Haloalkanes and Haloarenes

Question1

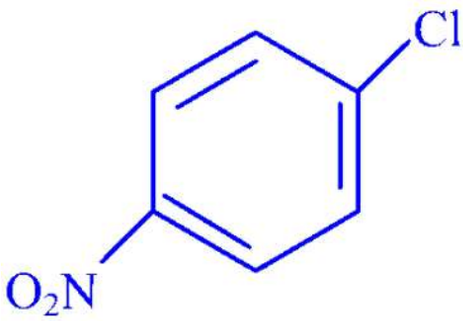
Identify the compound which is least reactive towards nucleophilic substitution reactions.

AP EAPCET 2025 - 26th May Morning Shift

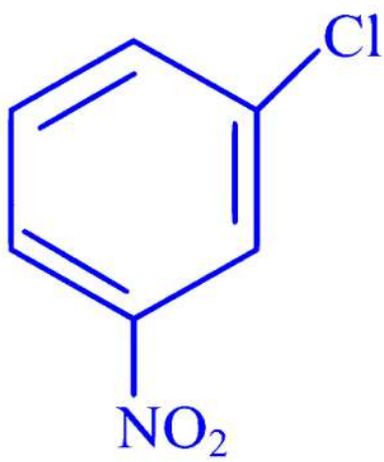
Options:

A.

B.



C.

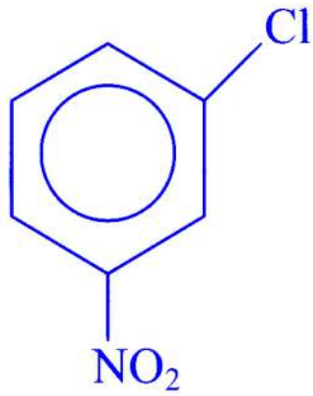


D. $CH_2 = CH - CH_2Cl$

Answer: C

Solution:

The presence of e^-withdrawing group like $-NO_2$ at meta positions decreases the reactivity of haloamines Thus among the given options



is least reactive towards nucleophilic substitution

Question2

Which of the following will undergo methylation with CH_3Cl /anhy. $AlCl_3$?

I. Aniline

II. Chlorobenzene

III. Benzoic acid

IV. Anisole

AP EAPCET 2025 - 26th May Evening Shift

Options:

A.

I, IV

B.

II, III

C.

II, IV

D.

I, III

Answer: C

Solution:

Among the given options chlorobenzene and anisole will undergo methylation with CH_3Cl/ anhy. $AlCl_3$.

Question3

Which one of the following halogen compounds is least reactive towards hydrolysis by S_N1 mechanism?

AP EAPCET 2025 - 24th May Morning Shift

Options:

A.

Tertiary butylchloride

B.

Isopropyl chloride

C.

Allyl chloride

D.

Ethyl chloride

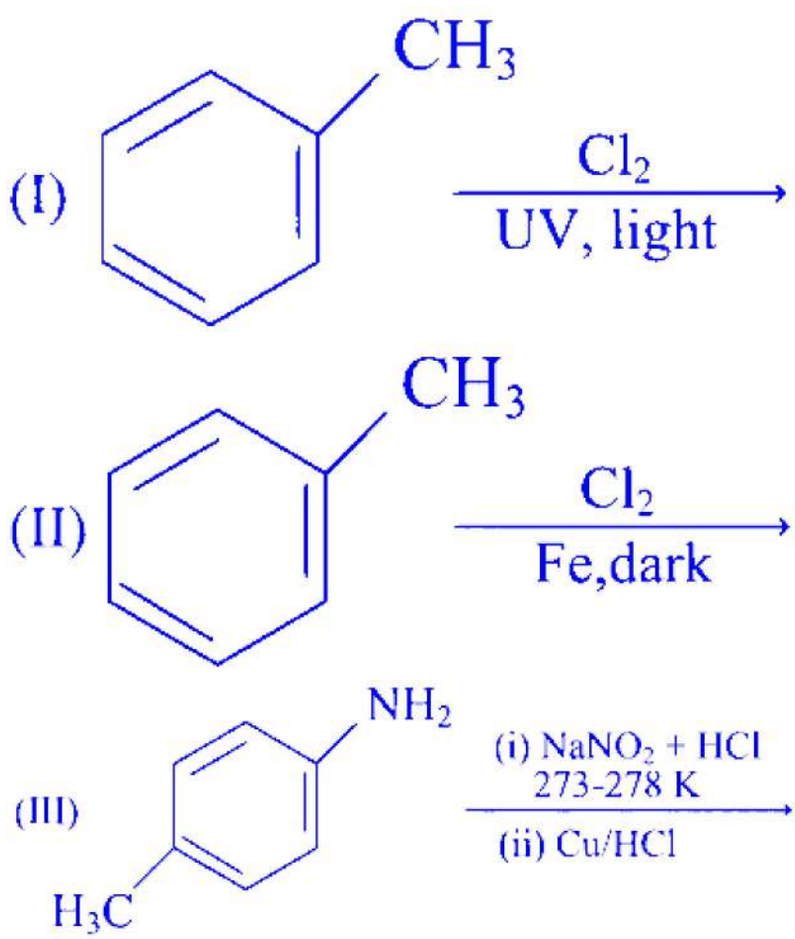
Answer: D

Solution:

Ethyl chloride is least reactive towards hydrolysis by S_N1 reaction. In S_N1 reaction, the rate determining step involves the formation of carbocation. The stability of carbocation directly affects the reactivity $CH_3CH_2^+$ is least stable carbocation.

Question4

p-chlorotoluene is the major product in which of the following reactions?



AP EAPCET 2025 - 24th May Morning Shift

Options:

A.

I, III only

B.

I, II only

C.

II, III only

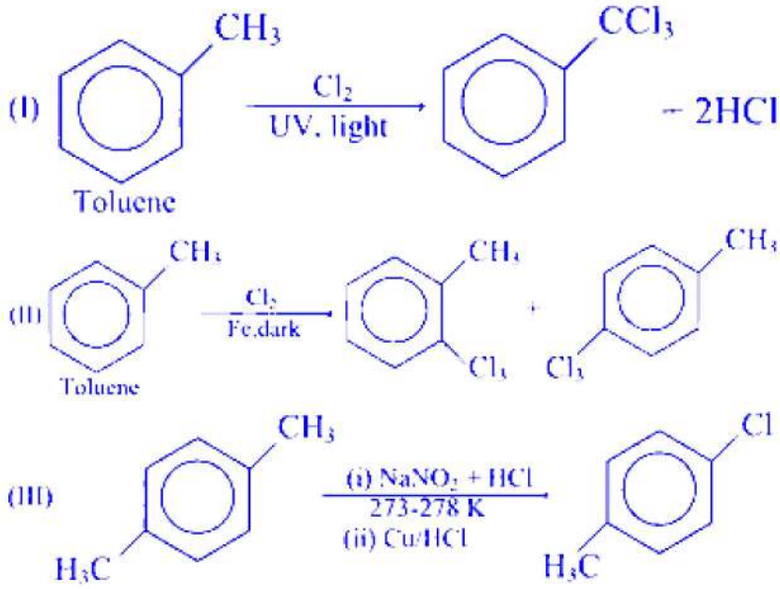
D.

I, II, III

Answer: C

Solution:

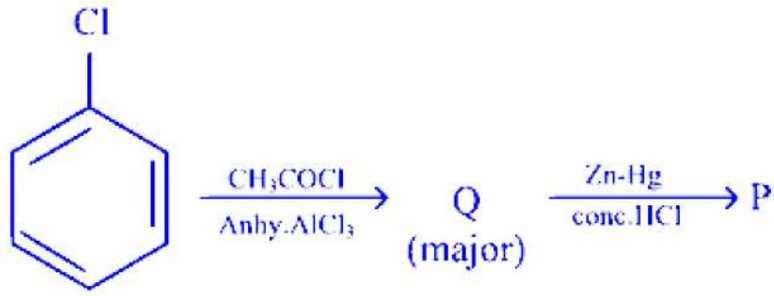
The complete reaction sequence are as follows



Thus, *p*-chlorotoluene is the major product formed in II and III.

Question5

What is the ratio of sp^3 carbons to sp^2 carbons in the product ' P ' of the given sequence of reactions?



AP EAPCET 2025 - 24th May Morning Shift

Options:

A.

3 : 1

B.

2 : 1

C.

1 : 2

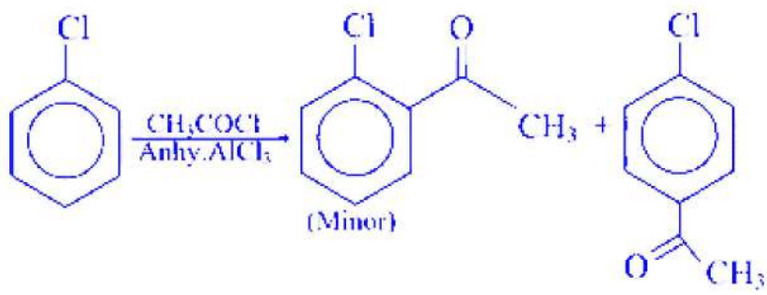
D.

