Organic Compounds Containing Halogens

TOPIC 1 Haloalkane

01 In the following sequence of reactions, [2021, 01 Sep Shift-II]

 $C_{3}H_{6} \xrightarrow{H^{+}/H_{2}O} A \xrightarrow{KIO} B + C$

The compounds B and C respectively are (a)Cl₃COOK, HCOOH (b)Cl₃COOK,CH₃I (c)CH₃I,HCOOK (d)CHI₃, CH₃COOK

Ans. (d)

Propene (C₃H₆) undergoes acidic hydrolysis to give A which is 2° alcohol. This alcohol undergoes iodoform reaction in presence of KIO and dil. KOH to give iodoform alongwith potassium salt of carboxylic acid.

This reaction is known as iodoform test.





C₂H₅OH



Ans. (d)

In the given reaction E2 elimination reaction takes place in which two substituents are removed from a molecule to form double bond (alkene).



1-methyl cyclopent -1-3-diene (Major product)

03 The correct order of reactivity of the given chlorides with acetate in acetic acid is [2021, 31 Aug Shift-I]





Ans. (a)

The correct order of reactivity of chlorides with acetate in acetic acid is



The given chlorides undergoes $S_N 1$ reaction. So, as the stability of carbocation formed increases, rate of reaction increases.

Stability of carbocation is as follows





Ans. (b)

On reaction of haloalkane with methoxide ion, alkene is formed.



Mechanism



• OCH₃ will act as a base due to its small size and high electron density and therefore, abstracts proton to form double bond which is in conjugation with aromatic ring.

 The O CH₃ when acts as nucleophile undergoes nucleophilic substitution and replaces Br[⊖] to form ether, which is a minor product.





05 In the following sequence of reactions the *P* is [2021, 27 Aug Shift-I]



Ans. (a)

In the first step, Grignard reagent is obtained. In the second step, acid-base reaction occurs. Due to presence of an acidic hydrogen in alcohol, neutralisation reaction takes place that produces alkane and water. The reaction is



06 The major product formed in the following reaction is [2021, 26 Aug Shift-I]







This addition is known as 1, 4-addition. Mechanism This reaction can undergoes two pathways





Out of the two intermediates formed in two paths, the path *B* intermediate is more stable as it has more stable carbocation. So, major product will be formed because of path *B*.



1, 2-addition Br⊖



1, 2-addition product is formed at low temperature and will be less stable as double bond is less substituted. 1, 4-addition is thermodynamically stable product as double bond is more substituted. As diene is in excess and HBr is limited in reaction, so diene cannot be formed. So option (b) is incorrect.

07 Excess of isobutane on reaction with Br₂ in presence of light at 125°C gives which one of the following, as the major product? [2021, 26 Aug Shift-I]



Ans. (d)

Excess of isobutane reacts with Br_2 in presence of light at 125°C gives 2-bromo-2-methyl propane as major product.



Mechanism The above reaction is halogenation of alkane *via* free radical substitution reaction. Initiation step

 $Br_2 \xrightarrow{hv} Br^{\bullet} + Br^{\bullet}$

Propagation step





Termination step





Reactivity order of abstraction of H towards bromination of alkane as more stable alkyl free radical is formed as follows

3°H > 2°H > 1°H Since, isobutane is in excess, so dibromination of single isobutane is not favourable reaction. This make (a) and (b) incorrect options.

08 Reaction of Grignard reagent,

 $C_{2}H_{5}MgBr$ with $C_{8}H_{8}O$ followed by hydrolysis gives compound 'A' which reacts instantly with Lucas reagent to give compound *B*, $C_{10}H_{13}CI$.

The compound B is [2021, 18 March Shift-I]



Ans. (c)

Reaction of Grignard reagent, C_2H_5MgBr with C_8H_80 followed by hydrolysis gives compound A, which reacts instantly with Lucas reagent to give compound B, $C_{10}H_{13}CI$. It will show instant turbidity. Step (i) $C_8H_80 \xrightarrow[H^+]{H^+} (A)$ Step (ii) (A) $\xrightarrow[Lucas reagent]{Lucas reagent} (B) C_{10}H_{13}CI$ Complete reaction is as follows



Ans. (d)

Alkene undergoes electrophilic addition with HBr to give a major product by Markownikoff rule by S_N 1 mechanism. **Step 1.** Addition of electrophile to form carbocation.



2° carbocation undergoes methyl shift to form more stable 3° carbocation.



Step 2. Attack of nucleophile on carbocation.



Ċl Identify the reagent(s) 'A' and condition(s) for the reaction: [2021, 16 March Shift-II]

(a) A = HCI, anhydrous AICI₃ (b) A = HCI, ZnCl₂

(c) $A = Cl_2$, UV light

(d) $A = Cl_2$, dark, anhydrous $AlCl_3$

Ans. (c)

The reaction can be achieved by $\rm Cl_2$ /UV light (A). Given, reaction follows free radical substitution mechanism.



1, 4-dichloro cyclohexene

Mechanism

(I) Initiation : This involves formation of radicals.

 (II) Propagation : Reactive free radicals react with stable molecules to form new free radicals.

$$C|^{\bullet} + \bigcup_{(M_{n+1}, \dots, n+k) \in \mathbb{Z}} + HC|$$





CI

Similarly second Cl atom is also attached at allylic position.







The product A and B formed in above reactions are



Ans. (c)

Alcohols undergo dehydration (removal of water molecule) in the presence of protic acids (conc. H_2SO_4 , H_3PO_4) at high temperature to give Saytzeff alkene (more alkylated) as major product.



Bulky bases like tert-butoxide, due to steric hindrance, a bulky base abstracts a less hindered proton, that leads to formation of the less substituted product as, the major one, called the Hofmann product.



12 Identify A and B in the chemical reaction. [2021, 25 Feb Shift-I] OCH₃





Ist reaction is Markownikoff's addition of HCI on double bond while 2nd reaction is halide substitution by Finkelstein reaction in which chlorine get displaced by iodine.



