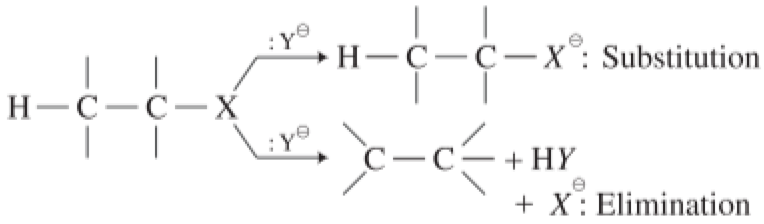
Haloalkanes and Haloarenes

Case Study Based Questions

Case Study 1

Substitution reactions involve the replacement of one atom or group (X) by another (Y):
RX + Y ---- RY+X
The halogenation of alkanes is a substitution reaction, in which a hydrogen atom is replaced by a halogen atom (X = H, Y = halogen). Reactions of this type proceed by radical-chain mechanisms in which the bonds are broken and formed by atoms or radicals as reactive intermediates. This mode of bond-breaking, in which one electron goes with R and the other with X, is called homolytic bond cleavage:
R: X+Y ----- X+R: Y
(a homolytic substitution reaction)
There are a large number of reactions, usually occurring in solution, that do not involve atoms or radicals but rather involve ions. They occur by heterolytic cleavage as opposed to homolytic cleavage of electron-pair bonds. In heterolytic bond cleavage, the electron pair can be considered to go with one or the other of the group R and X when the bond is broken. As one example, Y is a group such that it has an unshared electron pair and also is a negative ion. A heterolytic substitution reaction in which the R: X bonding pair goes with X would lead to RY and : Xs.
R: X+:Y --- X+R:Y
(a heterolytic substitution reaction.) Substitution reactions can proceed by ionic or polar mechanism in which the bonds cleave heterolytically elimination reactions that result in the formation of carbon-carbon multiple bonds:



These reactions often are influenced profoundly by seemingly minor variations in the structure of the reactants, in the solvent, or in the temperature.

Read the given passage carefully and give the answer of the following questions.

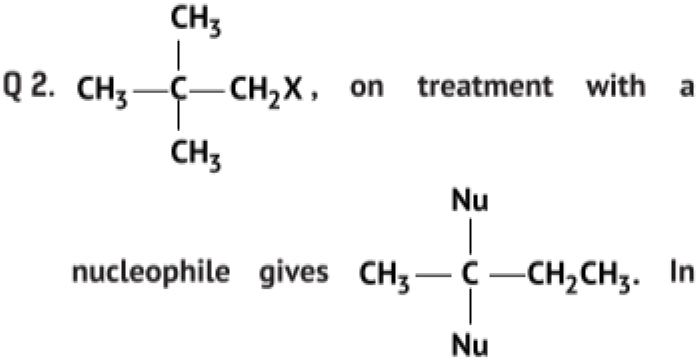
Q1. In a nucleophilic substitution reaction, the least reactive compound is:

a. CH_2CH_2CL

b. $(CH_3)_3CCL$

C. CH_2=CHCL

d. CH_2=CHCH2CL



Q 2. $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2X$, on treatment with a nucleophile gives $CH_3-\overset{Nu}{\underset{Nu}{C}}-CH_2CH_3$. In

which condition, the product yield will be maximum?

a. CCL_4 as a solvent, X = Cl

b. H_2O as a solvent, X = Cl

c. CCL_4 as a solvent, X =I

d. H_2O as a solvent, X=I

Q3. n-butane on monobromination gives three isomers. The product obtained when the major monobromo product is heated with alc. KOH will be:

a. but-1-ene

b. but-2-ene

c. 2-ethoxybutane

d. butan-2-ol

Q4. Reaction of tert-butyl bromide with aqueous sodium hydroxide follows:

a. 5,1 mechanism

b. 5,2 mechanism

c. Any of the above two depending upon temperature of reaction

d. E, mechanism

Answers

1. (c) CH_2=CHCL
2. (d) H_2O as a solvent, X = I
3. (b) but-2-ene
4. (a) 51 mechanism

Case Study 2

The substitution reaction of alkyl halide mainly occurs by S or S2 mechanism. Whatever mechanism alkyl halides follow for the substitution reaction to occur, the polarity of the carbon halogen bond is responsible for these substitution reactions. The rate of S1 reactions are governed by the stability of carbocation whereas for S2 reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation, which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.
Read the given passage carefully and give the answer of the following questions: (CBSE 2020)

Q1. Predict the stereochemistry of the product formed if an optically active alkyl halide undergoes substitution reaction by SN1 mechanism.

Q2. Name the instrument used for measuring the angle by which the plane polarised light is rotated.

Q3. Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.

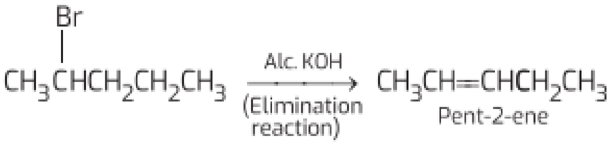
Q4. Write the structures of the products formed when anisole is treated with HI.