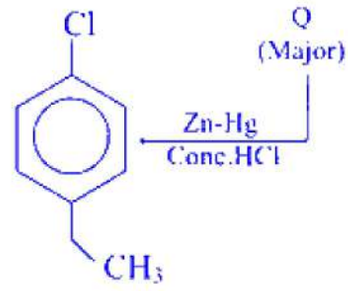
1 : 3

Answer: D

Solution:

The complete reaction sequence is as follows





(P)

Now number of sp^3 carbon are 2 while number of sp^2 carbons are 6 . So, their ratio is 2 : 6 or 1 : 3.

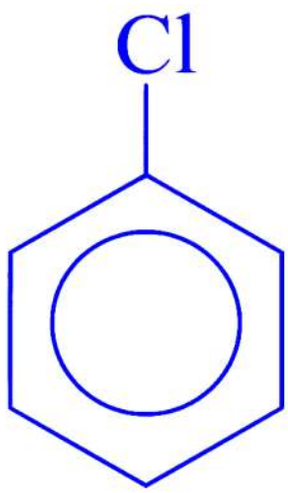
Question6

The most reactive compound towards nucleophilic substitution with an aqueous NaOH is

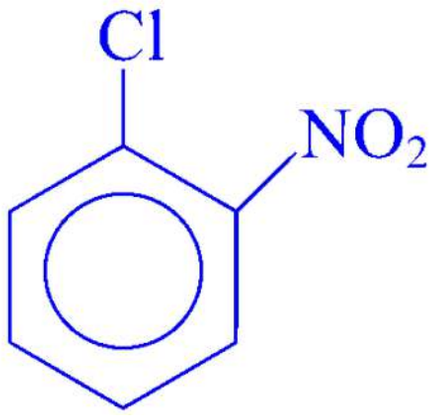
AP EAPCET 2025 - 23rd May Evening Shift

Options:

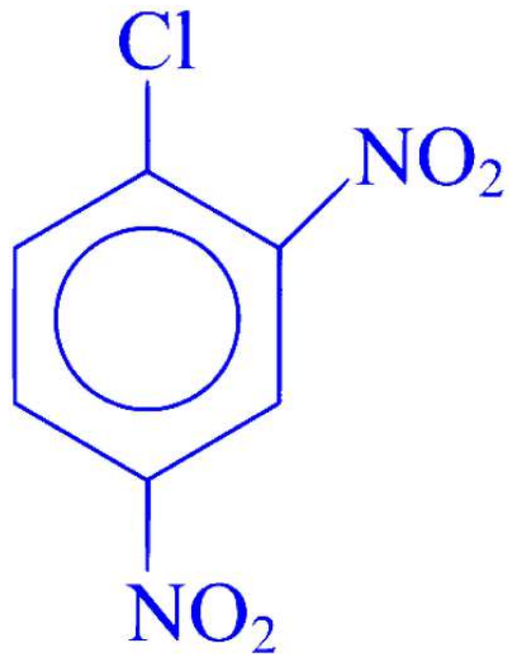
A.



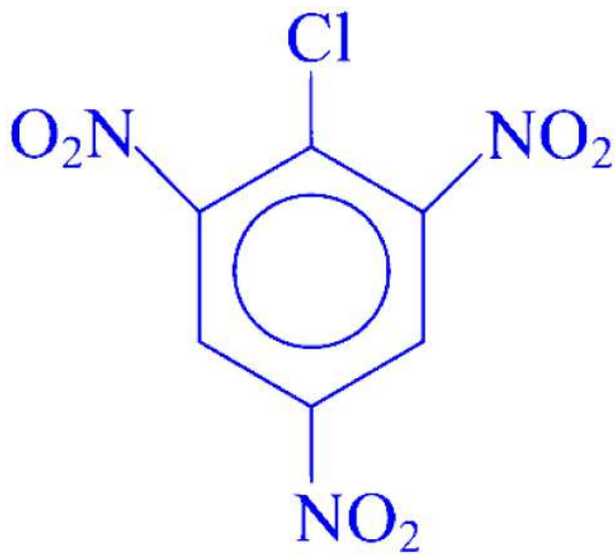
B.



C.



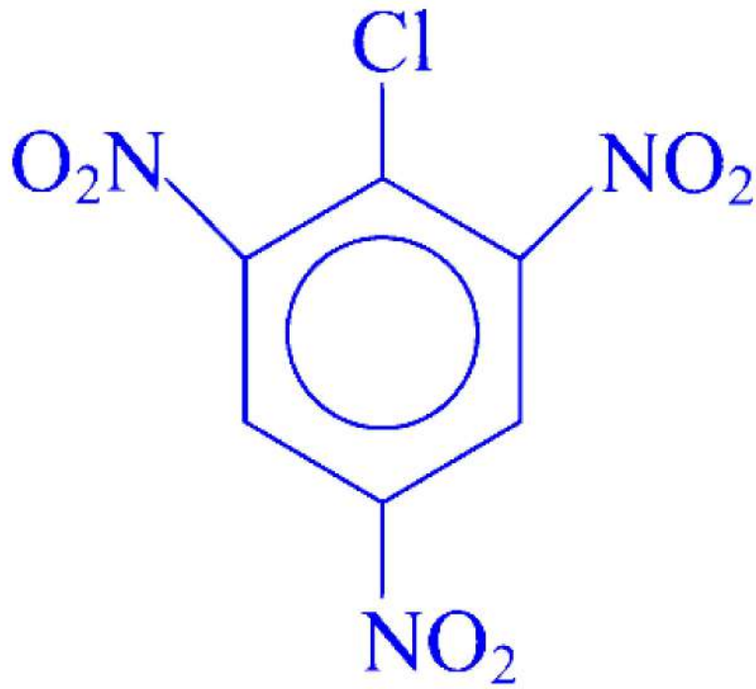
D.



Answer: D

Solution:

The presence of an electron withdrawing group like $-NO_2$ at ortho and para positions increases the reactivity of haloarenes. Thus among the given options



is most reactive towards nucleophilic substitution with an aqueous NaOH .

Question7

Identify the correct set from the following

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Options:

A.

$CHCl_3$ - used in production of freon - 12.

B.

CCl_4 - used in production of freon - 22.

C.

CH_2Cl_2 - used as propellant in aerosols.

D.

DDT - first chlorinated organic herbicide.

Answer: C

Solution:

The correct statement is CH_2Cl_2 - used as propellant in aerosols.

Question8

The preferred reagent for the preparation of pure alkyl chloride from alcohol is

AP EAPCET 2025 - 22nd May Evening Shift

Options:

A.

$HCl + ZnCl_2$

B.

PCl_5

C.

$SOCl_2$

D.

PCl_3

Answer: C

Solution:

- **Option A: HCl + $ZnCl_2$ (Lucas Reagent)**
  - Reaction: $\mathrm{ROH + HCl \xrightarrow{ZnCl_2} RCl + H_2O}$
  - Byproduct: Water (H_2O). Water needs to be separated from the alkyl chloride, which can be challenging, especially for lower molecular weight alkyl chlorides that may be soluble in water or form azeotropes. This makes obtaining *pure* alkyl chloride directly difficult.
- **Option B: PCl_5 (Phosphorus Pentachloride)**
  - Reaction: $\mathrm{ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl}$
  - Byproducts: Phosphorus oxychloride ($POCl_3$) and hydrogen chloride (HCl). $POCl_3$ is a liquid, and HCl is a gas. The separation of these byproducts from the desired alkyl chloride may require careful distillation or other purification steps, affecting the direct purity.
- **Option C: $SOCl_2$ (Thionyl Chloride)**
  - Reaction: $\mathrm{ROH + SOCl_2 \xrightarrow{Pyridine} RCl + SO_2\uparrow + HCl\uparrow}$
  - Byproducts: Sulfur dioxide (SO_2) and hydrogen chloride (HCl). Both of these are gases. They readily escape from the reaction mixture as they are formed. This leaves behind a relatively pure alkyl chloride, making the purification process very simple and efficient. This is often considered the best method for preparing pure alkyl halides because the gaseous byproducts automatically separate from the desired product.
- **Option D: PCl_3 (Phosphorus Trichloride)**
  - Reaction: $\mathrm{3ROH + PCl_3 \rightarrow 3RCl + H_3PO_3}$
  - Byproduct: Phosphorous acid (H_3PO_3). This is a non-volatile solid or viscous liquid. It needs to be separated from the alkyl chloride, typically by distillation or extraction, which adds purification steps.

Conclusion:

Among the given reagents, $SOCl_2$ (thionyl chloride) is the preferred reagent for the preparation of pure alkyl chloride from alcohol because the byproducts (SO_2 and HCl) are gases that escape from the reaction mixture, leaving behind a pure alkyl chloride.