Ans. (d)

Here, in first step only one mole of Mg/Et₂O attacks on bromine and form two 2MgBr in the first step.



On further moving in the reaction, two MgBr are eliminated to form alkene in respective positions.

14 What is the major product formed by HI on reaction with



(c)
$$CH_3 \longrightarrow CH_3 - CH_2 - CH_3$$

(d) $CH_3 \longrightarrow CH_3 - CH_3 -$

Ans. (b)

The major product formed is 2-iodo-2, 3-dimethylbutane. Steps involved in the reaction are as follows :

Step 1 It is electrophilic addition reaction, π -bond of alkene attack H⁺ ion of HI and form more stable carbocation.

Step 2 Formation of more stable 3° carbocation take place by 1, 2 shifting of —Me group.

Step 3 Direct addition of I^{\ominus} ion . Mechanism



15 Which of the following compounds will form the precipitate with aq. AgNO₃ solution most readily? [2020, 4 Sep Shift-II]





Ans. (b)

All given species in the question are alkyl halide. They react with aqueous $AgNO_3$ solution with different rate.

Reaction undergoes as follows:

$$R \longrightarrow X + \operatorname{AgNO}_{3}(aq) \xrightarrow{\operatorname{RDS}} R^{+} + \operatorname{AgX}_{\operatorname{Precipitate}}$$

Hence, rate precipitate formation of AgX depends on stability of carbocation $(R^{+}).$

In the given question all formed carbocation will be



carbocation (a) is most stable due to



precipitate with aqueous AgNO₃ solution most readily.

16 Which of the following compounds will show retention in configuration on nucleophilic substitution by OH⁻ ion? [2020, 2 Sep Shift-I]

(a)
$$CH_3 - CH - Br \\ C_6H_5$$

(b) $CH_3 - CH - CH_2Br \\ C_2H_5$
(c) $CH_3 - CH - Br \\ CH_3$



Ans. (b)

In (a) and (d), carbon atoms bearing the leaving group (Br atom) are chiral. So, their configurational change will take place with OH⁻ ion by $S_N 2 \text{ or } S_N 1$ pathway.

 $\stackrel{\text{le}}{\xrightarrow{}} Br \qquad \stackrel{\text{Me}}{\xrightarrow{}} Br \qquad Br$

In (c), $(CH_3)_2$ CH—Br does not have any chiral centre. So, no comment on configuration will arise with (c).

In option (b), the α -carbon (with respect to —CH₂Br with which S_N2 reaction will take place) is only chiral. This α -carbon remains unaffected in S_N2 pathway. So, it will show retention in configuration.

17 Consider the reaction sequence given below :



Which of the following statements is true?

[2020, 2 Sep Shift-II]

- (a) Changing the base from OH[⊖] to [⊖]OR will have no effect on reaction (2)
- (b) Changing the concentration of base will have no effect on reaction (1)
- (c) Doubling the concentration of base will double the rate of both the reactions
- (d) Changing the concentration of base will have no effect on reaction (2)

Ans. (b)

Reaction (1)

Rate = k[t-BuBr], it is a first order nucleophilic substitution reaction (S_N 1), so, rate of this reaction will depend only on the concentration of the substrate, i.e. t-BuBr.

So, option (b) is correct, but option (c) is not correct.



Reaction (2)

Rate = k[t-ByBr][OH⁻], it is a second (base)

order α , β -elimination reaction (E₂), because t-BuBr undergoes dehydrohalogenation (—HBr) with a strong base (alcoholic or ethanolic OH⁻) to give an alkene. So, rate of the reaction depends on concentrations of substrate (t-ByBr) and base (OH/alc.). So, option (a) is not correct.

 ${O}R$ is a stronger base than ${O}H$. So, use of

 ${OR}$ will make the ${E}_2$ reaction faster.

Hence, option (a) is also not correct.

18 The total number of

monohalogenated organic products in the following (including stereoisomers) reaction is

 $\begin{array}{c} A \\ \text{(Simplest optically} \\ \text{active alkene)} \end{array} \xrightarrow{(i) H_2/Ni/\Delta} \\ \text{(ii) } X_2/\Delta \end{array}$

[2020, 3 Sep Shift-I]

Ans. (8.00)

$$\begin{array}{c} \mathsf{CH}_{3}\mathsf{CH}_{2} - \underbrace{\mathsf{CH}}_{|} - \underbrace{\mathsf{CH}}_{|} = \operatorname{CH}_{2} \xrightarrow{(i)\mathsf{H}_{2} / \mathsf{Ni}/\Delta}_{(ii) X_{2} / \Delta} \\ & \mathsf{CH}_{3}_{(A)} \end{array}$$

(Simplest optically active alkene)



In the reaction, total number of monohalogenated products (including stereoisomers)

P = 2, Q = 4, R = 1, S = 1, i.e. Total = 8

19 The mechanism of S_N 1 reaction is

given as :

$$R \longrightarrow X \longrightarrow R^{\bigoplus} X^{\ominus} \rightarrow R^{\bigoplus} || X^{\ominus}$$

$$\stackrel{\text{Solvent}}{\underset{pair}{Y^{\ominus}}} R \xrightarrow{Y^{\ominus}} R \xrightarrow{Y^{+}} Y + X^{\ominus}$$

A student writes general characteristics based on the given mechanism as :

- (A) The reaction is favoured by weak nucleophiles.
- (B) R^{\oplus} would be easily formed if the substituents are bulky.
- (C) The reaction is accompanied by recemisation.
- (D) The reaction is favoured by non-polar solvents.
- Which observations are correct? [2020, 3 Sep Shift-I]

$\Delta ns(c)$	
c)(A),(B)and(C)	(d)(B)and(D)
a)(A)and(B)	(b)(A)and(C)

$$R \longrightarrow \overset{\oplus}{R} X^{\ominus} \longrightarrow \overset{\oplus}{R} || X^{\ominus} \xrightarrow{Y^{\ominus}} R \longrightarrow \overset{\oplus}{R} || X^{\ominus} \xrightarrow{Y^{\ominus}} X^{\ominus} \longrightarrow R \longrightarrow Y + X^{\Theta}$$

It indicates R^{\oplus} (carbocation) formation takes place and R^{\oplus} got stabilised by electronic factors and polar solvent molecules because solvent separation of R^{\oplus} is possible.