Answers

1. During S1 reactions, optically active alkyl halides give racemic products.

2. A polarimeter is used for measuring the angle by which the plane polarised light is rotated.

3. Pent-2-ene.



$$CH_3\underset{}{\overset{Br}{C}}HCH_2CH_2CH_3 \xrightarrow[\text{(Elimination reaction)}]{\text{Alc. KOH}} \underset{\text{Pent-2-ene}}{CH_3CH{=}CHCH_2CH_3}$$

4. CH_2I and C6H5OH are the products formed.

Case Study 3

The polarity of C-X bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reaction with metal atoms to form organometallic compounds. Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution of arenes. Nucleophilic substitution reactions are categorised into S1 and S2 on the basis of their kinetic properties. Chirality has a profound role in understanding the S1 and S2 mechanism.

Read the given passage carefully and give the answer of the following questions: (CBSE 2023)

Q1. What happens when bromobenzene is treated with Mg in the presence of dry ether?

Q2. Which compound in each of the following pairs will react faster in S1 reaction with OH-?

(i) CH_2=CH-CH_2-CL

or CH_3-CH2-CH2-CL

(ii) (CH_3),C-CL or CH,CL

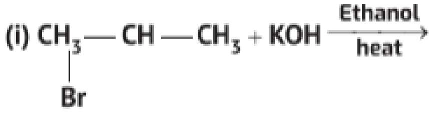
Q3. Write the equations for the preparation of 1-iodobutane from:

(i) 1-chlorobutane and

(ii) but-1-ene.

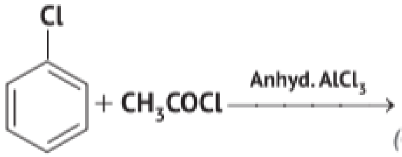
OR

Write the structure of the major products in each of the following reactions:



$$\text{(i) } CH_3-\underset{Br}{CH}-CH_3 + KOH \xrightarrow[\text{heat}]{\text{Ethanol}}$$

(ii)



(CBSE 2023)

Answers

1. When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.

2. (1) CH_2

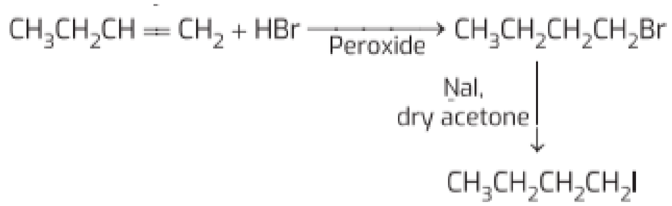
CH2-CH_2- CL_2 will react faster because allylic halides show high reactivity towards the SN_1 reaction

(ii) $(CH_3)_3$ C-Cl will react faster because the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion. Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction.

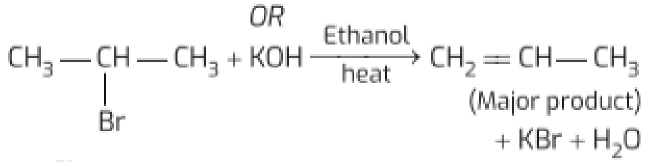
3. (i) Preparation of 1-iodobutane from 1-chlorobutane: It occurs in the presence of dry acetone [Finkelstein reaction].

$$CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow[\text{Acetone}]{CH_3OH} CH_3CH_2CH_2CH_2I + NaCl$$

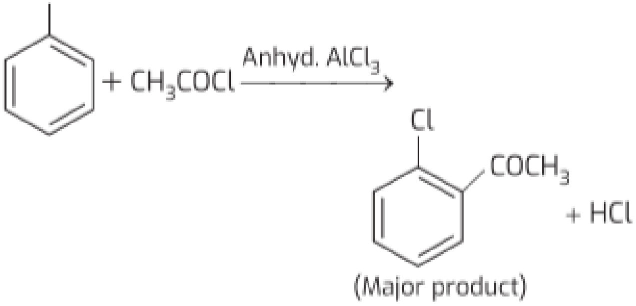
(ii) Preparation of 1-iodobutane from but-1-ene:
It occurs by using peroxide [Anti-Markovnikov's addition]



OR

(i)


$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 + KOH \xrightarrow[\text{heat}]{\text{Ethanol}} \underset{\text{(Major product)}}{CH_2=CH-CH_3} + KBr + H_2O$$

(ii)


Solutions for Questions 4 to 13 are Given Below

Case Study 4

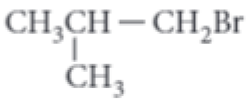
Read the passage given below and answer the following questions :

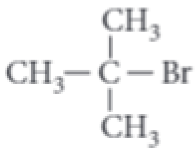
A primary alkyl halide (*A*) C_4H_9Br reacted with alcoholic KOH to give compound (*B*). Compound (*B*) is reacted with HBr to give compound (*C*) which is an isomer of (*A*). When (*A*) reacted with sodium metal, it gave a compound (*D*) C_8H_{18} that is different than the compound obtained when *n*-butyl bromide reacted with sodium metal.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound (*A*) is

(a) $CH_3CH_2CH_2CH_2Br$

(b) 
$CH_3\underset{\underset{CH_3}{|}}{CH}-CH_2Br$

(c) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

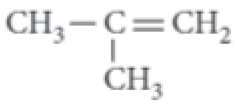
(d) $CH_3CH_2CH_2Br$

(ii) Which type of isomerism is present in compound (*A*) and (*C*)?

(a) Positional (b) Functional (c) Chain (d) Both (a) and (c)

OR

Identify compound (*B*).