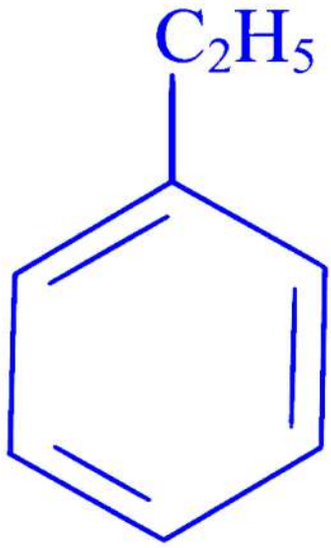
The final answer is $\boxed{SOCl_2}$.

Question9

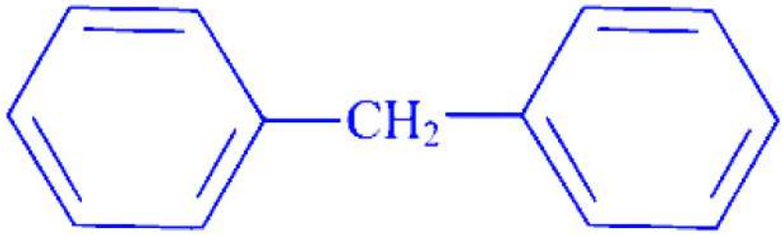
Which of the following is the product of Fittig reaction?

AP EAPCET 2025 - 22nd May Morning Shift

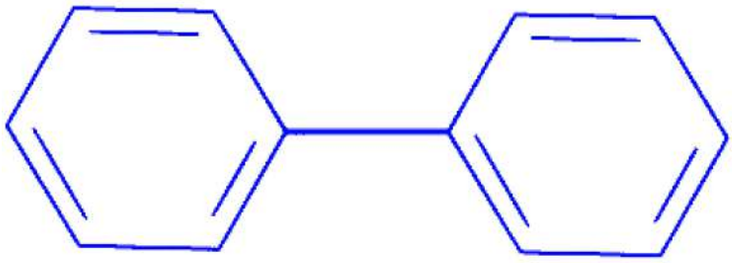
Options:

A. 

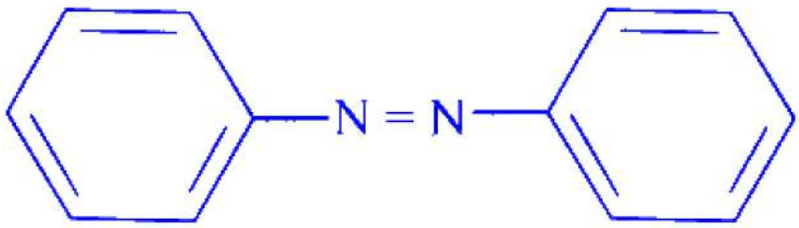
B.



C.



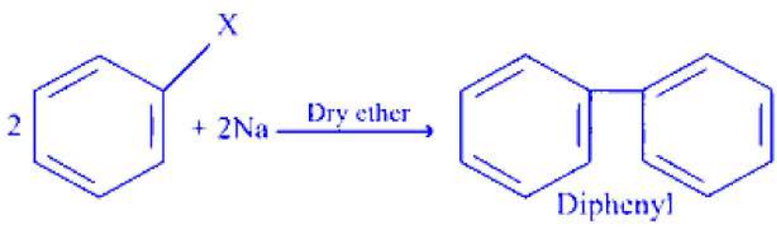
D.



Answer: C

Solution:

Fittig reaction : When aryl halide react with sodium in presence of dry ether to form a biaryl compound.



Question10

Match the following

List-I (Halide type)		List-II (Example)	
(A)	Vinyl	(I)	1-bromo-1-phenylethane
(B)	Allyl	(II)	3-bromotoluene
(C)	Benzyl	(III)	1-bromo-3-methylcyclohexene
(D)	Aryl	(IV)	3-bromo-4-methylcyclohexene

Correct answer is

AP EAPCET 2025 - 22nd May Morning Shift

Options:

A.

A-III, B-IV, C-II, D-I

B.

A-III, B-IV, C-I, D-II

C.

A-II, B-III, C-I, D-IV

D.

A-I, B-II, C-IV, D-III

Answer: B

Solution:

Let's define each type of halide and then match it with the given examples.

Definitions:

- **Vinyl Halide:** A compound in which the halogen atom (X) is directly attached to an sp^2 hybridized carbon atom of an alkene. The general structure is R-CH=CX-R' or R_2C=CX-R'.
- **Allyl Halide:** A compound in which the halogen atom (X) is attached to an sp^3 hybridized carbon atom that is adjacent to a carbon-carbon double bond (an allyl group). The general structure is R-CH=CH-CH_2-X.
- **Benzyl Halide:** A compound in which the halogen atom (X) is attached to an sp^3 hybridized carbon atom that is directly attached to an aromatic ring (a benzyl group). The general structure is Ar-CH_2-X. The carbon bearing the halogen can be primary, secondary, or tertiary.
- **Aryl Halide:** A compound in which the halogen atom (X) is directly attached to an sp^2 hybridized carbon atom of an aromatic ring. The general structure is Ar-X.

Matching the Examples:

- **(A) Vinyl Halide:**
  - (III) **1-bromo-3-methylcyclohexene**: In this molecule, the double bond can be assumed to be between C1 and C2. If the bromine is at C1, then C1 is part of the double bond (sp^2 hybridized). Thus, it's a vinyl halide.
  - *Match: A - (III)*
- **(B) Allyl Halide:**
  - (IV) **3-bromo-4-methylcyclohexene**: If the double bond is between C1 and C2, then C3 is an sp^3 hybridized carbon adjacent to the double bond. If bromine is at C3, it is attached to an allylic carbon.
  - *Match: B - (IV)*
- **(C) Benzyl Halide:**
  - (I) **1-bromo-1-phenylethane**: The structure is C_6H_5-CH(Br)-CH_3. The carbon bearing the bromine is an sp^3 hybridized carbon atom and is directly attached to the phenyl group (an aromatic ring). This is a secondary benzyl halide.
  - *Match: C - (I)*
- **(D) Aryl Halide:**
  - (II) **3-bromotoluene**: The structure is CH_3-C_6H_4-Br (meta-bromotoluene). The bromine atom is directly attached to one of the sp2 hybridized carbon atoms of the benzene ring.
  - *Match: D - (II)*

Summary of Matches:

- A - III
- B - IV
- C - I

- D - II

Comparing this with the given options, Option B is the correct answer.

The final answer is Option BOption B

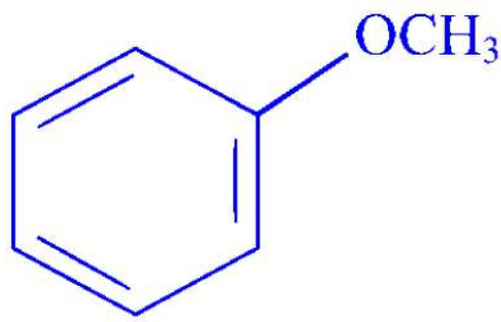
Question11

Which of the following does not involve in Friedel-Craft reaction?

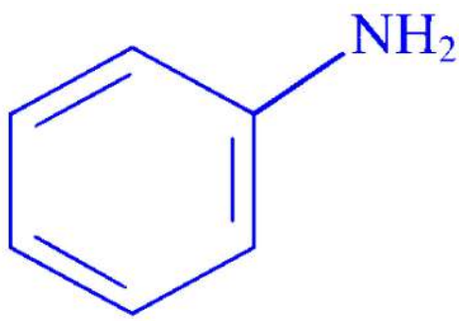
AP EAPCET 2025 - 21st May Evening Shift

Options:

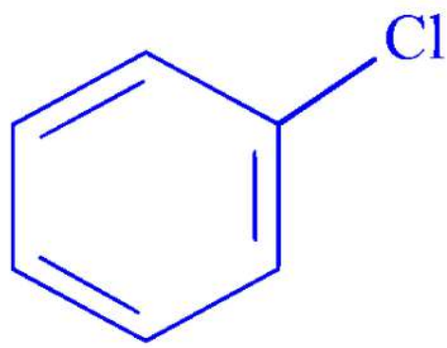
A.



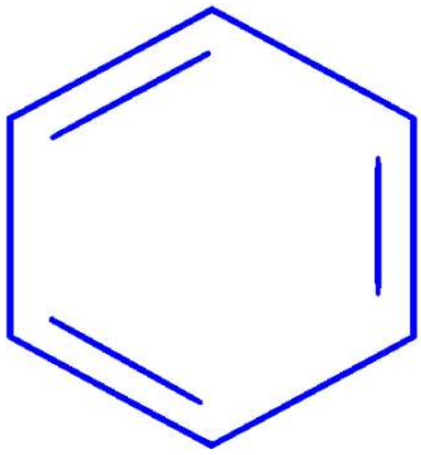
B.



C.



D.



