrow In the S_N1 reaction the leaving group begins to acquire a negative charge as the transition state is reached. Stabilisation of this developing negative charge at the leaving group stabilises the transition state and this lowers the free energy of activation and there by increases the rate of reaction. Leaving ability of halogen is $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

7. Stereochemistry of S_N1 reactions \rightarrow In the S_N1 mechanism, the carbocation intermediate is sp^2 hybridized and planar. A nucleophile can attack on the carbocation from either face, if reactant is chiral then attack of nucleophile from both faces gives enantiomers as the product, which is called racemisation.

Mechanism of racemisation (S_N1) \rightarrow



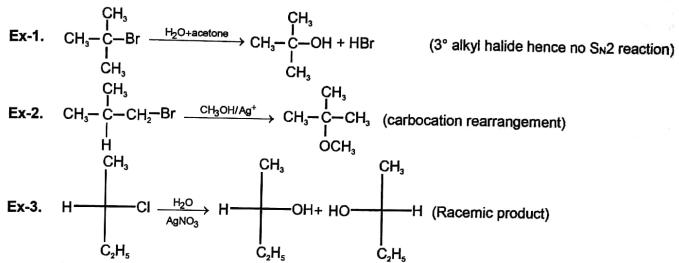
Reagents for alkyl halide are : H_2O , RCOOH , ROH & RSH

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ADV ORM III- 2

Organic Reaction Mechanisms-III



(2) S_N1 Reaction of Alcohols

(i) Reaction with hydrogen halides

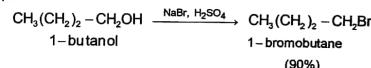
A common method is to treat the alcohol with a hydrohalic acid, usually HCl or HBr . These acids are used to convert alcohols into the corresponding alkyl halides.

(i) In acidic solution, an alcohol is in equilibrium with its protonated form. Protonation converts the hydroxy group from a poor leaving group (OH^-) into a good leaving group (H_2O). If the alcohol is protonated all the usual substitution and elimination reactions are feasible, depending on the structure (1°, 2°, 3°) of the alcohol.

(ii) Halides are anions of strong acids, so they are weak bases. Solutions of HBr and HI contain nucleophilic Br^- and I^- ions.

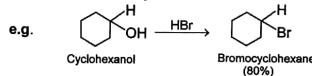
(iii) Concentrated hydrobromic acid rapidly converts t-Butyl alcohol to t-Butyl bromide. The strong acid protonates the hydroxyl group, converting it into a good leaving group. The hindered tertiary carbon atom cannot undergo S_N2 displacement, but it can ionise to a tertiary carbocation. Attack by bromide ion gives the alkyl bromide. The mechanism is similar to S_N1 mechanism.

(iv) 1-Butanol reacts with sodium bromide in concentrated sulfuric acid to give 1-Bromobutane by an S_N2 displacement.



Protonation converts the hydroxy group to a good leaving group, but ionization to a primary carbocation is unfavourable. The protonated unbranched primary alcohol is well suited for the S_N2 displacement.

(v) Secondary alcohols also react with HBr to form alkyl bromides usually by the S_N1 mechanism.



(vi) HCl (Hydrochloric acid) reacts with alcohols in much the same way that as the hydrobromic acid.

(vii) Chloride ion is a weaker nucleophile than bromide ion because it is smaller and less polarizable. Lewis acid, such as ZnCl_2 , is sometimes necessary to promote the reaction of HCl with primary and secondary alcohols.

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Organic Reaction Mechanisms-III

Nucleophilic substitution reaction (S_N) :

Replacement (displacement) of an atom or group by an other atom or group in a molecule is known as substitution reaction. If substitution reaction is brought about by a nucleophile then it is known as nucleophilic substitution reaction. Generally substitution takes place at sp^3 carbon.



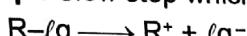
Types of nucleophilic substitution reaction :

- (I) S_N1 (II) S_N2 (III) S_Ni

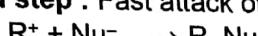
Section (A) : Unimolecular nucleophilic substitution reaction (S_N1)

Nucleophilic substitution which involves two step process

- (a) First step : Slow step which involves ionisation (to form carbocation)

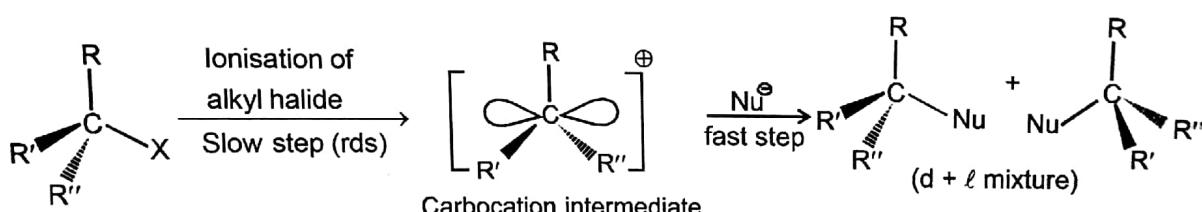


- (b) Second step : Fast attack of nucleophile on carbocation results into product.



(1) S_N1 Reaction of Alkyl halide

Mechanism :



Characteristics of S_N1 reactions :

1. It is unimolecular, two step process.
2. Carbocation intermediate is formed, so rearrangement is possible in S_N1 reaction.
3. It is first order reaction.
4. Kinetics of the reaction Rate \propto [Alkyl halide]

Rate of S_N1 reaction is independent of concentration and reactivity of nucleophile.

5. Energetics of the S_N1 reaction :

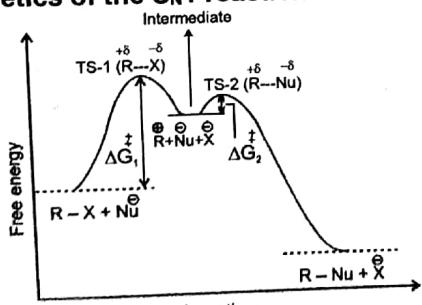


Figure : Free energy diagram for the S_N1 reaction.

6. Factors affecting the rate of S_N1 reaction :

- (i) The structure of the substrate : The rds of the S_N1 reaction is ionization step, a carbocation is formed in this step. This ionisation is strongly endothermic process, rate of S_N1 reaction depends strongly on carbocation stability because carbocation is the intermediate of S_N1 reaction which determines the energy of activation of the reaction.