(a) 
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$

(b) $CH_3-CH=CH-CH_3$

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

(d) None of these

(iii) IUPAC name of compound (*D*) is

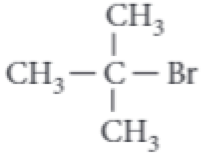
(a) *n*-octane

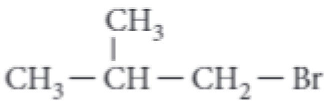
(b) 2,5-dimethylhexane

(c) 2-methylheptane

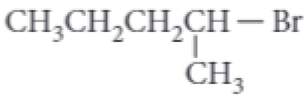
(d) 3,4-dimethyl hexane.

(iv) When compoound (*C*) is treated with alc. KOH and then treated with HBr in presence of peroxide, the compound obtained is

(a) 
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$

(b) 
$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-Br$

(c) $CH_3CH_2CH_2CH_2Br$

(d) 
$CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{CH}-Br$

Case Study 5

Read the passage given below and answer the following questions :

Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular (S_N2) and substitution nucleophilic unimolecular (S_N1) depending on molecules taking part in determining the rate of reaction. Reactivity of alkyl halide towards S_N1 and S_N2 reactions depends on various factors such as steric hindrance, stability of intermediate or transition state and polarity of solvent. S_N2 reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in case of S_N1 reactions.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following is most reactive towards nucleophilic substitution reaction?

(a) C_6H_5Cl (b) $CH_2{=}CHCl$ (c) $ClCH_2CH{=}CH_2$ (d) $CH_3CH{=}CHCl$

(ii) Isopropyl chloride undergoes hydrolysis by

(a) S_N1 mechanism (b) S_N2 mechanism

(c) S_N1 and S_N2 mechanism (d) neither S_N1 nor S_N2 mechanism.

(iii) The most reactive nucleophile among the following is

(a) CH_3O^- (b) $C_6H_5O^-$ (c) $(CH_3)_2CHO^-$ (d) $(CH_3)_3CO^-$

(iv) Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of

(a) insolubility (b) instability

(c) inductive effect (d) stearic hindrance.

OR

Which of the following is the correct order of decreasing S_N2 reactivity?

(a) $RCH_2X > R_2CHX > R_3CX$ (b) $R_3CX > R_2CHX > RCH_2X$

(c) $R_2CHX > R_3CX > RCH_2X$ (d) $RCH_2X > R_3CX > R_2CHX$

Case Study 6

Read the passage given below and answer the following questions :

A chlorocompound (*A*) on reduction with Zn-Cu and ethanol gives the hydrocarbon (*B*) with five carbon atoms. When (*A*) is dissolved in dry ether and treated with sodium metal it gave 2,2,5,5-tetramethylhexane. The treatment of (*A*) with alcoholic KCN gives compound (*C*).

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The compound (*A*) is

(a) 1-chloro-2, 2-dimethylpropane (b) 1-chloro-2, 2-dimethyl butane

(c) 1-chloro-2-methyl butane (d) 2-chloro-2-methyl butane.

(ii) The reaction of (*C*) with Na, C_2H_5OH gives

(a) $(CH_3)_3C\,CH_2CONH_2$ (b) $(CH_3)_3C\,NH_2$

(c) $(CH_3)_3C\,CH_2CH_2NH_2$ (d) $(CH_3)_2CHCH_2NH_2$

(iii) The reaction of (*C*) with Na, C_2H_5OH is called

(a) Gilman reaction (b) Mendius reaction

(c) Grooves process (d) Swart's reaction.

OR

The reaction of (A) with aq. KOH will preferably favour

(a) S_N1 mechanism (b) S_N2 mechanism (c) E_1 mechanism (d) E_2 mechanism.

(iv) Compound (B) is

(a) n-pentane (b) 2, 2-dimethylpropane

(c) 2-methylbutane (d) none of these.

Case Study 7

Read the passage given below and answer the following questions :

When haloalkanes with β-hydrogen atom are boiled with alcoholic solution of KOH, they undergo elimination of hydrogen halide resulting in the formation of alkenes. These reactions are called β-elimination reactions or dehydrohalogenation reactions. These reactions follow Saytzeff's rule. Substitution and elimination reactions often compete with each other. Mostly bases behave as nucleophiles and therefore can engage in substitution or elimination reactions depending upon the alkyl halide and the reaction conditions.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Among the following the most reactive towards alcoholic KOH is

(a) $CH_2{=}CHBr$ (b) $CH_3COCH_2CH_2Br$

(c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$

(ii) The general reaction, $R—X \xrightarrow{\text{aq. OH}^-} ROH + X^-$, is expected to follow decreasing order of reactivity as in

(a) t-BuI > t-BuBr > t-BuCl > t-BuF (b) t-BuF > t-BuCl > t-BuBr > t-BuI

(c) t-BuBr > t-BuCl > t-BuI > t-BuF (d) t-BuF > t-BuCl > t-BuI > t-BuBr

(t-Bu = tertiary Butyl group)

(iii) Reaction of t-butyl bromide with sodium methoxide produces

(a) sodium t-butoxide (b) t-butyl methyl ether

(c) *iso*-butane (d) *iso*-butylene.