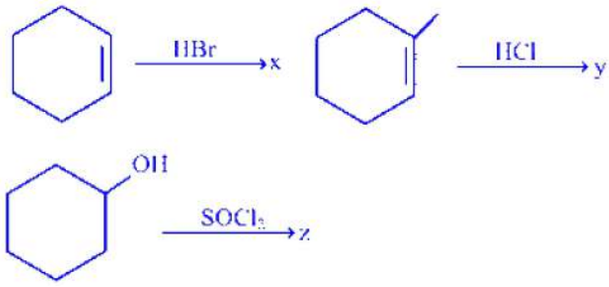
Answer: B

Solution:

Aniline does not undergoes Friedel-Craft reaction due to the Lewis basicity of nitrogen atom in aniline, which react with Lewis acid catalyst ($AlCl_3$), forming complex that deactivates the benzene ring and undergoes further electrophilic substitution.

Question12

Observe the following reactions Observe the following reactions



The order of reactivity of x,y,z towards SN1 reaction is

AP EAPCET 2025 - 21st May Morning Shift

Options:

A. x>z>y

B. x>y>z

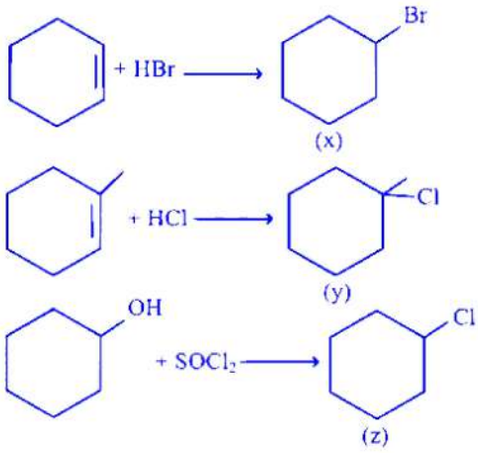
C. y>x>z

D. y>z>x

Answer: C

Solution:

The complete reaction sequence is as follow



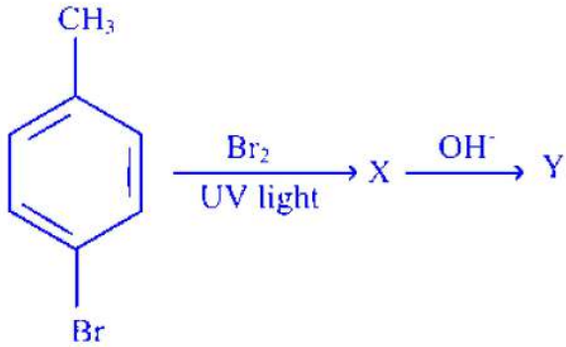
Now, we know that order for SN1 reaction is 3∘ halide >2∘ halide >1∘ halide >CH3X and

R−I>R−Br>R−Cl>R−F

Thus, the correct order is y>x>z

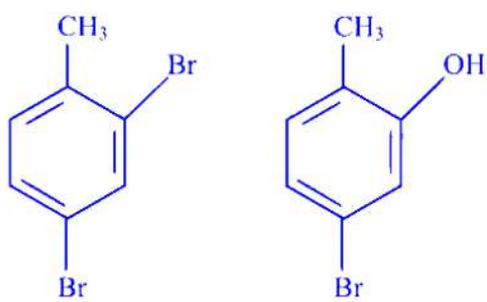
Question13

What are X and Y respectively in the following reactions?

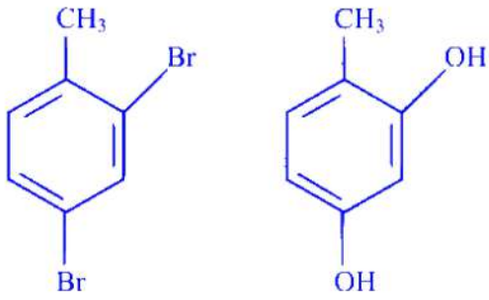


AP EAPCET 2024 - 23th May Morning Shift

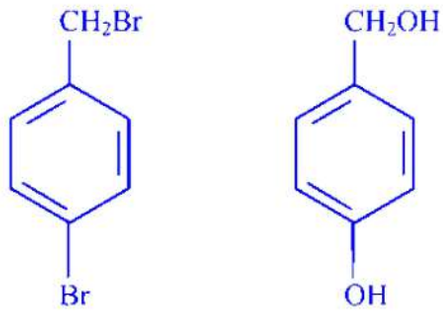
Options:

A. 

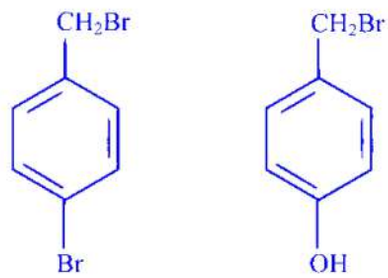
B.



C.

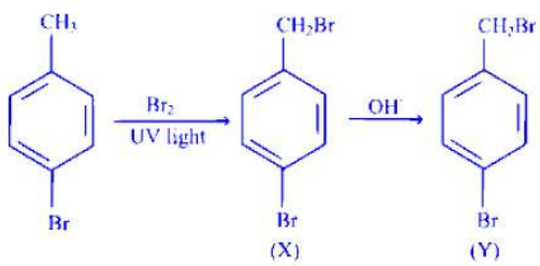


D.

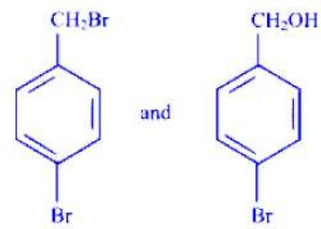


Answer: C

Solution:



Thus X and Y are



and

Question14

The sequence of reagents required to convert ethylbromide to propanal is

AP EAPCET 2024 - 23th May Morning Shift

Options:

A. CH_3COOAg,DIBAL - H, H_2O

B. CH_3COOAg,$LiAlH_4$,H_2O

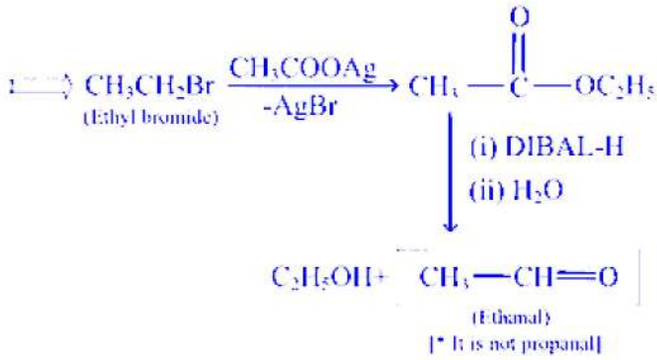
C. Mg/ether ,HCHO ,H_2O

D. CH_3COOH,$LiAlH_4$,H_2O

Answer: A

Solution:

The sequence of reagents required to convert ethylbromide to propanal is CH_3COOAg, DIBAL-H and H_2O.



Question15

Which of the following is not an example of allylic halide?

AP EAPCET 2024 - 22th May Evening Shift

Options:

A. 4-chlorobut - 1-ene

B. 1-chlorobut -2-ene

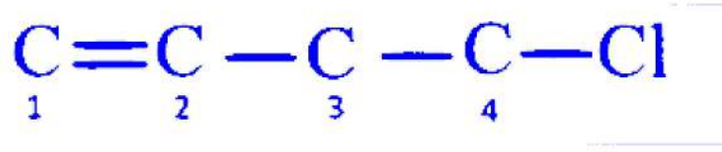
C. 3-chloro - 2 - methyl but-1 - ene

D. 4 - chloropent - 2 - ene

Answer: A

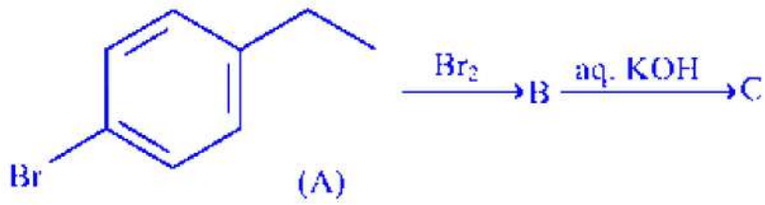
Solution:

Allylic halides are those compound 156 where the halogen group is attached to a sp^3 hybridised carbon atom and at α- to the carbon-carbon double bond. 4-chlorobut-1-ene is not allylic halide.



Question16

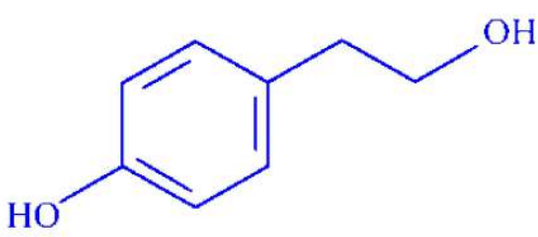
The product (C) in the following reaction sequenceis



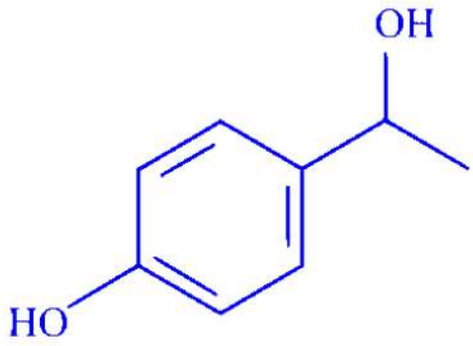
AP EAPCET 2024 - 22th May Morning Shift

Options:

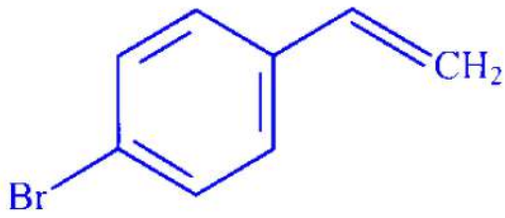
A.



