Haloalkanes and Haloarenes

Question1

The following reaction method

$$\begin{array}{c|c}
 & CH_3 \\
 & + X_2 \xrightarrow{\text{dark}}
\end{array}$$

$$\begin{array}{c|c}
 & CH_3 \\
 & + \\
 & X & X
\end{array}$$

$$\begin{array}{c|c}
 & CH_3 \\
 & + \\
 & X & X
\end{array}$$

is not suitable for the preparation of the corresponding haloarene products, due to high reactivity of halogen, when X is :

[NEET 2024 Re]

Options:

A.

E.

В.

C.

Cl

D.

Br

Answer: A

Solution:

- \bullet Aryl chlorides and bromides can easily be prepared by electrophilic substitution of arenes (toluene) with Cl_2 and Br_2 respectively in the presence of Lewis acid catalyst (Fe in dark).
- Reaction with I2 is reversible and requires the presence of oxidising agent.
- Corresponding fluoroarene is not prepared by this method due to high reactivity of fluorine.

Hence, 'X' is F.

Question2

The major product C in the below mentioned reaction is:

$$CH_{3}CH_{2}CH_{2}Br \xrightarrow{\qquad \text{alc. KOH} \qquad} A \xrightarrow{\qquad \text{HBr} \qquad} B \xrightarrow{\qquad \text{aq. KOH} \qquad} C$$





[NEET 2024 Re]

Options:

A.

Propan-1-ol

В.

Propan-2-ol

C.

Propane

D.

Propyne

Answer: B

Solution:

$$\begin{array}{cccc} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} & \xrightarrow{\text{alc. KOH}} & \text{CH}_3\text{CH} = \text{CH}_2 & \xrightarrow{\text{HBr}} & \text{CH}_3 - \text{CH} - \text{CH}_3 \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & \\ & & \\ & & \\ & \\ & & \\ & & \\ & \\ & & \\ & & \\ &$$

Question3

Identify ' \boldsymbol{X} ' in the following reaction.

Br
$$\longrightarrow$$
 Cl +Mg $\xrightarrow{\text{dry}}$ Intermediate $\xrightarrow{D_2O}$ X [1.0 mol]

[NEET 2024]

Options:

A.

В.

C.

$$D - \hspace{-1em} \bigwedge \hspace{-1em} -D$$

D.

Answer: A

Solution:

$$Br - Cl \xrightarrow{Mg} BrMg - Cl$$

$$D_2O$$

$$D - Cl$$

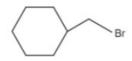
Question4

The compound that will undergo $S_N\mathbf{1}$ reaction with the fastest rate is

[NEET 2024]

Options:

A.



В.

C.

D.



Answer: D

Solution:

Reactivity towards $S_N 1$ depends upon stability of carbocation.

Order of stability is

Question5

The products A and B obtained in the following reactions, respectively, are

 $3 \text{ ROH} + \text{PCl}_3 \longrightarrow 3 \text{ RCl} + A$ $\text{ROH} + \text{PCl}_5 \longrightarrow \text{RCl} + \text{HCl} + B$

[NEET 2024]

Options:

A.

 $POCl_3$ and H_3PO_3

В.

 $\ensuremath{\mathsf{POCl}}_3$ and $\ensuremath{\mathsf{H}}_3\ensuremath{\mathsf{PO}}_4$

C

 $\ensuremath{\text{H}_3\text{PO}_4}$ and $\ensuremath{\text{POCl}_3}$

D.

 $\rm H_3PO_3$ and $\rm POCl_3$

Answer: D

Solution:



These reactions are preparation of haloalkanes from alcohols.

$$3~\text{ROH} + \text{PCl}_3 \longrightarrow 3~\text{RCl} + \text{H}_3\text{PO}_3 \label{eq:ROH}$$
 (A)

$$ROH + PCl_5 \rightarrow RCl + HCl + POCl_3$$
(B)

A and B are H₃PO₃ and POCl₃ respectively.

Question6

Identify the major product C formed in the following reaction sequence:

$$\mathbf{CH_3} - \mathbf{CH_2} - \mathbf{CH_2} - \mathbf{I} - \mathbf{NaCN} - \mathbf{A} - \mathbf{OH} - \mathbf{B} - \mathbf{B} - \mathbf{B} - \mathbf{B} - \mathbf{C}$$

$$\mathbf{Partial hydrolysis} - \mathbf{Br_2} - \mathbf{Partial hydrolysis} - \mathbf{Br_2} - \mathbf{C}$$

[NEET 2024]

Options:

A.

propylamine

В.

butylamine

C.

butanamide

D.

 $\alpha\text{-bromobutanoic}$ acid

Answer: A

Solution:

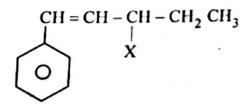
$$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2-1 \xrightarrow{\text{NaCN}} \text{CH}_3\text{CH}_2\text{CH}_2-\text{CN} \xrightarrow{\text{Partial hydrolysis}} & \text{CH}_3\text{CH}_2-\text{CH}_2-\text{C}-\text{NH}_2\\ \text{(A)} & \text{(B)} & \\ & \downarrow \text{NaOH/Br}_2\\ & \text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2\\ & \text{(C)}\\ & \text{(Propyl amine)} \end{array}$$

- \bullet Step-I is $\mathbf{S}_{\mathbf{N}}$ reaction with $\overset{\ominus}{\mathbf{C}}\mathbf{N}$ nucleophile.
- · Step-II will give amide.
- · Step-III is Hoffmann bromamide degradation reaction.

Question7



The given compoundis an example of



[NEET 2023]

Options:

A.

Aryl halide

В.

Allylic halide

C.

Vinylic halide

D.