(iv) In the elimination reactions, the reactivity of alkyl halides follows the sequence

(a) $R-F > R-Cl > R-Br > R-I$ (b) $R-I > R-Br > R-Cl > R-F$

(c) $R-I > R-F > R-Br > R-Cl$ (d) $R-F > R-I > R-Br > R-Cl$

OR

The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is

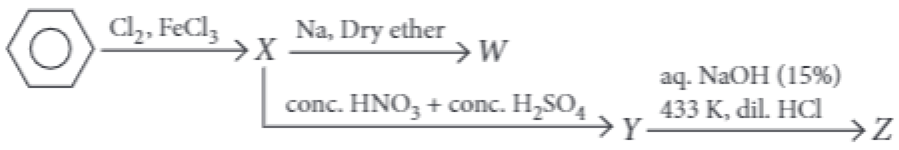
(a) 3° < 2° < 1° (b) 3° > 2° > 1°

(c) 3° < 2° > 1° (d) 3° > 2° < 1°

Case Study 8

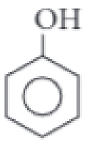
Read the passage given below and answer the following questions :

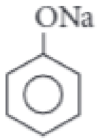
Consider the given sequence of reactions :



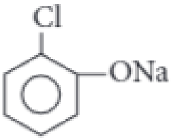
The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Identify *W*.

(a) 

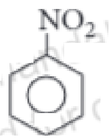
(b) 

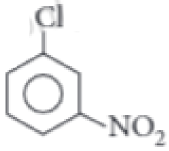
(c) 

(d) 

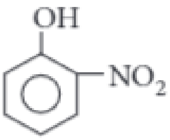
OR

Compound *Y* is

(a) 

(b) 

(c) 

(d) 

(ii) When *X* reacts with CH_3COCl in presence of anhy. $AlCl_3$, the reaction is known as

(a) Fittig reaction (b) Ullmann reaction

(c) Wurtz-Fittig reaction (d) Friedel–Crafts acylation reaction.

(iii) When *X* is treated Ni-Al/NaOH the product obtained is

(a) benzene (b) phenol (c) *p*-chlorophenol (d) triphenyl.

(iv) Compound *Z* is

(a) phenol (b) *p*-chlorophenol (c) *p*-nitrophenol (d) nitrobenzene.

Case Study 9

Read the passage given below and answer the following questions :

Haloarenes are less reactive than haloalkanes. The low reactivity of haloarenes can be attributed to

- resonance effect
- sp^2 hybridisation of C — *X* bond
- polarity of C — *X* bond
- instability of phenyl cation (formed by self-ionisation of haloarene)
- repulsion between the electron rich attacking nucleophiles and electron rich arenes.

Reactivity of haloarenes can be increased or decreased by the presence of certain groups at certain positions for example, nitro ($-NO_2$) group at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilc substitution reactions.

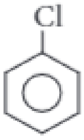
The following questions are multiple choice questions. Choose the most appropriate answer :

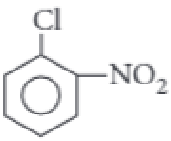
(i) Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to

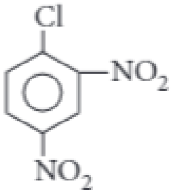
(a) the formation of less stable carbonium ion (b) resonance stabilisation

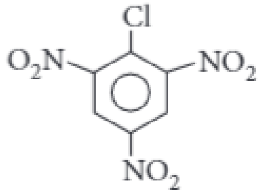
(c) larger carbon-halogen bond (d) inductive effect.

(ii) Which of the following aryl halides is the most reactive towards nucleophilic substitution?

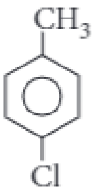
(a) 

(b) 

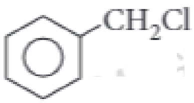
(c) 

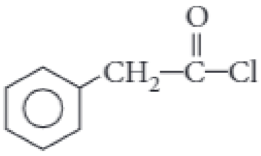
(d) 

(iii) Which one of the following will react fastest with aqueous NaOH?

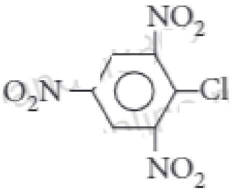
(a) 

(b) 

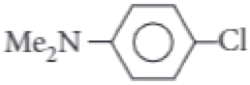
(c) 

(d) 

(iv) Which chloro derivative of benzene among the followings would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative?

(a) 

(b) 

(c) 

(d) C_6H_5Cl

OR

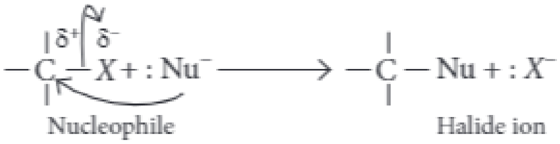
The reactivity of the compounds (i) MeBr, (ii) $PhCH_2Br$, (iii) MeCl, (iv) *p*-$MeOC_6H_4Br$ decreases as

(a) (i) > (ii) >(iii) > (iv)
(b) (iv) > (ii) >(i) > (iii)
(c) (iv) > (iii) >(i) > (ii)
(d) (ii) > (i) >(iii) > (iv)

Case Study 10

Read the passage given below and answer the following questions :

In haloalkanes, when a nucleophile stronger than the halide ion approaches the positively charged carbon atom of an alkyl halide, the halogen atom along with its bonding electron pair gets displaced and a new bond with the carbon and the nucleophile is formed. These reactions are called nucleophilic substitution reactions.



$$CH_3CH_2Br + \underset{\text{Nucleophile}}{OH^-} \longrightarrow CH_3CH_2OH + :Br^-$$

In these reactions the atom or group of atoms which loses its bond from carbon and takes on an additional pair of electrons is called leaving group. Halide ions are good leaving groups. Some important nucleophilic substitution reactions of haloalkanes with common nucleophiles are given in the table below.