So, statement (D) is not correct.

Here, X^{\ominus} (leaving group) of R - X is substituted by Y^{\ominus} , (nucleophile) via the formation of carbocation (R^{\oplus}) intermediate. So, it is an S_N 1reaction. S_N 1mechanism supports weaker nucleophiles. So, statement (A) is correct.

S_N1reaction is accompanied by inversion and retention in configuration, i.e. racemisation provided '*R*' of *R*—X is chiral. So, statement (C) is correct.

Attachment of bulkier substituents or 3° -nature of the carbon atom of C—X bond of R—X will favour formation of R^{\oplus} (carbocation). So, statement (B) is also correct.

20 The major product in the following reaction is







Ans. (b)

Complete reaction is as follows :



More substituted Alkene (major)

> The alkene formed is stable according to Saytzeff's rule. It states that alkenes with less number of hydrogen on the double bonded carbon atoms are preffered product.

21 The decreasing order of reactivity of the following organic molecules towards AgNO₃ solution is [2020, 4 Sep Shift-I]

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

(a) (A)>(B)>(C)>(D) (b) (C)>(D)>(A)>(B) (c) (B)>(A)>(C)>(D)

(d) (A) > (B) > (D) > (C)

Ans. (c)

 $\begin{array}{l} \mbox{General reaction}: \\ \mbox{AgNO}_3 + X(Halogen) \longrightarrow \mbox{Ag}X + NO_3^2 \\ \mbox{It follows} \, S_N \mbox{1reaction}. \\ \mbox{In} \, S_N \mbox{1reaction}, \\ \mbox{Rate of reaction} \propto \mbox{stability of} \\ \mbox{carbocation} \end{array}$



Stability of carbocation is (ii)>(i)>(iii)> (iv).

So, the reactivity order towards $AgNO_3$ solution is (B)>(A)>(C)>(D).

22 Among the following compounds, which one has the shortest C–Cl bond? [2020, 4 Sep Shift-II]



Ans. (b)

In option (c) vinyl chloride, C—Cl bond is shortest due to resonance of lone pair of — Cl(chlorine atom).

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Due to resonance C — Cl bond aquire partial double bond character.

Hence, vinyl chloride have least C — Cl bond length.



23 The major product formed in the following reaction is

 $CH_{3}CH = CHCH(CH_{3})_{2} \xrightarrow{HBr}$ [2020, 5 Sep Shift-II]

(a) $CH_3CH(Br)CH_2CH(CH_3)_2$ (b) $CH_3CH_2CH(Br)CH(CH_3)_2$ (c) $Br(CH_2)_3CH(CH_3)_2$ (d) $CH_3CH_2CH_2C(Br)(CH_3)_2$ **Ans.** (d)

$$\begin{array}{c} \mathsf{CH}_{3} - \mathsf{CH} = & \mathsf{CH} - & \mathsf{CH} - & \mathsf{CH}_{3} \xrightarrow{\mathsf{HBr}} \\ & \mathsf{CH}_{3} & \xrightarrow{\mathsf{CH}_{3}} \\ & \mathsf{CH}_{3} - & \mathsf{CH}_{2} - & \overset{\oplus}{\mathsf{CH}_{3}} \\ & & \mathsf{CH}_{3} \end{array}$$

1, 2–H shift (for more stable carbon cation)



24 The increasing order of the boiling points of the major products *A*, *B* and *C* of the following reactions will be [2020, 6 Sep Shift-II]



Ans. (a)

Complete reaction of I, II and III are as follow:



RX are polar, therefore intermolecular forces of attraction (e.g., dipole-dipole and van der Waals') are stronger in *RX*.

Hence, the boiling point of *RX* is greater than those of hydrocarbons of comparable molecular masses.

Branching decreases the surface area as in alkane because the branched *C* chains are more spherical -like, which results in lower boiling point.

Hence, the boiling point of isomeric RX decreases with increase in branching, hence the order will be B < C < A.

25 1-methyl ethylene oxide when treated with an excess of HBr produces : [2020, 7 Jan Shift-I]



Ans. (a)

The given reaction is completed as follows :





26 For the following reactions :



(a) $\mu_B > \mu_A$ and $k_e(B) > k_e(A)$ (b) $\mu_B > \mu_A$ and $k_e(A) > k_e(B)$ (c) $\mu_A > \mu_B$ and $k_e(A) > k_e(B)$ (d) $\mu_A > \mu_B$ and $k_e(B) > k_e(A)$

Ans. (d)



When alkyl halides react with nucleophiles (*Z*⁻), both substitution and elimination reactions can be expected. 1° alkyl halides generally favour substitution, but stronger bases favour elimination. So, in the above reactions in which (CH₃—CH₂—CH₂—Br is 1° alkyl halide, CH₃CH₂—O⁻ is a strong base), reasonable amounts of substitution and elimination products can form between $A = CH_3CH_2O^-$ and alkyl halide.

(A) is an unhindered nucleophile, so it can give substitution better than (B) which is hindered (more crowded or sterically hindered). But (B) tends to give elimination better than (A) due to the same reason also.

$$\therefore \qquad \mu = \frac{\kappa_s}{k_e} \text{ is in the order } A > B$$

and k_e is in the order B > A.