Benzylic halide

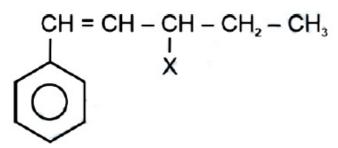
Answer: B

Solution:

 α -carbon is sp^3 carbon which is right next to >C = C<

This α -position is known as allylic position

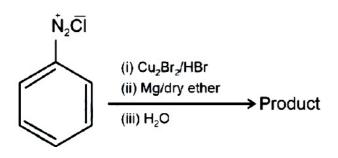
Hence,



is allylic halide

Question8

Identify the product in the following reaction:



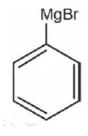
[NEET 2023]

Options:

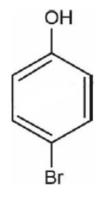
A.



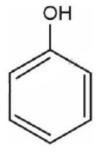
В.



C.



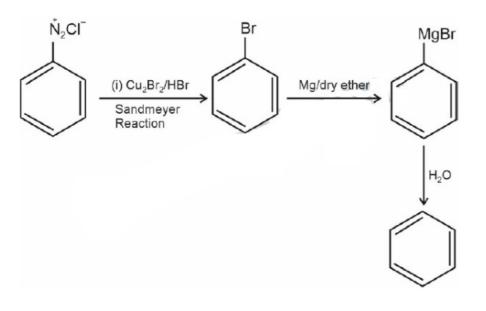
D.



Answer: A

Solution:





Identify the final product [D] obtained in the following sequence of reactions.

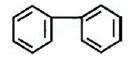
$$\mathsf{CH_3CHO} \xrightarrow{i) \, \mathsf{LiAlH_4}} [\mathsf{A}] \xrightarrow{\mathsf{H_2SO_4}} [\mathsf{B}]$$

$$\xrightarrow{\mathsf{HBr}} [C] \xrightarrow{\mathsf{Na/dry ether}} [D]$$

[NEET 2023]

Options:

A.



В.

 C_4H_{10}

C.

 $HC \equiv C^{\Theta}Na^{+}$

D.



Answer: C

Solution:

Which amongst the following reactions of alkyl halides produces isonitrile as a major product?

- (A) $R X + HCN \rightarrow$
- (B) $R X + AgCN \rightarrow$
- (C) $R X + KCN \rightarrow$
- (D) $R X + NaCN \xrightarrow{C_2H_5 OH}$

Choose the most appropriate answer from the options given below:

[NEET 2023 mpr]

Options:

A.

(D) only

В.

(C) and (D) only

C.

(B) only

D.

(A) and (B) only

Answer: C

Solution:

$$[B]R - X + Ag - C \equiv N \longrightarrow R - NC$$
Isonitrile



Choose the correct sequence of reagents in the conversion of 4-nitrotoluene to 2-bromotoluene.

[NEET 2023 mpr]

Options:

A.

 $NaNO_2/HCl; Sn/HCl; Br_2; H_2O/H_3PO_2$

В.

Sn/HCl; NaNO₂/HCl; Br₂; H₂O/H₃PO₂

C.

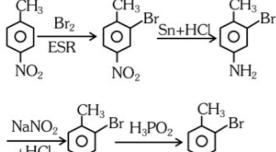
 Br_2 ; $\mathrm{Sn/HCl}$; $\mathrm{NaNO}_2/\mathrm{HCl}$; $\mathrm{H2O/H}_3\mathrm{PO}_2$

D.

Sn/HCl; Br_2 ; $NaNO_2/HCl$; H_2O/H_3PO_2

Answer: C

Solution:



+HCl \oplus \otimes N_2Cl

Question12

Identify the product in the following reaction

(i) KCN
(ii)
$$H_2O/HCl$$
, Δ
Product
(iii) Br_2/red phosphorus
(iv) H_2O

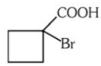
[NEET 2023 mpr]

Options:

A.



В.



C.

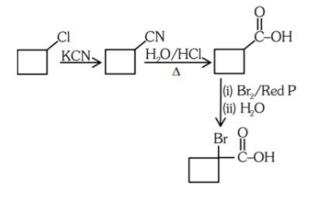


D.



Answer: B

Solution:



Question13

The incorrect statement regarding chirality is [NEET-2022]

Options:

A. $\boldsymbol{S}_{N} \, \boldsymbol{1}$ reaction yields $\boldsymbol{1} : \boldsymbol{1}$ mixture of both enantiomers

B. The product obtained by $\boldsymbol{S}_{N}^{}\,2$ reaction of haloalkane having chirality at the reactive site shows inversion of configuration

C. Enantiomers are superimposable mirror images on each other

D. A racemic mixture shows zero optical rotation

Answer: C

Solution:

The stereoisomers related to each other as non-superimposable mirror image are called enantiomers.

Question14

Which of the following sequence of reactions is suitable to synthesize chlorobenzene? [NEET-2022]

Options:

A. Benzene, Cl₂, anhydrous FeCl₃

B. Phenol, N aN O_2 , H Cl , CuCl

C.

D

Answer: A

Solution:

Benzene reacts with chlorine in presence of anhydrous $FeCl_3$ to give chlorobenzene

Question15

Given below are two statements : one is



labelled as Assertion (A) and the other is labelled as Reason (R).

Assertion (A):

Chlorine is an electron withdrawing group but it is ortho, para directing in electrophilic aromatic substitution.

Reason (R):

Inductive effect of chlorine destabilises the intermediate carbocation formed during the electrophilic substitution, however due to the more pronounced resonance effect, the halogen stabilises the carbocation at ortho and para positions.