	Reagent	Nucleophile (Nu^-)	Substitution product R — Nu	Class of main product
1.	NaOH or KOH or moist Ag_2O	^-OH	ROH	Alcohol
2.	H_2O	H_2O	ROH	Alcohol
3.	NaI	I^-	R — I	Alkyl iodide
4.	$R'NH_2$	$R'\ddot{N}H_2$	RNHR′	Sec. amine
5.	KCN	$\bar{C}{\equiv}N\colon$	RCN	Nitrile (cyanide)
6.	KNO_2	$O{=}N{-}O^-$	$R{-}O{-}N{=}O$	Alkyl nitrite

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Alkyl halides are hydrolysed to alcohols by moist silver oxide.
Reason : *R*Cl is hydrolysed to *R*OH easily but reactions slow down on addition of KI.

(ii) **Assertion :**Alkyl halides form alkenes when heated above 300°C.
Reason : CH_3CH_2I reacts slowly with strong base as compared to CD_3CH_2I.

(iii) **Assertion :***R*Br reacts with $AgNO_2$ to give nitroalkane.
Reason : Silver nitrite ($AgNO_2$) is an ionic compound, therefore the negative charge on nitrogen is the attacking site.

(iv) **Assertion :** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.
Reason : Vinyl group is electron donating group.

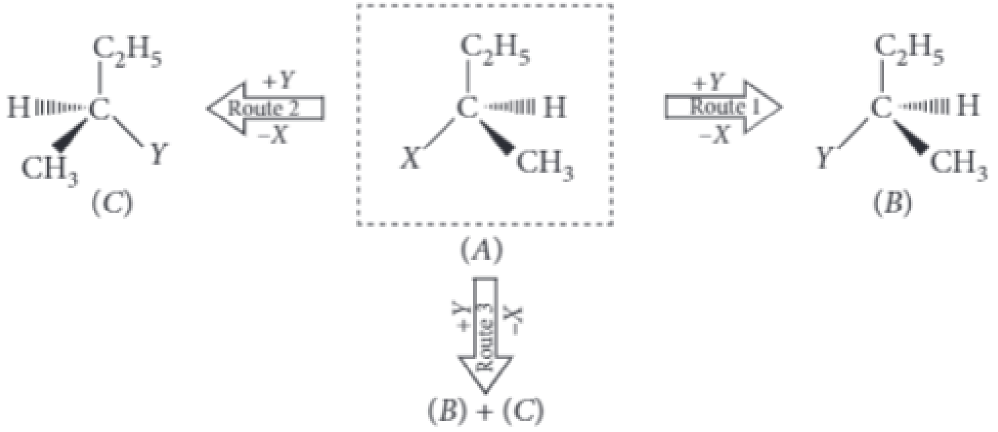
OR

Assertion : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as the major product.
Reason : 1-Butene is less stable than 2-butene.

Case Study 11

Read the passage given below and answer the following questions :

When a chemical reaction involves bond cleavage or bond formation at an asymmetric carbon atom, three different products may be formed. For example, during the substitution of a group *X* by *Y* in the following reaction, the three possible products may be shown below :



(i) If *B* is the only product, the process is called retention of configuration because *B* has the same configuration as the starting reactant (*A*).
(ii) If *C* is the only product, the process is called inversion of configuration because *C* has the configuration opposite to the starting reactant (*A*).
(iii) If an equimolar mixture of *B* and *C* (*i.e.*, a 50 : 50 mixture) is formed, then the process is called racemisation and the product is optically inactive because one isomer will rotate the light in the direction opposite to another.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** A reaction is said to be stereospecific if a particular stereoisomer of the reactant produces a specific stereoisomer of the product.
Reason : Bromination of *cis*-2-butene gives *meso*-2, 3-dibromobutane which is stereospecific.

(ii) **Assertion :** Addition of Br_2 to *cis*-but-2-ene is stereoselective.
Reason : S_N2 reactions are stereospecific as well as stereoselective.

(iii) **Assertion :** Optically active 2-iodobutane on treatment with NaI in acetone undergoes recemization.
Reason : Repeated Walden inversions on the reactant and its product eventually gives a racemic mixture.

(iv) **Assertion :** S_N2 reaction of an optically active alkyl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason : S_N2 reactions always proceed with inversion of configuration.

OR

Assertion : Nucleophilic substitution reaction of an optically active alkyl halide gives a mixture of enantiomers.
Reason : The reaction occurs by S_N1 mechanism.

Case Study 12

Read the passage given below and answer the following questions :

The order of reactivity towards S_N1 reaction depends upon the stability of carbocation in the first step. Greater the stability of the carbocation, greater will be its ease of formation from alkyl halide and hence faster will be the rate of the reaction. As we know, 3° carbocation is most stable, therefore, the *tert*-alkyl that halides will undergo S_N1 reaction very fast. For example, it has been observed that the reaction $(CH_3)_3CBr$ with OH^- ion to give 2-methyl-2-propanol is about 1 million times as fast as the corresponding reaction of the methyl bromide to give methanol.

The primary alkyl halides always react predominantly by S_N2 mechanism. On the other hand, the tertiary alkyl halides react predominantly by S_N1 mechanism. Secondary alkyl halides may react by either mechanism or by both the mechanisms without much preference depending upon the nature of the nucleophile and solvent.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Low concentration of nucleophile favours S_N1 mechanism.
Reason : 2° alkyl halides are less reactive than 1° towards S_N1 reactions.

(ii) **Assertion :** Polar solvent slows down S_N2 reactions.
Reason : CH_3–Br is less reactive than CH_3Cl.

(iii) **Assertion :** Benzyl bromide when kept in acetone- water it produces benzyl alcohol.
Reason : The reaction follows S_N2 mechanism.