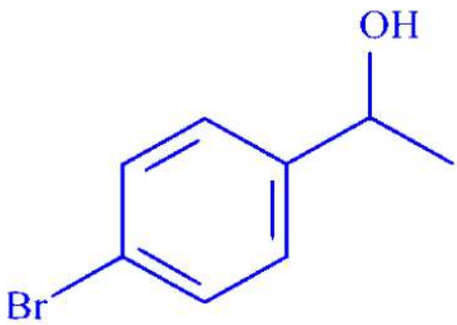
B.



C.



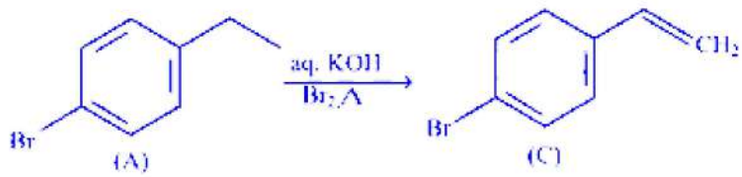
D.



Answer: D

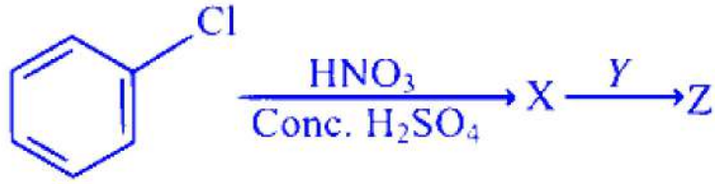
Solution:

The product *C* formed will be as follows



Question17

What are Y and Z respectively in the following reaction sequence?

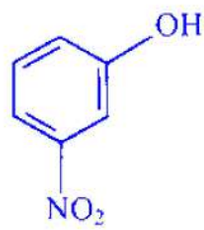


AP EAPCET 2024 - 21th May Evening Shift

Options:

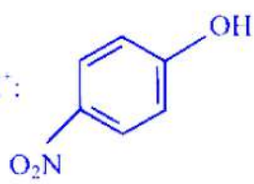
A.

(i) NaOH,443K,H^+:



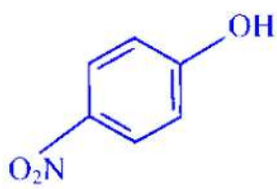
B.

(i) NaOH,443K,(ii)H^+:



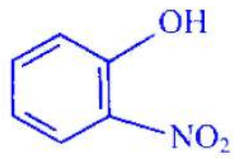
C.

H_2O,Δ:



D.

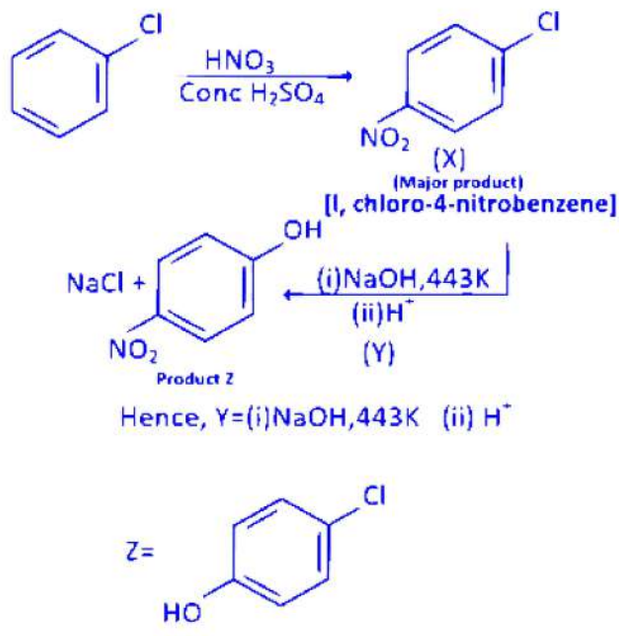
H_2O,Δ;



Answer: B

Solution:

The complete reaction is as follows.



Question18

Which of the following alkenes does not undergo anti Markownikoff addition of HBr ?

AP EAPCET 2024 - 21th May Morning Shift

Options:

A. Propene

B. 1-butene

C. 2-butene

D. 3-methyl-2-pentene

Answer: C

Solution:

In the presence of peroxide, addition of HBr to unsymmetrical alkenes takes place contrary to the Markownikoff rule. In case of 2-butene both double bonded carbons are identical. Therefore, it does not observe anti-Markownikoff addition of HBr .

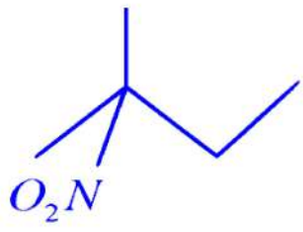
Question19

An isomer of C_5H_{12} on reaction with Br_2 /light gave only one isomer $C_5H_{11}Br(X)$. Reaction of X with $AgNO_2$ gave Y as major product. What is Y ?

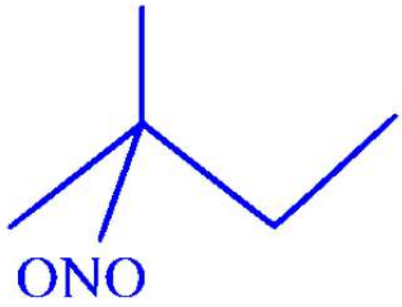
AP EAPCET 2024 - 21th May Morning Shift

Options:

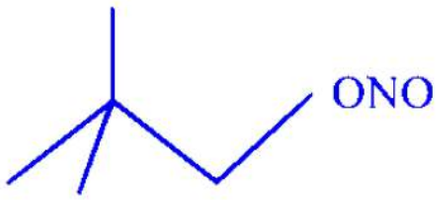
A.



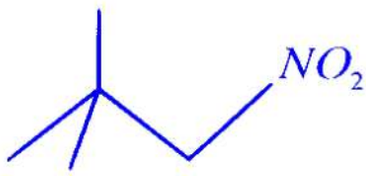
B.



C.

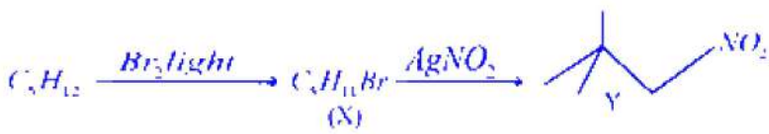


D.



Answer: A

Solution:



Question20

What are the major products X and Y respectively in the following reactions?

$$(CH_3)_3CONa + CH_3CH_2Br \longrightarrow X$$
$$(CH_3)_3CBr + CH_3CH_2ONa \longrightarrow Y$$

AP EAPCET 2024 - 21th May Morning Shift

Options:

A. $CH_2 = CH_2, (CH_3)_3COCH_2CH_3$

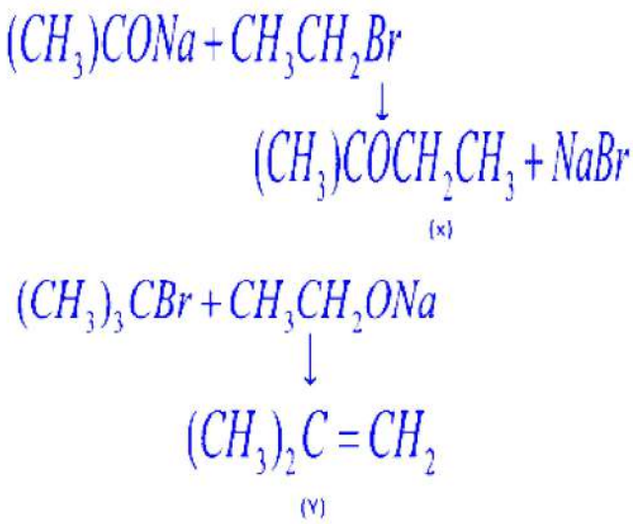
B. $(CH_3)_3COCH_2CH_3, (CH_3)_3COCH_2CH_3$

C. $CH_2 = CH_2, (CH_3)_2C = CH_2$

D. $(CH_3)_3COCH_2CH_3, (CH_3)_2C = CH_2$

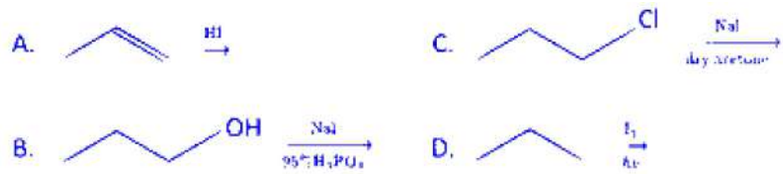
Answer: D

Solution:



Question21

Which of the following are general methods for the preparation of 1 -iodopropane?