In the light of the above statements, choose the most appropriate answer from the options given below:
[NEET Re-2022]

Options:

- A. (A) is not correct but (R) is correct.
- B. Both (A) and (R) are correct and (R) is the correct explanation of (A).
- C. Both (A) and (R) are correct but (R) is not the correct explanation of (A).
- D. (A) is correct but (R) is not correct.

Answer: D

Solution:

Halogen are electron withdrawing groups due to high electronegativity. They have high electron withdrawing inductive effect. In electrophilic substitution reaction it shows both electron withdrawing inductive effect and electron donating resonance effect, but inductive effect overpowers resonance effect so, it deactivates benzene ring and directs the incoming electrophile to ortho and para positions. So, here assertion is correct and Reason is false.

Question16

Predict the order of reactivity of the following four isomers towards $\boldsymbol{S}_{N}\,\boldsymbol{2}$ reaction.

- (I) CH₃CH₂CH₂CH₂Cl
- (II) CH₃CH₂CH(Cl) CH₃
- (III) (CH₃)₂CHCH₂Cl

(IV) $(CH_3)_3 CCl$ [NEET Re-2022]

Options:

A. (IV) > (II) > (III) > (I)

B. (IV) > (III) > (II) > (I)

C. (I) > (II) > (III) > (IV)

D. (I) > (III) > (IV)

Answer: D

Solution:

Greater the steric hindrance, lesser will be the rate of $S_N 2$ reaction. So order of reactivity of $S_N 2$ reaction is- (I) > (III) > (IV)

Question17

The major product of the following chemical reaction is:

$$CH_3$$
 $CH-CH=CH_2+HBr \xrightarrow{(C_6H_5CO)_2O_2}$?

[NEET 2021]

Options:

A.

$$CH_3$$
 $CH-CH_2-CH_2-Br$

В.

$$CH_3$$
 $CH-CH_2-CH_2-O-COC_6H_5$
 CH_3

C.

D.

Answer: A

Solution:



$$CH_3$$
 $CH-CH=CH_2+HBr$
 CH_3
 CH_3
 CH_3
 $CH-CH_2-CH_2Br$
 CH_3

Mechanism: Peroxide effect proceeds via free radical chain mechanism.

(i)
$$C_6H_5 - \overset{O}{C} / \overset{O}{C} - \overset{O}{C} - C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5 - \overset{O}{C} - \overset{O}{C}:$$

$$2\dot{C}_6H_5 + CO_2$$

(ii)
$$\dot{C}_e H_e + H - Br \xrightarrow{Homolysis} C_e H_e + \dot{B}r$$

free radical

(iv)
$$CH_3$$
 $CH-CH-CH_2-Br+H-Br$ $OH-CH_3$ Homolysis

 CH_3 $CH-CH_2-CH_2-Br$
 CH_3 $CH-CH_2-CH_2-Br$

Major product

Question18

 $CH_{3}CH_{2}COO^{-}N a^{+N_{aOH,+}}CH_{3}CH_{3} + N a_{2}CO_{3}$

Consider the above reaction and identify the missing reagent/chemical. [NEET 2021]

Options:

- A. B_2H_6
- B. Red Phosphorus
- C. CaO
- D. DI BAL H

Answer: C

Solution:

Alkane is produced by heating sodium salt of carboxylic acid with sodalime (NaOH and CaO in the ratio of 3:1)



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Question19

Elimination reaction of 2-Bromo-pentane to form pent-2-ene is:

- (A) β-Elimination reaction
- (B) Follows Zaitsev rule
- (C) Dehydrohalogenation reaction
- (D) Dehydration reaction [2020]

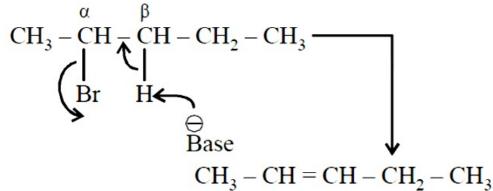
Options:

- A. (A), (C), (D)
- B. (B), (C), (D)
- C. (A), (B), (D)
- D. (A), (B), (C)

Answer: D

Solution:

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3 -$$



It is an β elimination reaction as β hydrogen is abstracted and results more substituted alkene. which follows Zaitsev's rule

Since 'H' and 'Br' are removed, it is dehydrohalogenation.

Question20

Which of the following alkane cannot be made in good yield by Wurtz reaction?
[2020]

Options:

A. 2,3-Dimethylbutane

B. n-Heptane

C. n-Butane

D. n-Hexane

Answer: B

Solution:

Wurtz reaction is used to prepare symmetrical alkanes like \boldsymbol{R}_1 – \boldsymbol{R}_1 , as

$$\mathbf{R_1 - X} \ + 2 \, \mathbf{N} \ \mathbf{a} + \mathbf{X} \ - \mathbf{R_1} \stackrel{\mathrm{Dry \ ether}}{\longrightarrow} \mathbf{R_1} - \mathbf{R_1} + 2 \, \mathbf{N} \ \mathbf{aX}$$

If $\boldsymbol{R}_{\!1}$ and $\boldsymbol{R}_{\!2}$ are different, then mixture of alkanes may be obtained as

$$R_1 - X + 2Na + R_2 - X \xrightarrow{Dry etner} R_1 - R_1 + R_1 - R_2 + R_2 - R_2 + 2NaX$$

Question21

The hydrolysis reaction that takes place at the slowest rate, among the following is (Odisha NEET 2019)

Options:

A.

В.

$$H_3C$$
— CH_2 — Cl $\xrightarrow{aq \cdot NaOH}$ $\xrightarrow{H_3C}$ \xrightarrow{CH} \xrightarrow{CH} \xrightarrow{CH}

C.

$$H_2C=CH-CH_2Cl\xrightarrow{aq\cdot NaOH}$$
 $H_2C=CH-CH_2OH$

D.