(iv) **Assertion :** Rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason : Hydrolysis of methyl chloride follows second order kinetics.

OR

Assertion : S_N1 reaction is carried out in the presence of a polar protic solvent.
Reason : A polar protic solvent increases the stability of carbocation due to solvation.

Case Study 13

Read the passage given below and answer the following questions :

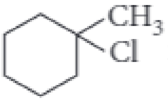
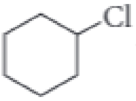
The aryl halides are relatively less reactive towards nucleophilic substitution reactions as compared to alkyl halides. This low reactivity can be attributed to the following factors :

- The C — *X* bond in halobenzene has a partial double bond character due to involvement of halogen electrons in resonance with benzene ring.
- The C — *X* bond in aryl halides is less polar as compared to that in alkyl halides as sp^2 hyridised carbon is more electronegative than sp^3 hybridised carbon.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Primary benzylic halides are more reactive than primary alkyl halides towards S_N1 reactions.
Reason : Reactivity depends upon the nature of the nucleophile and the solvent.

(ii) **Assertion :**  is more reactive than  towards nucleophilic substitution reactions.

Reason : Tertiary alkyl halides react predominantly by S_N1 mechanism.

(iii) **Assertion :** Chlorobenzene is more reactive than *p*-chloroanisole to nucleophilic substitution reactions.
Reason : Greater the stability of carbanion, greater is its ease of formation and hence, more reactive is the aryl halide.

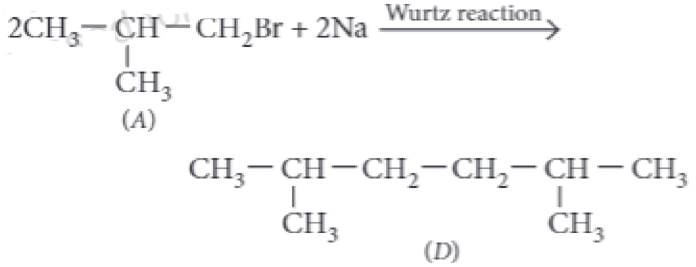
OR

Assertion : 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.
Reason : Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

(iv) **Assertion :** Chlorobenzene is less reactive than benzene towards the electrophilic substitution reaction.
Reason : Resonance destabilises the carbocation.

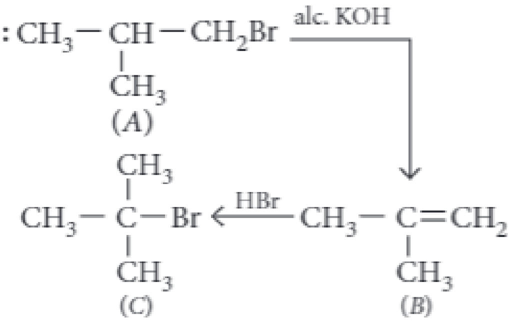
4. (i) (b): When compound (*A*) reacted with Na–metal, it gave a compound $D(C_8H_{18})$ which is different from the compound obtained when *n*-butyl bromide reacted with Na metal and hence the compound (*A*) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$



$$\underset{(A)}{2CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br} + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{(D)}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3}$$

(ii) (d):

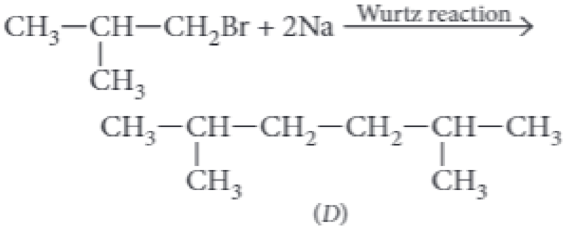


$$\underset{(A)}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br} \xrightarrow{\text{alc. KOH}} \underset{(B)}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2} \xrightarrow{HBr} \underset{(C)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-Br}$$

OR

(a)

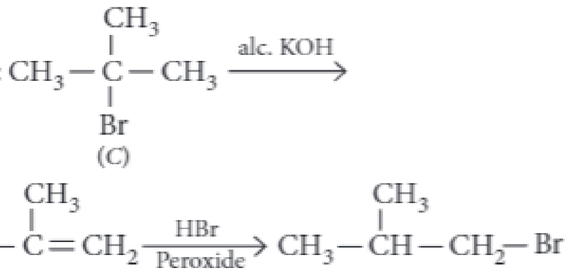
(iii) (b):



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br + 2Na \xrightarrow{\text{Wurtz reaction}} \underset{(D)}{CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3}$$

2,5-Dimethylhexane

(iv) (b):



$$\underset{(C)}{CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3} \xrightarrow{\text{alc. KOH}} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-Br$$

5. (i) (c) : Allylic chlorides are most reactive.

(ii) (c) : 2°- alkyl halides undergo hydrolysis by S_N1 or S_N2 mechanism.

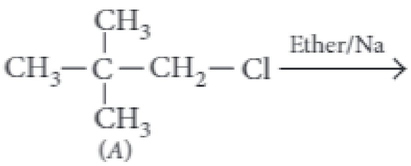
(iii) (a) : Smaller the size of the nucleophile (*i.e.*, CH_3O^-), more reactive it is.

(iv) (d) : Stearic hindrance due to bulky alkyl groups prevents the attack of the nucleophile in S_N2 mechanism.