AP EAPCET 2024 - 20th May Evening Shift

Options:

A. A, B

B. B, C

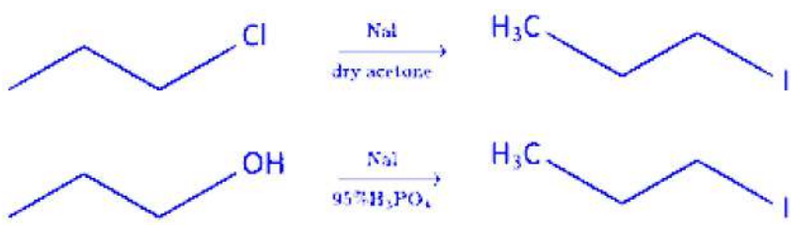
C. C, D

D. A, D

Answer: B

Solution:

Among the given reaction 1 -iodopropane can be prepared by reactions given are *B* and *C* only.



Question22

Which of the following sequence of reagents convert propene to 1-chloropropane?

AP EAPCET 2024 - 20th May Evening Shift

Options:

A. (i) $(BH_3)_2$ (ii) H_2O_2/OH^- : $HCl, ZnCl_2$

B. (i) $(BH_3)_2$ (ii) H_2O_2/OH^- : $NaCl$

C. (i) dil. H_2SO_4 : $HCl, ZnCl_2$

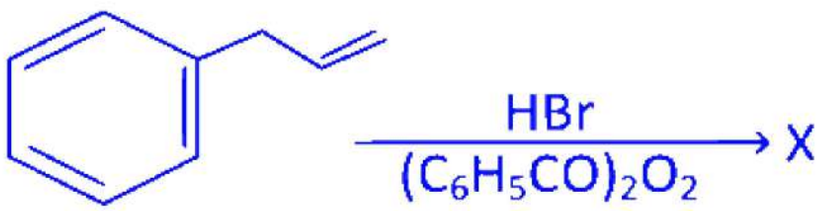
D. (i) dil. H_2SO_4 : Conc. HCl

Answer: A

Solution:

Question23

The major product (X) formed in the given reaction is an example of



AP EAPCET 2024 - 19th May Evening Shift

Options:

A. secondary alkyl halide

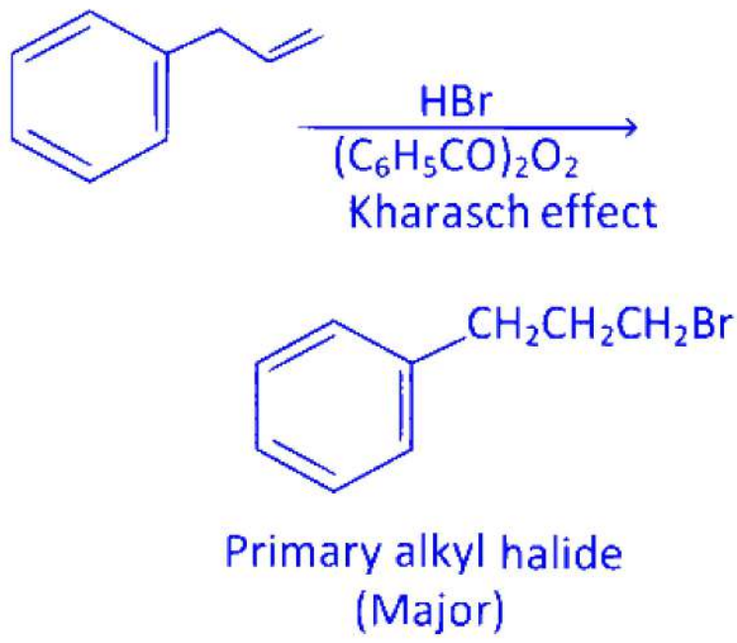
B. primary alkyl halide

C. tertiary alkyl halide

D. benzylic halide

Answer: B

Solution:



Question24

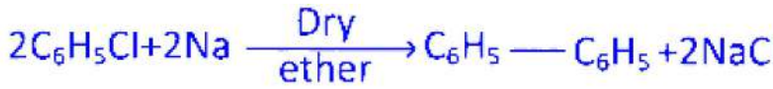
Identify the Swarts reaction from the following

AP EAPCET 2024 - 19th May Evening Shift

Options:

A. 

B. 

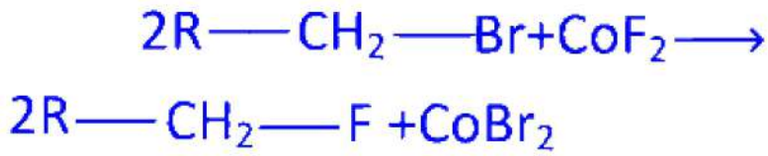
C. 

D. 

Answer: D

Solution:

When alkyl chloride/bromide is heated in presence of fluoride of same heavy metal alkyl fluoride is obtained. This reaction is named as Swarts reaction.



Question25

Chlorobenzene (X) when reacted with reagent (A) geb converted to phenol (Y). The major product obtained from nitration of (X) gets converted to p-nitrophend (Z) by reaction with reagent (B). What are A and B respectively?

AP EAPCET 2024 - 18th May Morning Shift

Options:

A. $\mathrm{A} =$ (i) NaOH, 623 K, 300 atm (ii) H^{+}; $B =$ (i) NaOH, 443 K (ii) H^{+}

B. $A =$ (i) $NaOH$, 443 K (ii) H^+; $B = H_2O$. Δ

C. $A =$ (i) $NaOH$, 323 K (ii) H^+; $B =$ (i) $NaOH$, 443 K (ii) H^+

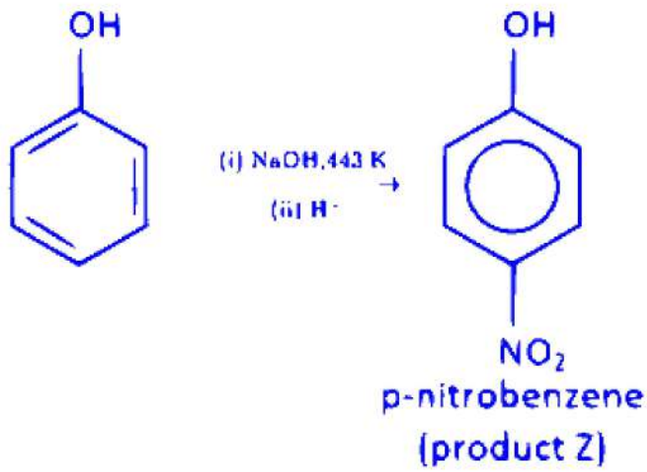
D. $A =$ (i) $NaOH$, 623 K, 300 atm (ii) H^+; $B = H_2O$. Δ

Answer: A

Solution:

When chlorobenzene (X) is reacted with reagent NaOH (A) it produce phenol.

When chlorobenzene goes through nitration.



Hence, $A =$ (i) $NaOH$, 623 K, 300 atm (ii) $H^+ B =$ (i) $NaOH$, 443 K (ii) H^+

Question26

Match the following reactions with the prodact obtained from them.

List-I	List-II
A Sandmeyer reaction	I $R - I$
B Finkelstein reaction	II $R - F$

C Swarts reaction	III $\mathrm{Ar-Br}$
	IV $R-\mathrm{Br}$

AP EAPCET 2024 - 18th May Morning Shift

Options:

A. A− III, B−I,C−IV

B. A−IV,B=II,C−I

C. A−III,B−IV,C−II

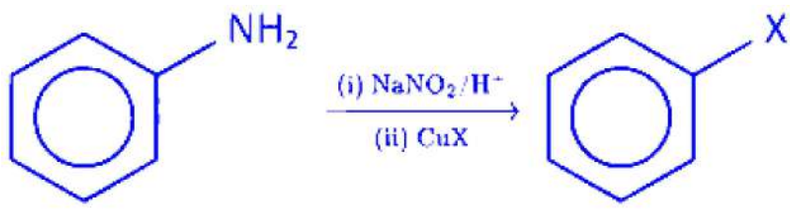
D. A= III, B-I, C - II

Answer: D

Solution:

The correct match is A-III, B-I, C-II.

Sandmeyer reaction is a reaction used to synthesis aryl halides from aryl diazonium salt.



Finkelstien reaction is a halogen (X) exchange method. It is used to prepare alkyl iodide by reaction of alkyl chlorides/bromides with NaI in dry acetone.

$$\underset{(x=\mathrm{Cl,Br})}{R-X}+\mathrm{NaI}\xrightarrow{\text{Acetone}}R\mathrm{I}+\mathrm{NaX}$$

Swartz reaction is used to get alkyl fluorides from alkyl chlorides.

$R-\mathrm{Br}+\mathrm{AgF}\longrightarrow R-\mathrm{F}+\mathrm{AgBr}$

Question27

An alkyl halide $\mathrm{C_3H_7CL}$. on reaction with a reagent X gave the major product Y $(\mathrm{C_4H_7\ N})$. Y on hydrolysis released gas. Which turns red litmus to blue. What are X and Y ?