Answer: A



Solution:

Aryl halides are less reactive as compared to alkyl halides as the halogen atom in these compounds is firmly attached and cannot be replaced by nucleophiles such as OH^- , NH_2^- , etc. In chlorobenzene, the electron pair of chlorine atom is in conjugation with π -electrons of benzene ring. Thus C-Cl bond acquires double bond character and is difficult to break.

Question22

The compound A on treatment with Na gives B, and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order (NEET 2018)

Options:

A. C_2H_5OH , C_2H_6 , C_2H_5Cl

B. C_2H_5OH , C_2H_5Cl , C_2H_5ONa

C. C_2H_5Cl , C_2H_6 , C_2H_5OH

D. C_2H_5 OH, C_2H_5 ONa, C_2H_5 Cl

Answer: D

Solution:

$$C_{2}H_{5}OH \xrightarrow{Na} C_{2}H_{5}O^{-}Na^{+}$$

$$(A) \qquad (B)$$

$$\downarrow PCl_{5}$$

$$C_{2}H_{5}Cl$$

$$(C)$$

$$C_{2}H_{5}O^{-}Na^{+} + C_{2}H_{5}Cl \xrightarrow{S_{N}^{2}} C_{2}H_{5}OC_{2}H_{5}$$

$$(B) \qquad (C)$$

$$C_{2}H_{5}O^{-}Na^{+} + C_{2}H_{5}Cl \xrightarrow{Williamson's Synthesis} C_{2}H_{5}OC_{2}H_{5}$$

$$Diethyl ether$$

Question23

The compound C_7H_8 undergoes the following reactions:

$$\mathbf{C_7H_8} \xrightarrow{\mathrm{3Cl_2/\Delta}} \mathbf{A} \xrightarrow{\mathrm{Br_2/Fe}} \mathbf{B} \xrightarrow{\mathrm{Zn/HCl}} \mathbf{C}$$

The product C is.

(NEET 2018)

Options:



A. m -bromotoluene

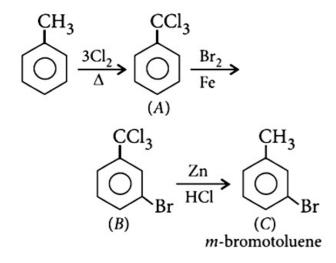
B. o -bromotoluene

C. 3 -bromo- 2,4,6 -trichlorotoluene

D. p -bromotoluene

Answer: A

Solution:



Question24

Identify A and predict the type of reaction.

$$\begin{array}{c}
\text{OCH}_{3} \\
\text{Br}
\end{array}$$

(NEET 2017)

Options:

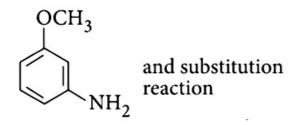
A.

В.

C.

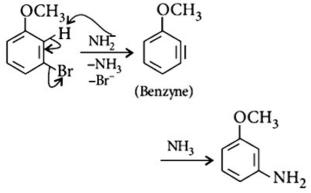
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D.



Answer: D

Solution:



 \ensuremath{m} -Bromoanisole gives only the respective meta substituted aniline. This is a substitution reaction which goes by an elimination-addition pathway.

Question25

Consider the reaction, $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$. This reaction will be the fastest in (NEET-II 2016)

Options:

A. ethanol

B. methanol

C. N, N'-dimethylformamide (DMF)

D. water. (NEET -II2016)

Answer: C



Solution:

The reaction, $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr follows S_N^2$ mechanism which is favoured by polar aprotic solvent i.e., N, N' dimethylformamide (DMF), $H - \overset{\circ}{C} - N(CH_3)_2$

Question26

Which of the following biphenyls is optically active? (NEET-I 2016)

Options:

A.

В.

$$CH_3$$
 CH_3

C.

D.

Answer: D

Solution:

For the following reactions:

(A)
$$CH_3CH_2CH_2Br + KOH \longrightarrow$$

 $CH_3CH = CH_2 + KBr + H_2O$

(B)
$$H_3C$$
 CH_3 + KOH \longrightarrow H_3C CH_3 + KBr

Which of the following statements is correct? (NEET-I 2016)

Options:

- A. (A) is elimination, (B) and (C) are substitution reactions.
- B. (A) is substitution, (B) and (C) are addition reactions.
- C. (A) and (B) are elimination reactions and (C) is addition reaction.
- D. (A) is elimination, (B) is substitution and (C) is addition reaction.

Answer: D

Solution:

 $CH_3CH_2CH_2Br + KOH \rightarrow CH_3CH = CH_2 + KBr + H_2O$

Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.

$$H_3C$$
 \leftarrow CH_3 + KOH \longrightarrow H_3C \leftarrow CH_3 + KBr

- Br group is replaced by - OH group hence, it is a substitution reaction.

$$\bigcirc + Br_2 \longrightarrow \bigcirc Br$$

$$Br$$

Addition of Br_2 converts an unsaturated compound into a saturated compound hence, it is an addition reaction.

Question28



Two possible stereo-structures of CH $_3$ CH OH COOH which are optically active are called (2015)

Options:

A. atropisomers

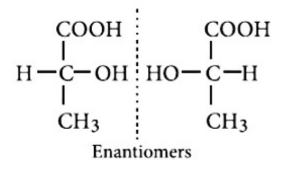
B. enantiomers

C. mesomers

D. diastereomers

Answer: B

Solution:



Question29

In an S_N 1 reaction on chiral centers, there is (2015)

Options:

A. inversion more than retention leading to partial racemisation

B. 100% retention

C. 100% inversion

D. 100% racemisation.

Answer: A

Solution:

In case of optically active alkyl halides, $S_{\rm N} 1$ reaction is accompanied by racemisation. The carbocation formed in the slow step being ${
m sp}^2$ hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of

products, one having the same configuration and other having inverted configuration. The isomer corresponding to inversion is present in slight excess because $S_{\rm N}1$ also depends upon the degree of shielding of the front side of the reacting carbon



The reaction of $C_6H_5CH = CHCH_3$ with HBr products (2015 Cancelled)

Options:

A. $C_6H_5CH_2CH_2CH_2Br$

В.