OR

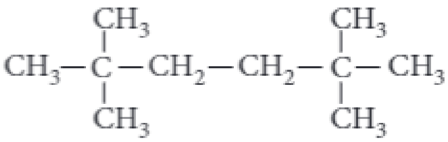
(a) : Larger the number of alkyl groups at α-carbon atom, more is the stearic hindrance and hence lesser the reactivity towards S_N2 mechanism.

6. (i) (a) :



$$\underset{(A)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-Cl} \xrightarrow{\text{Ether/Na}}$$

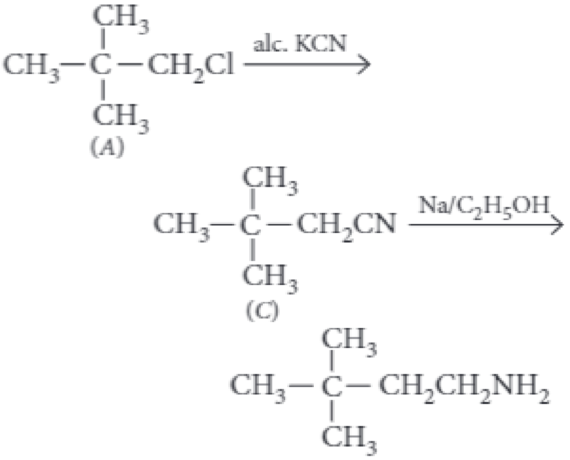
1-Chloro-2,2-dimethylpropane



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$$

2, 2, 5, 5- Tetramethylhexane

(ii) (c) :



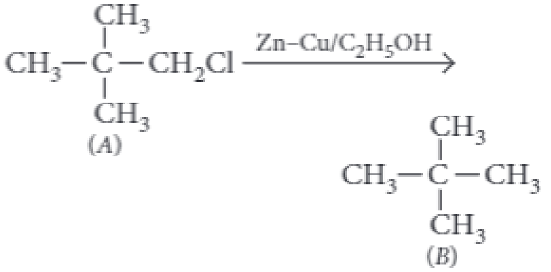
$$\underset{(A)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Cl} \xrightarrow{\text{alc. KCN}} \underset{(C)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CN} \xrightarrow{Na/C_2H_5OH} CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2CH_2NH_2$$

(iii) (b)

OR

(a)

(iv) (b):



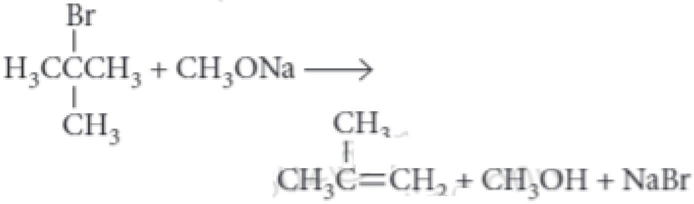
$$\underset{(A)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2Cl} \xrightarrow{Zn-Cu/C_2H_5OH} \underset{(B)}{CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3}$$

7. (i) (d): In alkyl halides, polarity of C – Br bond increases with increase in chain length.

(ii) (a): The order of reactivity of alkyl halides : iodide > bromide > chloride (nature of the halogen atom)

tertiary > secondary > primary (type of halogen atom).

(iii) (d) : *Iso*-butylene is obtained.



$$\mathrm{H_3C\overset{Br}{\underset{CH_3}{C}}CH_3 + CH_3ONa \longrightarrow CH_3\overset{CH_3}{C}{=}CH_2 + CH_3OH + NaBr}$$

(iv) (b): The order of bond dissociation energy : $R - F > R - Cl > R - Br > R - I$. During dehydrohalogenation C – I bond breaks more easily than C – F bond.

So reactivity order of halides

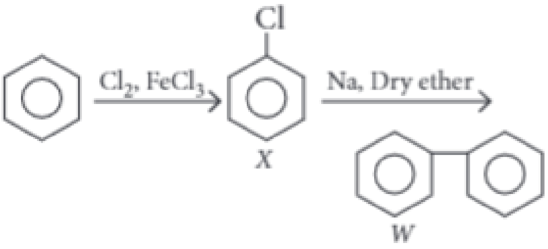
$R - I > R - Br > R - Cl > R - F$.

OR

(b) : The ease of dehydrohalogenation of alkyl halide with alcoholic KOH is 3° > 2° > 1°.

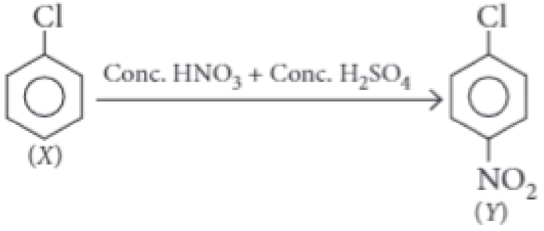
This order of alkyl halides can be explained on the basis of the stability of the alkene formed after dehydrohalogenation of haloalkanes. 3° alkyl halides on dehydrohalogenation forms more substituted alkenes, which being more stable and formed at faster rate, while primary alkyl halides yield least substituted alkenes, which being less stable and formed at slower rate.