27 The decreasing order of reactivity towards dehydrohalogenation (*E*₁) reaction of the following compounds is : **[2020, 8 Jan Shift-I]**



(a) B > A > D > C (b) B > D > A > C (c) D > B > C > A (d) B > D > C > A

Ans. (c)

 E_1 reaction proceeds *via* carbocation formation, therefore greater the stability of carbocation faster is the reaction. Carbocation formed by *D*, (2°, resonance stabilised the product is diene) is most stable followed by *B*, (1° and the product formed is diene). Further among *C* and *A*, the carbocation formed by *C* is more stable (2°) than *A*, (1°). Thus, the reactivity towards dehydrohalogenation follows the order :

D > B > C > A

28 Which of the following reactions will not produce a racemic product? [2020, 9 Jan Shift-I



Ans. (d)

Reaction (d) will not produce a racemic product whereas other reactions will form racemic mixture.



There is no chiral carbon atom present in the product.

.. Product would not be a racemic mixture.



(a) $CI = CII_2$ (b) H_2N — $CH = CH_2$ (c) CH_3O — $CH = CH_2$ (d) F_3C — $CH = CH_2$

Ans. (d)

Attachment of electron donating group (+ R or + I) with sp²-carbon of an unsymmetrical alkene supports Markownikov's addition rule through electrophilic-addition-pathway.

But, attachment of electron-withdrawing group (-R or -I) for the same will follow anti-Markownikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway. The product formed by given alkenes when treated with HCI.



Similarly,

30 The major product of the following reaction is



Ans. (c)

In the given question, the substrate is a 2° -halide (bromide) and the medium, CH₃OH(as well as a poor nucleophile) is protic in nature, So, the reaction will follow mainly S_N1pathways via the formation of a carbocation intermediate (I).



The intermediate, I can be rearranged into the more stable form I'(3°) by α -hydride shift. I 'will give the major product.



(2° carbocation)



31 The major product Y in the following reaction is



[2019, 10 April Shift-II]



Ans. (b)

The given reaction takes place as follows :



2-bromo-3-methyl 2-bromo-2-methyl butane(minor) butane(major)(Y)

32 The major product obtained in the given reaction is

CH-CI





Ans. (c)

The given reaction takes place as follows :



33 Heating of 2-chloro-1-phenyl butane with EtOK/EtOH gives X as the major product. Reaction of X with Hg(OAc)₂ / H₂O followed by NaBH₄ gives \overline{Y} as the major product. Y is [2019, 12 April Shift-II]



Ans. (c)

Heating of 2-chloro-1-phenylbutane with EtOK/EtOH gives 1-phenyl but-1-ene(X). Reaction of X with Hg(OAc)₂ /H₂O followed by NaBH₄ gives 1-phenyl butan-1-ol (Y). Reaction involved is as follows :





Ph



34 An Assertion and a Reason are given below. Choose the correct answer from the following options. [2019, 12 April Shift-II]

 $C_{2}H_{5}(Y)$

Assertion (A) Vinyl halides do not undergo nucleophilic substitution easily.

Reason(R) Even though the intermediate carbocation is stabilised by loosely held π -electrons, the cleavage is difficult because of strong bonding.

- (a) Both (A) and (R) are wrong statements.
- (b) Both (A) and (R) are correct statements and (R) is correct explanation of (A).
- (c) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A).
- (d) (A) is a correct statement but (R) is a wrong statement.

Ans. (c)

Vinyl halide (CH₂ == CH---Cl) do not undergo nucleophilic substitution reactions. This is because it forms highly unstable carbocation

 $(CH_2 = \overset{\oplus}{C}H)$. It cannot delocalise its

 π -electron. In vinyl halide C–Cl bond possess double bond character also.

$$\overbrace{CH_2}^{\checkmark} = CH \checkmark \overbrace{CH}^{\circ} \leftarrow \rightarrow \stackrel{\circ}{CH_2} - CH = \stackrel{\circ}{CH_2}$$

35 The major product of the following reaction is



Ans. (d)

It is a simple case of Markownikoff addition. The reaction proceeds as :



The structure of options given may confuse an aspirant with ring expansion but that is seen as the minor product only [Due to the formation of a 3° stable carbocation in the process] the major product is



36 The major product of the following reaction is [2019, 12 Jan Shift-II]

 $H_{3}C \longrightarrow CH_{2}CH_{3}$ $H_{3}C \longrightarrow CI \xrightarrow{Na0Et}{\Delta}$ $(a) CH_{3}CH_{2}C = CH_{2}$ $CO_{2}CH_{2}CH_{3}$ $(b) CO_{2}CH_{2}CH_{3}$ $CH_{3}C = CHCH_{3}$ $CH_{3}C = CHCH_{3}$ $(c) H_{3}C \longrightarrow C \xrightarrow{CH_{2}CH_{3}}{COOCH_{2}CH_{3}}$ $(c) H_{3}C \longrightarrow C \xrightarrow{CH_{2}CH_{3}}{COOCH_{2}CH_{3}}$ $(d) H_{3}CH_{2}C \longrightarrow C \xrightarrow{C}{C} \xrightarrow{CO_{2}CH_{2}CH_{3}}{CH_{3}}$

Ans. (b)

Presence of strong base (EtO⁻) and heat indicates elimination.

Thus, the compound undergo dehydrohalogenation and alkene is

produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:

(i) $CH_3CH_2 C = CH_2$

 $\dot{C}OOCH_2CH_3$ (ii) $CH_2CH = C - CH_3$

In accordance with Saytzeff rule

 $CH_3CH = C - CH_3$ | $COOCH_2CH_3$

will be the major product.