C.
$$C_6H_{5 \atop Br}^{CH} CH_2CH_3$$

D.
$$C_6H_5CH_2$$
 CH CH $_3$

Answer: C

Solution:

$$\begin{array}{c} & \bigcirc \\ \bigcirc \\ -\text{CH} = \text{CH} - \text{CH}_3 \xrightarrow{\text{HBr}} \\ & \triangle \\ \text{More stable} \\ & \text{(Benzyl carbocation)} \\ & \rightarrow \\ \bigcirc \\ -\text{CH} - \text{CH}_2 - \text{CH}_3 \\ & \text{Br} \end{array}$$

Question31

Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

(ii) CH ₃CH ₂CH ₂Cl

(iii)
$$H_3C - CH - CH_2Cl$$

CH₃

H C C₂H₅

(2014)

Options:

A. (i) and (ii)

B. (ii) and (iv)

C. (iii) and (iv)

D. Only (iv)

Answer: D

Solution:

Solution:

Only (iv) option will undergo racemization when the solution of KOH hydrolyzes because it is the only compound which contains a chiral carbon atom

Question32

Given:

I and II are (Karnataka NEET 2013)

Options:

A. identical

B. a pair of conformers

C. a pair of geometrical isomers

D. a pair of optical isomers.



Answer: B

Solution:

I and II are staggered and eclipsed conformers.

Question33

Which of the following acids does not exhibit optical isomerism? (2012)

Options:

- A. Maleic acid
- B. alpha -amino acids
- C. Lactic acid
- D. Tartaric acid

Answer: A

Solution:

Maleic acid shows geometrical isomerism and not optical isomerism.

$$C = C$$
HOOC

Maleic acid

COOH

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Question34

In the replacement reaction

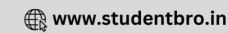
$$CI + MF \longrightarrow CF + MI$$

The reaction will be most favourable if M happens to be (Mains 2012)

Options:

- A. Na
- B. K
- C. Rb
- D. Li

Answer: C



Solution:

Tertiary halide shows S_N^1 mechanism i.e., ionic mechanism. In the given reaction negative ion will attack on carbocation. Thus greater the tendency of ionisation (greater ionic character in M-F bond more favourable will be reaction. The most ionic bond is Rb-F in the given examples thus most favourable reaction will be with Rb-F.

Question35

Consider the reactions.

(i)
$$(CH_3)_2CH - CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH - CH_2OC_2H_5 + HBr$$

(ii) $(CH_3)_2CH - CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH - CH_2OC_2H_5 + Br^-$
The mechanisms of reactions (i) and (ii) are respectively (Mains 2011)

Options:

A. $S_N 1$ and $S_N 2$

B. $S_N 1$ and $S_N 1$

 $C. S_N^2$ and S_N^2

D. $S_N 2$ and $S_N 1$

Answer: C

Solution:

Positive charge will be on the Carbon with 1° in Both Examples as order of Reaction for SN $_2$ is 1° > 2° > 3° So, Answer is S_{N^2} and S_{N^2}

Question36

Which one is most reactive towards $S_N 1$ reaction? (2010)

Options:

A. $C_6H_5CH(C_6H_5)Br$

B. C_6H_5 CH(CH₃) Br



C. $C_6H_5C(CH_3)(C_6H_5)$ Br

D. $C_6H_5CH_2Br$

Answer: C

Solution:

 ${\rm S}_{\rm N}{\rm 1}$ reactions proceed via the formation of a carbocation intermediate.

More stable is the carbocation more reactive is the alkyl/aryl halide towards $S_N 1$.

In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their -R effect and $-CH_3$ by its +I effect diminish the positive charge and make it stable.

$$\bigcirc - \stackrel{\scriptscriptstyle \downarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}{\stackrel{\scriptscriptstyle \leftarrow}}}}}}}}}}}}}}$$

Question37

The correct order of increasing reactivity of

$$X$$
 X
 X
 X
 NO_2
 NO_2
 I
 II
 IV
 NO_2
 II
 IV

C-X bond towards nucleophile in the following compounds is (2010)

Options:

A. I < II < IV < III

B. II < III < I < IV

C. IV < III < I < II

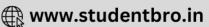
D. III < II < I < IV

Answer: A

Solution:

| < || < |V < |||

The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of C—X bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV) which in turn will be more stable than the arcnium ion (formed from I). Also, the aryl halide has a double bond character in the C—X bond which makes the cleavage more difficult. However, inspite of all the stated factors, II will be more reactive than I due to the presence of the electron withdrawing -N O_2 group. C—X bond becomes weak and undergoes nucleophilic substitution reaction



Options:

A. $C_6H_5CH_2OCH_2C_6H_5$

B. $C_6H_5CH_2OH$

C. $C_6H_5CH_3$

D. $C_6H_5CH_2CH_2C_6H_5$

Answer: C

Solution:

$$C_6H_5CH_2Br \xrightarrow{Mg, \text{ ether}} C_6H_5CH_2MgBr$$

$$\downarrow H_3O^+ Br$$

$$C_6H_5CH_3 + Mg < OH$$

Question39

Which of the following reactions is an example of nucleophilic substitution reaction? (2009)

Options:

A.
$$2RX + 2Na \rightarrow R - R + 2NaX$$

B. RX + H₂
$$\rightarrow$$
 RH + HX

C. RX + M g
$$\rightarrow$$
 RM gX

D. RX + KOH
$$\rightarrow$$
 ROH + KX

Answer: D

Solution:



 $KOH \rightarrow K^+ + OH^-, RX + OH^- \rightarrow R - OH + KX$

Nucleophile are either negative charge or a lone pair of ${\rm e}^-{\rm bearing}$ species, OH $^-$ etc.