8. **(i) (c) :**



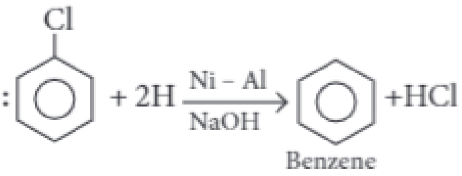
OR

(c) :



(ii) (d)

(iii) (a):

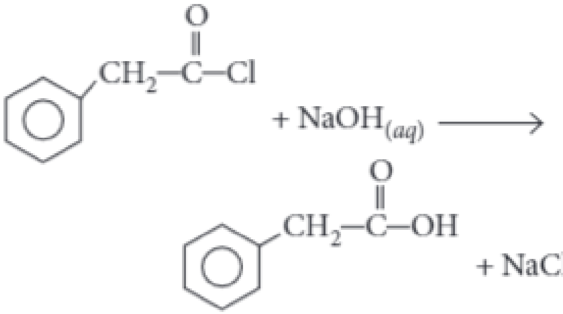


(iv) (c)

9. **(i) (b)**

(ii) (d): When in aryl halides the electron withdrawing groups are attached at ortho and para positions to the chlorine atom then the removal of chlorine atom as Cl− ion becomes easy, therefore, 2,4,6-trinitro chlorobenzene is the most reactive among given aryl halides.

(iii) (d):



(iv) (a): Cl in 2,4,6-trinitrochlorobenzene is activated by three NO_2 groups at *o*, and *p*-positions and hence undergoes hydrolysis most readily.

OR

(d) : The order of reactivity follows the sequence: benzyl halides > alkyl halides > aryl halides.

Out of chlorides and bromides, bromides are more reactive. Therefore, the correct order of reactivity is $PhCH_2Br(ii) > MeBr(i) > MeCl(iii) > p\text{-}MeOC_6H_4Br(iv)$

10. **(i) (c) :** KI reacts with *R*Cl to form *R*I. This *R*I molecule now hydrolysed easily to give *R*OH because alkyl iodide are more reactive than alkyl chloride. Thus, reaction becomes faster on addition of KI.

(ii) (c): CH_3CH_2I reacts more rapidly with strong base in comparison to CD_3CH_2I. The elimination of HI (or DI) in presence of strong base shows E_2 elimination. The rate determining step involves the breaking up of C — H (or C — D) bond. The C — D bond being stronger than C — H bond is difficult to break.

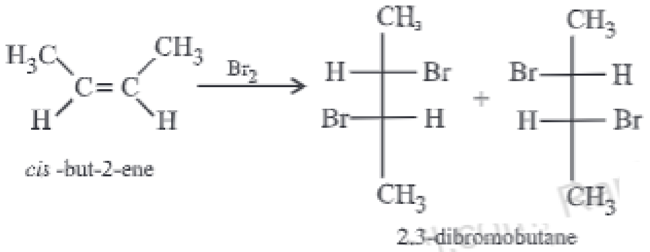
(iii) (c): Silver nitrite is a covalent compound and the bond between Ag — O is covalent. Therefore, it does not have a negative charge on the oxygen atom. Hence, the nucleophillic attack occurs through the lone pair on nitrogen forming nitroalkanes ($R - NO_2$).

(iv) (c): The carbon-halogen bond in vinyl halides has some double bond character and hence little difficult to break.

OR

(d): 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 2-butene as a major product.

11. **(i) (c) :** Bromination of *cis*-2-butene gives (±) 2,3-dibromobutane.



(ii) **(b)**

(iii) **(a)**

(iv) **(a)**

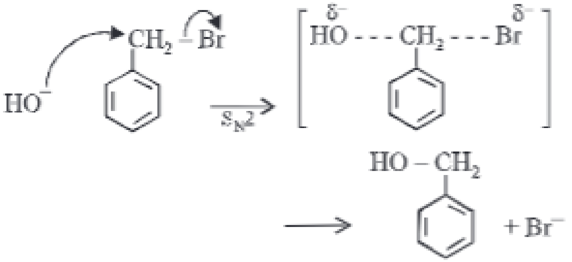
OR

(a) : In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. The carbocation formed is sp^2 hybridised and planar. The attack of the nucleophile may be accomplished from either side resulting in a mixture of products with opposite configuration *i.e.*, racemic mixture.

12. **(i) (c) :** Ability to accommodate a positive charge determines the ease of heterolysis leading to S_N1 mechanism. This ability to accommodate positive charge is more in the 2° alkyl halide since it has two alkyl groups as compared to one in 1° alkyl halide.

(ii) **(c) :** $CH_3—Br$ is more reactive than $CH_3—Cl$. The C — Br has bond dissociation energy of 293 kJ mol^{-1} while C — Cl bond has its dissociation energy of 351 kJ mol^{-1}. As the bond dissociation energy increases, the ease of breaking of C — *X* bond decreases and hence the reactivity of haloalkanes decreases.

(iii) **(a) : :**



(iv) **(a)**

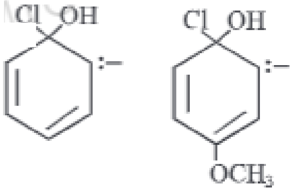
OR

(a)

13. **(i) (b):** Primary benzylic halides show higher reactivity in S_N1 reactions than primary alkyl halides. This is due to the greater stabilisation of the benzylic carbocation intermediates by resonance.

(ii) **(a)**

(iii) (a) : On comparing the relative stabilities of carbanion of chlorobenzene and *p*-chloroanisole,



the electron donating group (OCH_3) in anisole tends to intensify the negative charge relative to carbanion in chlorobenzene. Thus, *p*-chloroanisole is less reactive than chlorobenzene.

OR

(b) : As compared to chlorobenzene, the intermediate carbanion resulting from 4-nitrochlorobenzene is stabilized by –*R*-effect of the NO_2 group.

(iv) **(c) :** Chlorobenzene is less reactive than benzene towards the electrophilic substitution reactions due to –*I* effect.