37 Which hydrogen in compound (*E*) is easily replaceable during bromination reaction in presence of light?

$$\begin{array}{c} CH_{3} - CH_{2} - CH = CH_{2} \\ \delta & \gamma & \beta & \alpha \end{array}$$
(E)
(a) β -hydrogen
(b) δ -hydrogen

(c) γ-hydrogen

(d) α-hydrogen **[2019, 10 Jan Shift-I]**

Ans. (c)

The compound (*E*) has two allyl-hydrogen atoms (γ). When *E* reacts with Br₂ /*h*v, it readily undergoes allylic free radical substitution and forms 3, 3-dibromobut-1-ene

$$\begin{array}{c} \overset{\delta}{\mathsf{C}}\mathsf{H}_{3} & \overset{\gamma}{-} \overset{\beta}{\mathsf{C}}\mathsf{H}_{2} & \overset{\beta}{-} \mathsf{C}\mathsf{H}_{2} & \overset{\beta}{-} \overset{\mathsf{Br}_{2}/h_{V}}{} \\ \overset{\mathsf{But-l-ene}}{\mathsf{Br}} & \overset{\mathsf{H}_{2}}{-} \overset{-}{} \overset{\mathsf{H}\mathsf{Br}}{\mathsf{H}} \\ \overset{\mathsf{G}}{\mathsf{C}} & \mathsf{H}_{3} & \overset{\mathsf{G}}{-} \overset{\mathsf{C}}{\mathsf{C}}\mathsf{H} & \overset{\mathsf{G}}{-} \overset{\mathsf{C}}{\mathsf{C}}\mathsf{H} \\ \overset{\mathsf{G}}{} \overset{\mathsf{G}}{\mathsf{H}}_{3} & \overset{\mathsf{G}}{-} \overset{\mathsf{C}}{\mathsf{C}}\mathsf{H} & \overset{\mathsf{G}}{-} \overset{\mathsf{G}}{\mathsf{C}} \mathsf{H}_{2} \\ \overset{\mathsf{G}}{} \overset{\mathsf{G}}{\mathsf{J}} \overset{\mathsf{G}}{-} \overset{\mathsf{G}}{\mathsf{C}}\mathsf{H}_{3} & \overset{\mathsf{G}}{-} \overset{\mathsf{G}}{\mathsf{C}}\mathsf{H}_{3} \end{array}$$

$$\xrightarrow{\text{Br}_2/h_V}_{-\text{HBr}} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}_3} \xrightarrow{\text{L}_{\gamma}}_{I_{\gamma}} \xrightarrow{\text{CH}}_{\beta} \xrightarrow{\text{CH}}_{\alpha} \xrightarrow{\text{CH}}_{\gamma}$$

3,3- dibromobut-1-ene



Ans. (b)

Complete reaction can be represented as



Thus, the given reaction is dehydrohalogenation which is a β -elimination proceeding through $E_{\rm 2}$ mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H atoms.



39 The increasing order of reactivity of the following halides for the S_N^1 reaction is

I. CH₃CH(CI)CH₂CH₃

III.
$$p - H_3CO - C_6H_4 - CH_2CI$$

[JEE Main 2017]

(b)(II)<(I)<(III) (d)(II)<(III)<(I)

Ans. (d)

(a)(|||)<(||)<(|)

(C)(|) < (||) < (||)

- (i) The rate of S_N 1reaction depends only upon the concentration of the alkyl halide.
- (ii) S_N1reaction proceeds through the formation of carbocation.

The reactivity is decided by ease of dissociation of alkyl halide.

 $R \longrightarrow R^{\oplus} + X^{\ominus}$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N 1 reaction.

 $p - H_3CO - C_6H_4 - CH_2^{\oplus}$ is the most

stable carbocation due to resonance and then $CH_3 CHCH_2 CH_3 (2^{\circ} carbocation)$

while $CH_3CH_2CH_2(1^\circ)$ is least stable.

Thus, the correct increasing order of the reactivity of the given halides towards the S_N 1reaction is

$$\begin{array}{c} \operatorname{CH_3CH_2CH_2CI} < \operatorname{CH_3CH_2CH_2CH_3} \\ | \\ (II) \\ (II) \\ < p - \operatorname{CH_3CO} - \operatorname{C_6H_4} - \operatorname{CH_2CI} \\ (III) \\ (III) \end{array}$$

40 Which of the following, upon treatment with *tert*-BuONa followed by addition of bromine water, fails to decolourise the colour of bromine ? [JEE Main 2017]



Ans. (a)

To show decolourisation, compound must be unsaturated.



41 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is [JEE Main 2017]

(a) six
(b) Zero
(c) two
(d) four

Ans. (d)

The number of stereoisomers in molecules which are not divisible into two equal halves and have n number of asymmetric C-atoms $= 2^n$.

3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e.

2-bromo-3-methyl pentane. It has two chiral centres. Therefore, 4 stereoisomers are possible



Anti-Markownikoff's addition Four stereoisomers are possible (As molecule has two chiral centres and asymmetric).

42 The major product obtained in the following reaction is **[JEE Main 2017]**

 $\begin{aligned} &(a)(\pm) \, C_6 \, H_5 CH(O^t Bu) CH_2 C_6 H_5 \\ &(b) \, C_6 \, H_5 CH = \, CH C_6 \, H_5 \\ &(c)(+) \, C_6 H_5 CH(O^t Bu) CH_2 C_6 H_5 \\ &(d)(-) C_6 \, H_5 CH(O^t Bu) CH_2 C_6 \, H_5 \end{aligned}$

Ans. (b)

An alkyl halide in presence of a bulkier base removes a proton from a carbon adjacent to the carbon bonded to the halogen. This reaction is called E2 (β -elimination reaction).



43 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields [JEE Main 2016]



$$\begin{array}{c} \text{III. C}_2\text{H}_5\text{CH} = \begin{array}{c} \text{C} - \begin{array}{c} \text{CH}_3 \end{array} \\ \\ \text{CH}_3 \end{array}$$

(a) Both I and III(b) Only III(c) Both I and II(d) All of the above

Ans. (d)

Strong nucleophile (\overline{O} Me) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



(More yield) **44** The synthesis of alkyl fluorides is

best accomplished by

[JEE Main 2015]

CH3

(a) free radical fluorination(b) Sandmeyer's reaction(c) Finkelstein reaction(d) Swarts reaction

Ans. (d)

CH-

Alkyl fluorides can be prepared by action of mercurous fluoride or antimony trifluorides (inorganic fluorides) on corresponding alkyl halide. This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$

Methyl fluoride But, when action of Nal/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called 'Finkelstein reaction'.

$$C_2H_5CI \xrightarrow{Nal} C_2H_5I + NaCI$$

Free radical fluorination is highly explosive reaction. so not preferred for the preparation of fluoride.