Question40

How many stereoisomers does this molecule have? $CH_3CH = CHCH_2CHBrCH_3$ (2008)

Options:

A. 8

B. 2

C. 4

D. 6

Answer: C

Solution:

The given compound may be written as

$$CH_3$$
 $C=C$
 CH_2
 CH_2
 CH_3
 CH_3
 CH_3

Both geometrical isomerism (cis-trans form) and optical isomerism is possible in the given compound.

No. of optical isomer $= 2^n = 2^1 = 2$

(where n = no. of asymmetric carbon)

Hence total no. of stereoisomers = 2 + 2 = 4

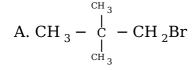
Question41

In a S_N 2 substitution reaction of the type

 $R - Br + Cl^{-\frac{DMF}{-----}}R - Cl + Br^{-}$ which one of the following has the highest relative rate? (2008)

Options:





B. CH₃CH₂Br

C. CH $_3$ CH $_2$ CH $_2$ Br

D. CH
$$_3$$
 – C $_{\stackrel{}{\underset{\text{CH}}{\mid}}_3}$ – CH $_2$ Br

Answer: B

Solution:

 S_N^2 mechanism is followed in case of primary and secondary alkyl halides i.e. S_N^2 reaction is favoured by small groups on the carbon atoms attached to halogen so, $CH_3 - X > R - CH_2 - X > R_2CH - X > R_3C - X$

Primary is more reactive than secondary and tertiary alkyl halides. $S_N 2$ order :Methyl > Ethyl > Isopropyl > Tertiary butyl > Allyl > Benzyl

Question42

If there is no rotation of plane polarised light by a compound in a specific solvent, though to be chiral, it may mean that (2007)

Options:

- A. the compound is certainly meso
- B. there is no compound in the solvent
- C. the compound may be a racemic mixture
- D. the compound is certainly a chiral.

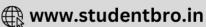
Answer: A

Solution:

Solution:

Meso compound does not rotate plane polarised light. Compound which contains tetrahedral atoms with four different groups but the whole molecule is achiral, is known as meso compound. It possesses a plane of symmetry and is optically inactive. One of the asymmetric carbon atoms turns the plane of polarised light to the right and other to the left and to the same extent so that the rotation due to upper half is compensated by the lower half, i.e., internally compensated, and finally there is no rotation of plane polarised light.

Question 43



 ${\rm CH_3-CHCl-CH_2-CH_3}$ has a chiral centre. Which one of the following represents its R -configuration? (2007)

Options:

A.

$$\begin{array}{c} C_2H_5 \\ H-C-CH_3 \\ Cl \end{array}$$

В.

C.

$$\begin{array}{c} \operatorname{CH}_3 \\ \operatorname{H-C-Cl} \\ \operatorname{C}_2\operatorname{H}_5 \end{array}$$

D.

$$H_3C-C-Cl$$

Answer: B

Solution:

R-configuration

Which of the following is not chiral? (2006)

Options:

- A. 2 -Hydroxypropanoic acid
- B. 2 -Butanol
- C. 2,3 -Dibromopentane
- D. 3 -Bromopentane

Answer: D

Solution:

Solution:

$$H_3C-CH_2-CH_2-CH_3$$
 Due to absence of asymmetric carbon atom.

Question45

Which of the following undergoes nucleophilic substitution exclusively by $S_N 1$ mechanism? (2005)

Options:

- A. Ethyl chloride
- B. Isopropyl chloride
- C. Chlorobenzene
- D. Benzyl chloride

Answer: D

Solution:

Solution:

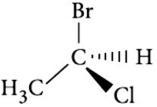
 $\mathrm{S}_{_{\mathrm{N}}}1$ reaction is favoured by heavy (bulky) groups on the carbon atom attached to halogens and nature of carbonium ion in substrate is

Benzyl > Allyl > Tertiary > Secondary > Primary> Methyl halides.





The chirality of the compound



is (2005)

Options:

A. R

B. S

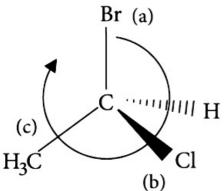
C. E

D. Z

Answer: A

Solution:

Solution:



Lowest priority atom is always away from the viewer. Priority is seen on the basis of atomic no. and if atomic no. are same then on the basis of atomic mass.

If clockwise then it is $\boldsymbol{R},$ if anticlockwise then it is $\boldsymbol{S}.$

Name of the molecule is, (R) 1 -bromo- 1 -chloroethane.