AP EAPCET 2024 - 18th May Morning Shift

Options:

A. KCN/C_2H_5OH 

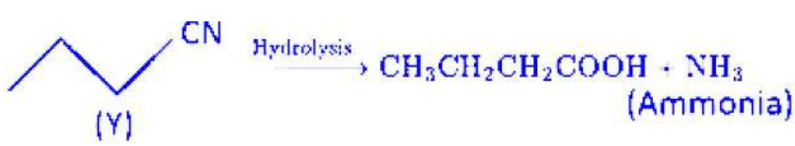
B. KCN/C_2H_5OH 

C. $AgCN/C_2H_5OH$ 

D. $AgCN/C_2H_5OH$ 

Answer: B

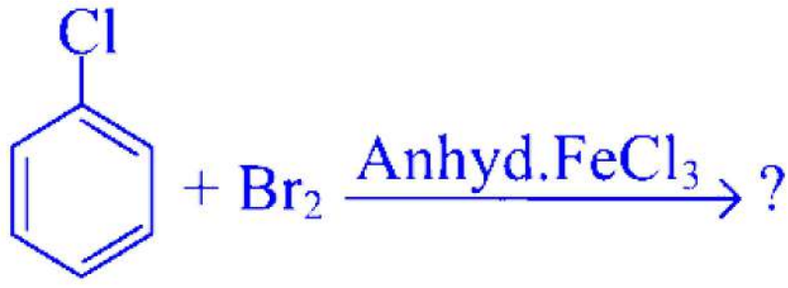
Solution:



The ammonia gas released will turn red litmus to blue. Thus, the compound X and Y are KCN/C_2H_5OH and $CH_3CH_2CH_2CN$.

Question28

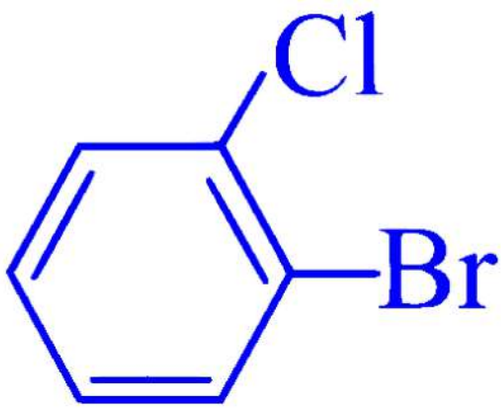
Identify the major product of the following reaction.



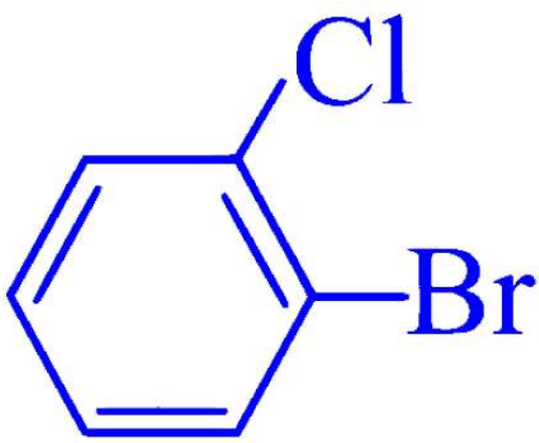
AP EAPCET 2022 - 5th July Morning Shift

Options:

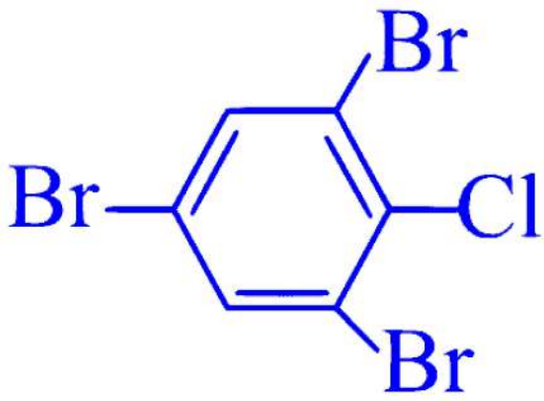
A.



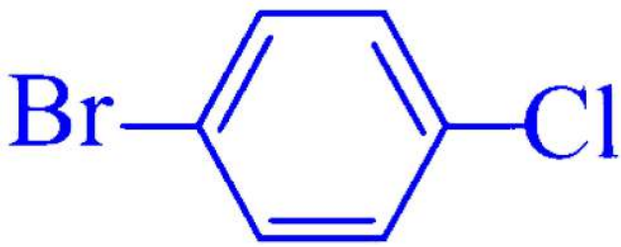
B.



C.

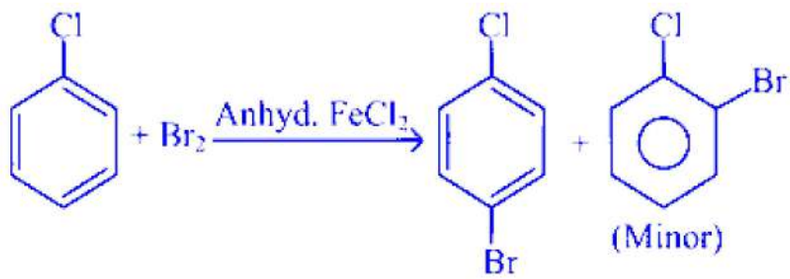


D.



Answer: D

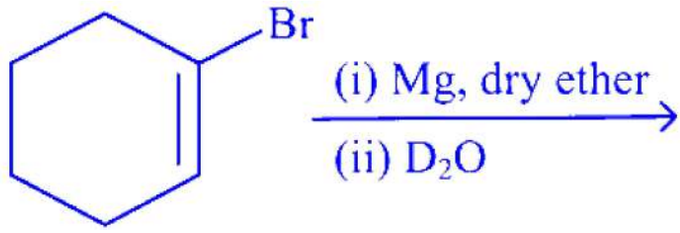
Solution:



Cl has $-I$ and $+R$-effect. Due to electron donating resonance effect it is ortho/para-directing and donates the electron density to benzene ring. Thus, the incoming electrophile -Br gets attached on para-position and para disubstituted product is obtained as major product and ortho as minor product.

Question29

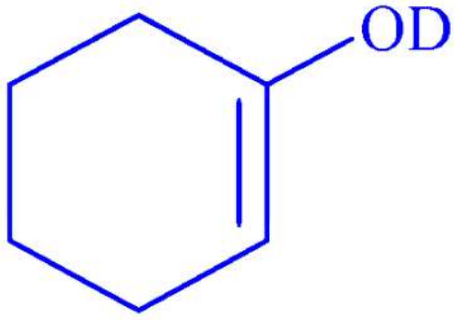
The major product of the following reaction is



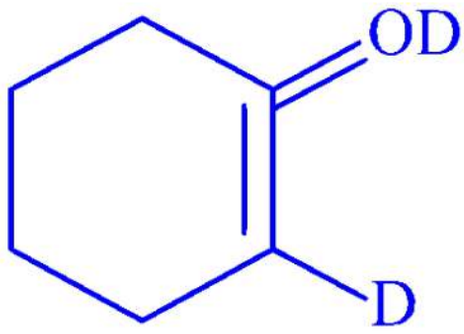
AP EAPCET 2022 - 4th July Evening Shift

Options:

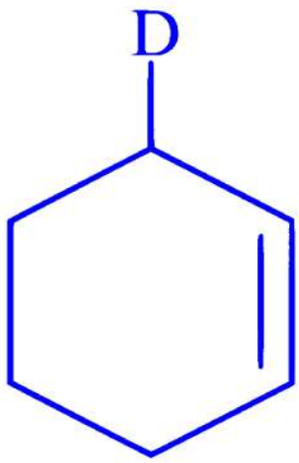
A.



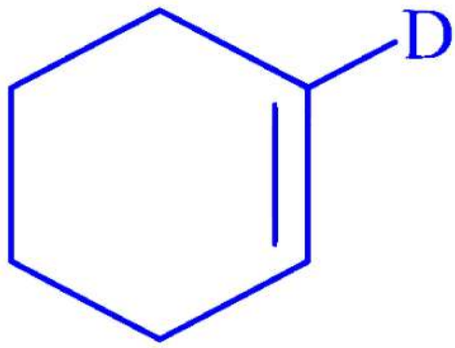
B.



C.



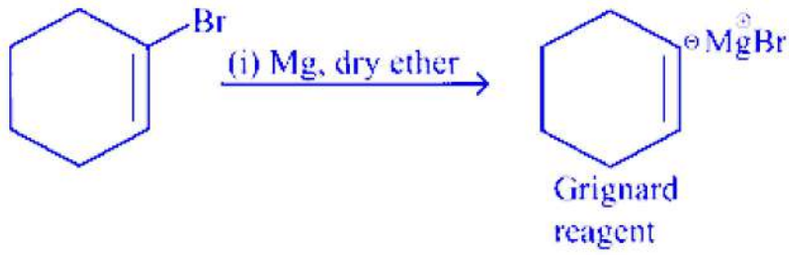
D.