45 How many chiral compounds are possible on monochlorination of 2-methyl butane? [AIEEE 2012] (a) 8 (b) 2 (c) 4 (d) 6

Ans. (b)

2-methylbutane an monochlorination gives 4 isomers, among which I and III are chiral in nature.

$$\begin{array}{c} CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{3} \longrightarrow CH_{3$$

Hence, 2 chiral compounds are formed in the above reaction.

46 Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide? [AIEEE 2012]

- (a) Tertiary butyl chloride
- (b) Neopentane
- (c) Isohexane
- (d) Neohexane

Ans. (b)

Molar mass = $72 = C_n H_{2n+2}$ = 12n + (2n + 2)n = 5

Thus, hydrocarbon is $C_5 H_{12}$. Since, it gives only single $C_5H_{11}CI$, This suggests that C_5H_{12} is symmetrical. Hence, it is containing all 12 equivalent H-atoms.



47 Consider the following bromides,



The correct order of S_N1reactivity is

Ans. (a)	
(c)(C)>(B)>(A)	(d)(A)>(B)>(C)
(a) (B)>(C)>(A)	(b)(B)>(A)>(C)

The reactivity of S_N 1 reaction depends upon the stability of the intermediate, carbocation formed during these reactions. The stabililty order of the carbocation formed from the given species is

Allylic carbocation (stabilises through resonance due to conjugution)

Me 2°carbocation (stabilises by hyperconjugation due to 6 α -H atoms)

Me

1°carbocation (stablises by hyperconjugation due to 2 α -H-atoms)

Hence, the reactivity order of the given bromide towards S_N 1 reaction is



48 The organic chloro compound, which shows complete stereochemical inversion during an $S_N 2$ reaction is [AIEEE 2008]

(a) (C₂H₅)₂ CHCI (b) (CH₃)₃ CCI (c) (CH₃)₂CHCI (d) CH₃CI

Ans. (d)

Nucleophilic substitution bimolecular (S_N2) prefers less sterically hindered site to attack. Lesser the steric hindrance faster the $S_N 2$ reaction. So ease of reaction is $1^{\circ} > 2^{\circ} > 3^{\circ}$.



 $S_N 2$ involves inversion of configuration stereo, chemically.

Since, 1° alkyl halides are prone to S_N2 reactions, therefore CH₃Cl undergoes complete strerochemical inversion.

- 49 Which of the following reactions will yield 2, 2-dibromopropane? [AIEEE 2007]
 - (a) $CH_3 \longrightarrow C \Longrightarrow CH + 2HBr \longrightarrow$
 - (b) $CH_3CH = CHBr + HBr \longrightarrow$
 - (c) $CH \equiv CH + 2HBr \longrightarrow$
 - (d) $CH_3 \longrightarrow CH \Longrightarrow CH_2 + HBr \longrightarrow$

Ans. (d)

(a)
$$CH_3 - C \equiv CH + HBr$$

 $\rightarrow CH_3 - C \equiv CH_2$
Br
 $\downarrow H^+$
 $\begin{pmatrix} Rearrangement \\ (Hydride transfer) \\ H_3C - CH_4 \\ H_7 \\ H_7$

50 HBr reacts with CH₂=CH—OCH₃ under anhydrous conditions at room temperature to give (a) CH₃CHO and CH₃Br [AIEEE 2006] (b) BrCH₂CHO and CH₃OH (c) $BrCH_2$ — CH_2 — OCH_3 (d) H₃C—CHBr—OCH₃ Ans. (d)

$$CH_2 = CH_OCH_3 \xrightarrow{HBr}$$

 $CH_3 \xrightarrow{CH}OCH_3$
 H
Br
First protonation occurs, two possible

intermediates are - CH → OCH

(-/ effect destabilises carbocation)

and CH₃—CH—O CH₃ (||) 📐

(+ M effect stabilises carbocation) II, is more favourable. Hence, Br^{\ominus} attacks and product is





Ans. (c)

In presence of Lewis acid, electrophilic halogenation reaction takes place at meta position to give



54 Among the following compounds I-IV, which one forms a yellow precipitate on reacting sequentially with (i)NaOH (ii) dil. HNO₃

[2021, 26 Aug Shift-I] ĊH₃ Br .CI CH₃ CH₂I Ш IV (b)IV (c)| (d) ||| (a)II



CH₂OH+Nal CH₂I

This compound halide will only give yellow ppt. as benzyl carbocation formed shown below is highly stable by conjugation.



Other compounds halide cannot be removed because their corresponding carbocation is highly unstable.



The given reaction can occur in the presence of (A) bromine water (B) Br₂ in CS₂ 273 K (C) Br₂ / FeBr₃ (D) Br₂ in CHCl₃, 273 K Choose the correct answer from the options given below [2021, 22 July Shift-I] (a)(B) and (D) only (b)(A) and (C) only

(c)(B),(C) and (D) only (d)(A), (B) and (D) only

Ans. (c)

Only bromine water gives tribromo products, while all other gives monobromo products in which para bromo is major product.



When phenol reacts with bromine in the presence of CS_2 , FeBr₃, CHCl₃0, it results in the formation of two products. The products is *ortho* bromophenol and *para* bromophenol. The major product of this reaction is *p*-bromophenol because no steric hindrance is present at *para* position.