Question47

Which of the following is least reactive in a nucleophilic substitution reaction? (2004)

Options:

A. $(CH_3)_3C - Cl$

 $\mathrm{B.}\;\mathrm{CH}_2=\mathrm{CHCl}$



 $C. CH_3CH_2Cl$

D. $CH_2 = CHCH_2Cl$

Answer: B

Solution:

The non-reactivity of the chlorine atom in vinyl chloride can be explained from the molecular orbital point of view as follows. If the chlorine atom has sp^2 hybridisation, the C-Cl bond will be a σ -bond and the two lone pairs of electrons would occupy the other two sp^2 orbitals. This would leave a p orbital containing a lone pair, and this orbital could now conjugate with the π -bond of the ethylenic link. Thus two M.O's will be required to accommodate these four π -electrons. Furthermore, since chlorine is more electronegative than carbon, the electrons will tend to be found in the vicinity of the chlorine atom. Nevertheless, the chlorine atom has now lost full control of the lone pair and so, is less negative than it would have been had there been no conjugation. since two carbon atoms have acquired a share in the lone pair, each carbon atom acquires a small negative charge. Hence, owing to delocalisation of bonds (through conjugation), the vinyl chloride molecule has an increased stability. Before the chlorine atom can be displaced by some other group, the lone pair must be localised again on the chlorine atom. This requires energy, and so the chlorine is more firmly bound.

$$H_2\overset{\longleftarrow}{C}=CH\overset{\longleftarrow}{C}I:\longleftrightarrow \bar{C}H_2-CH=\bar{C}I$$

Question48

Which of the following pairs of compounds are enantiomers? (2003)

Options:

Α.

$$\begin{array}{c|ccccc} H & \xrightarrow{CH_3} & & & & CH_3 \\ H & & OH & & HO & & H \\ HO & & H & & H & & OH \\ \hline & CH_3 & & & CH_3 & & \\ \end{array}$$

В.

C.

$$H \longrightarrow OH$$
 and $H \longrightarrow OH$ CH_3 CH_3 CH_3 CH_3



D.

$$HO \xrightarrow{CH_3} H$$
 and $HO \xrightarrow{CH_3} H$ $HO \xrightarrow{CH_3} H$ $HO \xrightarrow{CH_3} H$ $HO \xrightarrow{CH_3} H$

Answer: A

Solution:

Solution:

These two are non-superimposable mirror images of each other, so they are enantiomers.

Question49

Reactivity order of halides for dehydrohalogenation is (2002)

Options:

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

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

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

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

Answer: B

Solution:

I > Br > Cl > F→ atomic radii

F, Cl, Br, I belongs to the same group orderly.

Atomic radii go on increasing as the nuclear charge increases in preceeding downwards in a group. The decreasing order of bond length C – I > C – Br > C – Cl > C – F. 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 is, R-I > R-Br > R-Cl > R-F.

Question 50

$$\mathbf{CH_3CH_2Cl} \overset{\mathrm{NaCN}}{---} \mathbf{X} \overset{\mathrm{Ni}/\mathrm{H_2}}{---} \mathbf{Y} \overset{\mathrm{acetic}\,\mathrm{anhydride}}{----} \mathbf{Z}$$

Z in the above reaction sequence is (2002)



Options:

A. CH₃CH₂CH₂NHCOCH₃

B. CH₃CH₂CH₂NH₂

C. CH₃CH₂CH₂CONHCH₃

D. CH₃CH₂CH₂CONHCOCH₃

Answer: A

Solution:

Solution:

$$\text{CH}_3\text{CH}_2\text{Cl} \underbrace{\overset{\text{NaCN}}{-}}_{\text{(X)}} \text{CH}_3\text{CH}_2\text{CN} \underbrace{\overset{\text{Ni} \, / \, \text{H}_2}{-}}_{\text{(Y)}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \underbrace{\overset{\text{acetic anhydride}}{-}}_{\text{(Z)}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCOCH}_3$$

Question51

 $\mathbf{CH_3}$ – $\mathbf{CH_2}$ – $\mathbf{CH_3}$ obtained by chlorination of n -butane will be (2001)

Options:

A. meso form

B. racemic mixture

C. d -form

D. l -form.

Answer: B

Solution:

Chlorination of n -butane takes place via free radical formation. i.e. $\mathrm{Cl}_2 \to \mathrm{Cl} + \mathrm{Cl}$

 $\label{eq:ch3} \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \to \text{CH}_3 \text{ CHCH}_2\text{CH}_3 + \text{HCl} \\ \text{sp}^2 \text{ - hybrid planar shape intermediate and } \text{Cl may attack from either side to give} \end{array}$

CH₃ČHCH₂CH₃ + Čl —

$$CH_{3}$$
— CH_{2} CH_{3} + CH_{3} — CH_{2} CH_{3}

Racemic mixture

(Mixture of 50% d-form and 50% l-form)

An organic compound $A(C_4H_9Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then, A is (2001)

Options:

A. t -butyl chloride

B. s -butyl chloride

C. iso-butyl chloride

D. n -butyl chloride.

Answer: A

Solution:

Wurtz reaction: It involves the reaction of alkyl halides with Na in ether to form higher alkanes.

 $2R - X + 2 Na \rightarrow R - R + 2 NaX$

In the given problem,

$$2C_4H_9Cl + 2Na \xrightarrow{\text{Ether}} C_4H_9 \cdot C_4H_9 + 2NaCl$$

Compound A is t -butyl chloride, in this compound all - CH_3 groups have primary hydrogen only and able to give only, one chloro derivative.

 $(CH_3)_3 CC(CH_3)_3 \xrightarrow{CI_2} CH_2 Cl(CH_3)_2 C - C(CH_3)_3$

Question53

A compound of molecular formula ${\rm C_7H_{16}}$ shows optical isomerism, compound will be (2001)

Options:

A. 2,3 -dimethylpentane

B. 2,2 -dimethylbutane

C. 2 -methylhexane

D. none of these.

Answer: A

Solution:



Organic compounds exhibit the property of enantiomerism (optical isomerism) only when their molecules are chiral. Most chiral compounds have a chiral centre, which is an atom bonded to four different atoms or groups.

$$CH_3$$
 $CH - CH_2CH_3$ CH_3

2,3-Dimethylpentane has one chiral C-atom and do not have any symmetric element.

Question54

Which of the following compounds is not chiral? (1998)

Options:

A. CH₃CHDCH₂Cl

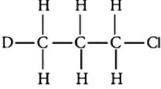
B. CH₃CH₂CHDCl

C. DCH₂CH₂CH₂Cl

D. CH₃CHClCH₂D

Answer: C

Solution:



The above compound has no chiral 'C'-atom. All the 'C' atoms are attached to two identical 'H' atoms, so they are not asymmetrical.