56 Main products formed during a reaction of 1-methoxy naphthalene with hydroiodic acid are



Ans. (b)

Given reaction is completed via SN2 mechanism. Methyl of methoxy group will be substituted by H⁺ ion to give —OH(hydroxy group) as

follows

Mechanism





57 Which of the following reaction is an example of ammonolysis? [2021, 17 March Shift-I]

 $(a)C_{6}H_{5}COCI + C_{6}H_{5}NH_{2} \longrightarrow$

C₆H₅CONHC₆H₅

$$(b)C_{6}H_{5}CH_{2}CN \xrightarrow{ \square } C_{6}H_{5}CH_{2}CH_{2}NH_{2}$$

$$(c)C_6H_5NH_2 \xrightarrow{HU} C_6H_5NH_3CI^-$$

 $(d)C_6H_5CH_2CI + NH_3 \longrightarrow C_6H_5CH_2NH_2$ **Ans.** (d)

Reaction of alkyl halide with ammonia is called ammonolysis reaction.

 $C_{6}H_{5}CH_{2}CI \xrightarrow{NH_{3}} C_{6}H_{5}CH_{2}NH_{2}$

Carbon-halogen bond in alkyl or benzyl halides can be easily cleaved by a nucleophile. Hence, an alkyl or benzyl halide on reaction with an ethanolic solution of ammonia undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (—NH₂) group.

This process of cleavage of the C—X bond by ammonia molecule is known as ammonolysis.



The above reaction requires which of the following reaction conditions? [2021, 17 March Shift-I] (a) 573 K, Cu, 300 atm (b) 623 K, Cu, 300 atm (c) 573 K, 300 atm (d) 623 K, 300 atm

Ans. (d)

When chlorobenzene is treated with NaOH at 623 K and 300 atm sodium phenoxide is formed by nucleophilic substitution.



Nucleophilic substitution is not preferred in aromatic compounds. So, to do such reactions high temperature and pressure are required.

59 Match List-I with List-II.





C. $2CH_3CH_2CI + 2Na \xrightarrow{Ether}$

$$\begin{array}{c} C_2H_5 - C_2H_5 + 2NaCI\\ D.2C_6H_5CI + 2Na \xrightarrow{\text{Ether}} \end{array}$$

List-II

(i) Wurtz reaction

(ii) Sandmeyer reaction

(iii) Fittig reaction

(iv) Gattermann reaction

Choose the correct answer from the options given below.

[2021, 26 Feb Shift-II]

	А	В	С	D	
a)	(iii)	(i)	(iv)	(ii)	
b)	(ii)	(i)	(iv)	(iii)	
c)	(ii)	(iv)	(i)	(iii)	
d)	(iii)	(iv)	(i)	(ii)	

Ans. (c)

Benzene diazonium chloride undergoes Sandmeyer reaction in presence of Cu_2Cl_2 while undergoes Gattermann reaction in presence of Cu/HCl to give chlorobenzene along with nitrogen gas (N₂).

⊕ ∈ N₂CI Benzene diazonium Cu₂Cl₂ chloride $-N_2$ (Sandmeyer reaction) $+ N_2$ Chlorobenzene Cu, HCI

(Gattermann reaction) So, (A) - (ii) Sandmeyer reaction (B)-(iv) Gattermann reaction (C) Ethyl chloride reacts with sodium in presence of dry ether to give *n*-butane. This reaction is known as Wurtz reaction.

 $2CH_3CH_2CI + 2Na \xrightarrow{Ether}$

Ethy^l chloride [Aliphatic 1º-halide]

CH₃CH₂ ----CH₂CH₃ + 2NaCl n-butane

It is Wurtz reaction in which an aliphatic 1° or 2° halides produces a symmetrical alkane like n-butane.

(D) Chlorobenzene reacts with sodium in presence of dry ether to give biphenyl. This is known as Fittig reaction.



It is Fittig reaction in which a halobenzene produces biphenyl. So, C - (i) Wurtz reaction D - (iii) Fittig reaction So, correct match is A-(ii), B-(iv), C-(i) and D-(iii).

60 For the given reaction,





Ans. (c)

When 3-ethyl benzonitrile undergoes photochemical reaction (UV) with bromine (1 equivalent), we get a monobrominated product 1 bromo -1(3 cyanophenyl) ethane (A) as the major product.







UV light -HBr

The reaction follows benzylic free radical substitution mechanism which has a 2° benzylic free radical intermediate (stable due to resonance with the benzene ring).

(i) Initiation step In this step radicals are generated via homolytic fission of covalent bond.

$\overrightarrow{Br} \xrightarrow{UV} Br^{\bullet} + Br^{\bullet}$

(ii) Propagation step 3-methyl benzonitrile reacts with bromine radical to give 1-bromo-1-(3-cyanophenyl) ethane along with H[•].



(iii) Termination step H[•] and Br[•] reacts to form HBr. $H^{\bullet} + Br^{\bullet} \longrightarrow HBr$



61 The decreasing order of reactivity of the following compounds towards nucleophilic substitution $(S_N 2)$ is



[2020, 3 Sep Shift-II]

 NO_2

(a) (||)>(||)>(|V)>(|) (b) (|V|) > (||) > (|||) > (||)(C) $(|||) > (||) > (|\wedge\rangle) > (|)$ (d) (||)>(||)>(|)>(|))

Ans. (a)

Rate of S_N2 reaction







So, the decreasing order of reactivity of the given compounds toward $S_N 2$ reaction is

 $(||) > (|||) > (|\vee) > (|\vee) > (|).$

62 In the following reaction sequence, [*C*] is



[2020, 4 Sep Shift-II]



Ans. (a)

CI













 possible?
 [2020, 7 Jan Shift-II]

 (a)(B) and (D)
 (b)(A) and (D)

 (c)(B), (C) and (D)
 (d)(A) and (B)

Ans. (a)

(A) and (C) are not possible : Aryl halides and vinyl halides in the presence of anhyd. $AICI_3$ do not act as electrophiles to give Friedel-Crafts reaction with benzene. Therefore, these reactions are not possible.



(D) + CH₂=CH—CH₂—CI (Allyl halide : easily form electrophile with AlCl₃ and can react with benzene to give Friedel-Craft's reaction)



64 Which of these will produce the highest yield in Friedel-Crafts reaction? [2020, 9 Jan Shift-I]



Ans. (b)

Friedel-Crafts reaction is an electrophilic substitution reaction. In general, the rate of these reactions is highest when benzene have some electron releasing groups, (i.e. $--NH_2$, --OH) attached to the nucleus.



-OH groups are deactivated because the

Lewis acid (anhydrous AICI_3) used in these reactions form an adduct with the '----NH₂' or ---OH groups and becomes ineffective.

'—Ċ—NH₂' is a electron withdrawing (deactivating) group.



withdrawing (deactivating) group, but among the given options, it is most reactive towards Friedel-Crafts reaction.

65 The major product of the following reaction is



[2019, 8 April Shift-II]





So, considering the second reaction condition, Cl⁻, H_2O , Δ in the statement of the question, the correct answer is option (d).

66 The major product of the following reaction is





Ans. (b)

In presence of alc. KOH, the given halide undergoes elimination reaction.



The alkene produced undergoes polymerisation *via* free radical mechanism. This process involve three steps, i.e. initiation, propagation and termination.



67 Increasing rate of S_N1reaction in the following compounds is [2019, 10 April Shift-I]



Ans. (b)

More stable the carbocation intermediate, higher will be the rate of ${\rm S}_{\rm N}$ 1reaction.

The reaction involving carbocation intermediate formation for the given compounds are as follows:





Stability of intermediates will follow the order

B' < A' < C' < D'(-/) (-HPC=3) (+HPC=6) (+HPC=3) +R=1

So, the rate of S_N 1 reaction with the given compounds will be, B < A < C < D

68 The major product of the following reaction is



Ans. (d)

The road map of the given reaction is :





69 The major product of the following reaction is



Ans. (a)

Key Idea The reaction involves hydrolysis or nucleophilic substitution in first step followed by oxidation and dehydration in last step. The most important fact is that, the Br group attached directly to aromatic ring will not undergo substitution in step (i) The road map of the given reaction is as follows:



It is aryl halide, remains unaffected under ordinary S_N2 reaction conditions



70 The compounds A and B in the following reaction are, respectively



- (a) A = Benzyl alcohol,
- B = Benzyl isocyanide
- (b) A = Benzyl alcohol,
- B = Benzyl cyanide
- (c) A = Benzyl chloride, B = Benzyl isocyanide
- (d) A = Benzyl chloride,B = Benzyl cyanide

[2019, 9 Jan Shift-I]

Ans. (c)

The mechanism of the given reaction is as follows:



Thus, both benzyl cyanide and benzyl isocyanide are the products of reaction but benzyl isocyanide being the major product gives the correct option as (c).

71 Which of the following compounds will produce a precipitate with AgNO₃? [2019, 11 Jan Shift-II]



Ans. (a)

Only ionic halides (X^-) give precipitate of AgX with AgNO₃ solution. So, an organic bromide able to produce R^{\oplus} (stable carbocation) and Br⁻ in aqueous solution will give precipitate of AgBr with AgNO₃.





precipitate of AgBr with AgNO₃ solution.

72 The major product in the following conversion is [2019, 12 Jan Shift-II]



Ans. (d)

Key Idea The excess of HBr and high temperature in given reaction serves for dual purpose :

(i) Hydrolysis of ether via S_N2 mechanism, i.e. Zeisel's method.

(ii) Markownikoff addition at double bond of the branch.

The road map of complete reaction is as





73 Compound (A), C₈H₉Br gives a white

precipitate when warmed with alcoholic AgNO₃. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anyhydride on heating. Identify the compound (A).





Ans. (d)

Compound A gives a precipitate with alcoholic AgNO₃ (here white is misprinting because the colour of ppt is light yellow), so it must contains Br in side chain. On oxidation, it gives $C_8 H_6 O_{4/2}$ which shows the presence of two alkyl chains attached directly with the benzene nucleus.

Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) position. Thus, A must be







74 A solution of

(-/)-chloro-1-phenylethane in toluene racemises slowly in the presence of a small amount of SbCl₅, due to the formation of [JEE Main 2013]

(a) carbanion (c) carbocation (d) free radical

(b) carbene

Ans. (c)

The given compound, (-l)chloro-1-phenylethane in the presence of SbCl₅ forms a carbocation.

CI CH CH₃
$$\xrightarrow{\text{SbCl}_5}$$

|
Ph
[Ph $\xrightarrow{+}$ CH CH₃]SbCl₆

Since, the carbocation is a planar species, therefore it can be attacked by SbCl₆ either from the front or back side of the carbocation with equal ease. As a result, 50:50 mixture of two enantiomers of

1-chloro-1-pheynylethane undergoes racemization due to the formation of a carbocation intermediate.



75 The structure of the major product formed in the following reaction is



Ans. (d)



Chloride present on 1° aliphatic carbon can be substituted easier than iodide because I is attached to benzene ring. Lone pair of e^- of I is involved in delocalisation with $\pi - e^-$ of benzene.



Hence, lis difficult to substitue.

76 The compound formed on heating chlorobenzene with chloral in the



 $\xrightarrow{\text{Conc} \times \text{H}_2\text{SO}_4} \text{DDT}$

77 Bottles containing C $_{6}H_{5}I$ and C $_{6}H_{5}CH_{2}I$ lost their original labels. They were labelled A and B for testing . A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO₃ and then some AgNO₃ solution was added. Substance B

B gave a yellow precipitate. Which one of the following statements is true for this experiment?

[AIEEE 2003]

(a) A was C₆H₅I (b) A was C₆H₅CH₂I (c) B was C₆H₅I (d) Addition of HNO₃ was unnecessary Ans. (a) In tube A $C_6H_5I \xrightarrow{NaOH}$ No reaction (:: pH -/ does not break) (i) Dil HNO 3 No (ii) AgNO 3 yellow ppt. of Agl In tube B (i) Dil HNO 3 NaOH, boil C₆H₅CH₂I Nal -C₆H₅CH₂OH (ii) AgNO _z Agl yellow ppt. (PhCH₂I bonds breaks) Thus, A was C₆H₅I.