Question55

Replacement of Cl of chlorobenzene to give phenol requires drastic conditions. But chlorine of 2,4 -dinitrochlorobenzene is readily replaced because (1997)

Options:

A. NO₂ donates e⁻ at meta position

B. NO₂ withdraws e⁻ from ortho/para positions

 $\mathrm{C.\ NO}_2$ make ring electron rich at ortho and para



D. NO₂ withdraws e⁻ from meta position.

Answer: B

Solution:

$$\bigvee_{NO_2}^{Cl} NO_2$$

Withdrawal of electrons by - NO_2 groups from ortho/para positions cause easier removal of - Cl atom due to the development of positive charge on o - positions.

Question56

The alkyl halide is converted into an alcohol by (1997)

Options:

A. elimination

B. dehydrohalogenation

C. addition

D. substitution.

Answer: D

Solution:

$$\begin{array}{c} {\rm C_2H_5\,Br} \ + \ {\rm KOH} \\ {\rm Ethyl\,bromide} \end{array} \xrightarrow{\rm (aqueous)} \begin{array}{c} {\rm C_2H_5\,OH} \ + \ {\rm KBr} \\ {\rm Ethyl\,Alcohol} \end{array}$$

Question57

Reaction of t -butyl bromide with sodium methoxide produces (1994)

Options:

A. sodium t -butoxide

B. t -butyl methyl ether



C. isobutane

D. isobutylene.

Answer: D

Solution:

Isobutylene is obtained.

$$H_3C-C-CH_3 + CH_3ONa \longrightarrow$$
 CH_3
 CH_3
 $CH_3C=CH_2 + CH_3OH + NaBr$

Thus, the reaction produces isobutylene.

Question58

Grignard reagent is prepared by the reaction between (1994)

Options:

A. magnesium and alkane

B. magnesium and aromatic hydrocarbon

C. zinc and alkyl halide

D. magnesium and alkyl halide.

Answer: D

Solution:

Grignard reagent is prepared by heating an alkyl halide with dry magnesium powder in dry ether.

Grignard reagent is prepared by
$$R - X + Mg \xrightarrow{Dryether} R - Mg - X$$
Gridnard reaction

.....

Question59

Benzene reacts with n -propyl chloride in the presence of anhydrous $AlCl_3$ to give (1993)



Options:

A. 3 -propyl-1-chlorobenzene

B. n -propylbenzene

C. no reaction

D. isopropylbenzene.

Answer: D

Solution:

$$C_6H_6 + CH_3CH_2CH_2Cl \xrightarrow{Anhy.} CH_3$$
 $C_6H_5 - CH - CH_3$
Isopropylbenzene

Question60

Industrial preparation of chloroform employs acetone and (1993)

Options:

A. phosgene

B. calcium hypochlorite

C. chlorine gas

D. sodium chloride.

Answer: B

Solution:

$$\begin{array}{l} \text{CaOCl}_{\,2} + \text{H}_{\,2}\text{O} \rightarrow \text{Ca(OH)}_{\,2} + \text{Cl}_{\,2} \\ \text{Cl}_{\,2} \text{ so obtained acts as a mild oxidising as well as chlorinating agent.} \\ \text{CH}_{\,3} - \overset{\text{C}}{\underset{\,}{\mid}} - \text{CH}_{\,3} + \text{CaOCl}_{\,2} \longrightarrow \text{CH Cl}_{\,3} \end{array}$$

Question61

Chlorobenzene reacts with Mg in dry ether to give a compound (A)



which further reacts with ethanol to yield (1993)

Options:

A. phenol

B. benzene

C. ethyl benzene

D. phenyl ether.

Answer: B

Solution:

$$C_6H_5Cl \xrightarrow{Mg} C_6H_5MgCl \xrightarrow{CH_3CH_2OH} C_6H_6 + CH_3CH_2OMgCl$$

Question62

When chlorine is passed through propene at 400°C, which of the following is formed? (1993)

Options:

A. PVC

B. Allyl chloride

C. Propyl chloride

D. 1,2 -Dichloroethane

Answer: B

Solution:

$$CH_3 CH = CH_2 \xrightarrow{Cl_2, 400^{\circ}C} ClCH_2 CH + CH_2$$
At 400°C temporature, substitution occurs instead of additional contents of addition

At $400^{\circ}\mathrm{C}$ temperature, substitution occurs instead of addition.

Question63

Which chloro derivative of benzene among the following would undergo



hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative? (1989)

Options:

A.

$$O_2N - \bigcirc O_2$$
 $O_2N - \bigcirc O_2$
 $O_2N - \bigcirc O_2$

В.

$$O_2N - \bigcirc - CI$$

C.

$$Me_2N$$
 — Cl

D. C_6H_5Cl

Answer: A

Solution:

Cl in 2, 4, 6-trinitrochlorobenzene is activated by three $-\mathrm{NO}_2$ groups at o -and p -positions and hence undergoes hydrolysis most readily.

Question64

Which of the following is an optically active compound? (1989)

Options:

A. 1 -Butanol

B. 1 -Propanol

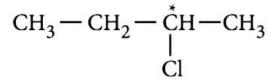
C. 2 -Chlorobutane

D. 4 -Hydroxyheptane

Answer: C

Solution:





2-Chlorobutane contains a chiral carbon atom and hence it is optically active compound.

Question65

Phosgene is a common name for (1988)

Options:

A. phosphoryl chloride

B. thionyl chloride

C. carbon dioxide and phosphine

D. carbonyl chloride.

Answer: D