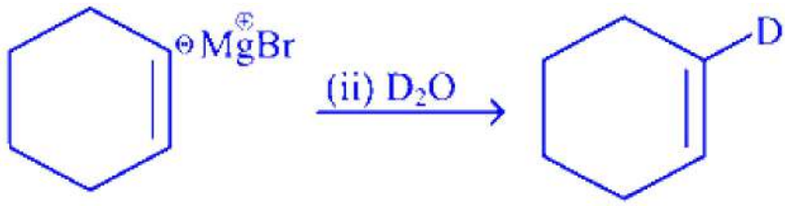
Answer: D

Solution:

Alkenyl bromide reacts with Mg in dry ether to form Grignard reagent.



Grignard reagent abstracts acidic proton. So, it takes D^+ form D_2O.



Question30

Finkelstein reaction is used for the synthesis of

AP EAPCET 2022 - 4th July Evening Shift

Options:

A. RF

B. RI

C. RCl

D. RBr

Answer: B

Solution:

Finkelstein reaction is an S_N2 reaction that involves the exchange of one halogen by iodine. In this reaction, alkyl chloride/bromides are treated with sodium iodide in acetone to form alkyl iodide and NaCl/NaBr. Acetone is used because NaCl/NaBr are less soluble in acetone hence, they can precipitate out.

$$R-\mathrm{Cl}+\mathrm{NaI}\xrightarrow{\text{Acetone}}R-\mathrm{I}+\mathrm{NaCl}\downarrow$$

Question31

Which among the following will have highest density?

AP EAPCET 2022 - 4th July Evening Shift

Options:

A. CCl_4

B. $n-C_3H_7I$

C. $n-C_3H_7Br$

D. $n-C_3H_7Cl$

Answer: B

Solution:

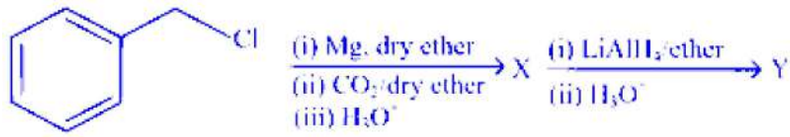
Density is directly proportional to mass. The molar masses of the compounds are as follows:

$$\begin{aligned}
CCl_4 &\rightarrow 12+142=154\ \mathrm{g/mol}\\
n-C_3H_7I &\rightarrow (12\times 3)+(7\times 1)+127=170\ \mathrm{g/mol}\\
n-C_3H_7Br &\rightarrow (12\times 3)+(7\times 1)+80=123\ \mathrm{g/mol}\\
n-C_3H_7Cl &\rightarrow (12\times 3)+(7\times 1)+35.5=78.5\ \mathrm{g/mol}
\end{aligned}$$

Since the molar mass of $n-C_3H_7I$ is the highest, it will also have the highest density.

Question32

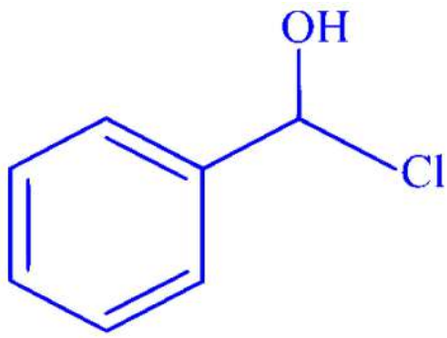
Identify the major product (Y) from the following reaction,



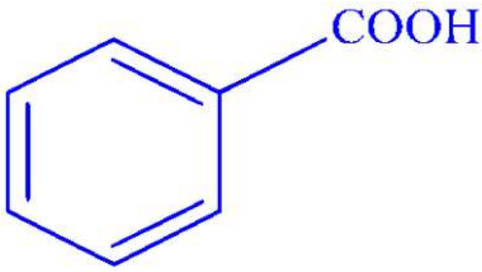
AP EAPCET 2022 - 4th July Evening Shift

Options:

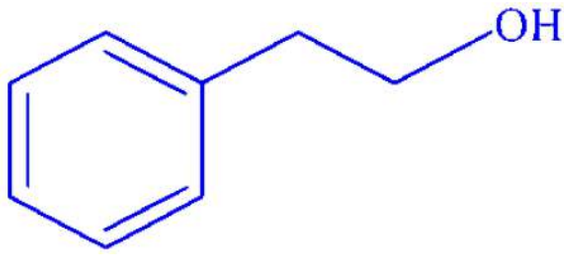
A.



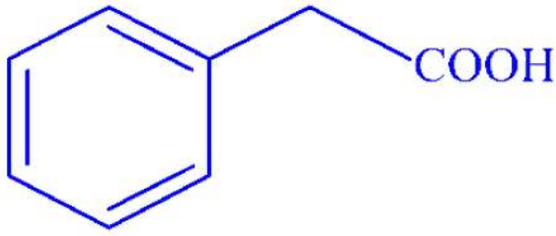
B.



C.



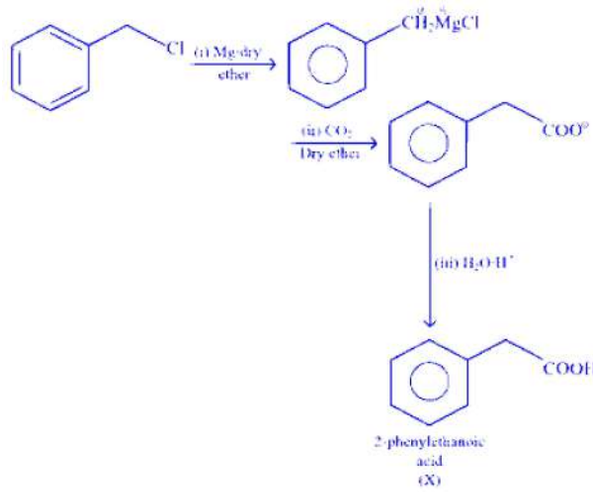
D.



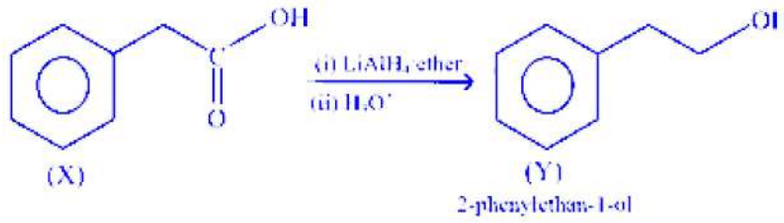
Answer: C

Solution:

Benzyl chloride reacts with Mg in presence of dry ether to form Grignard reagent (G.R.) and on treating with CO_2, G.R. form carboxylate ion which on hydrolysis give carboxylic acid.

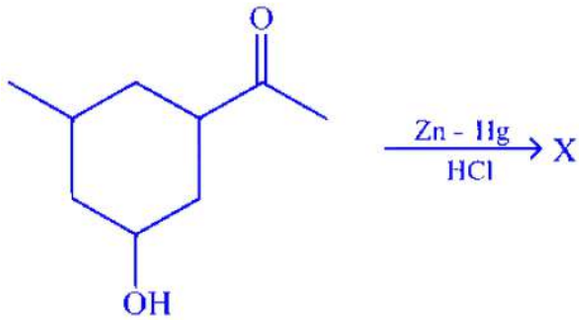


X on treatment with $LiAlH_4$ ether followed by acidic hydrolysis give alcohol as *Y* product.



Question33

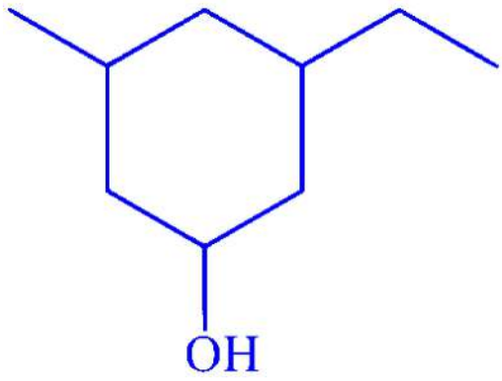
Identify the major product of the following reaction.



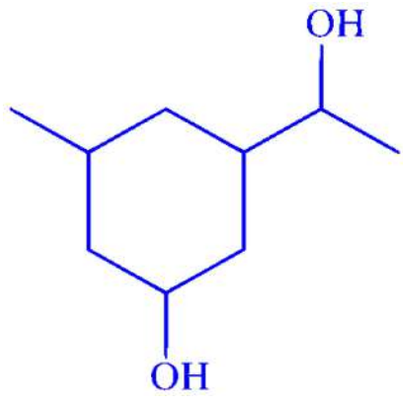
AP EAPCET 2022 - 4th July Evening Shift

Options:

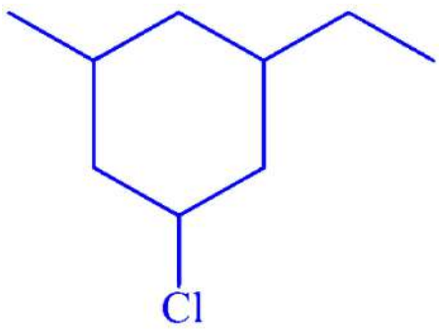
A.



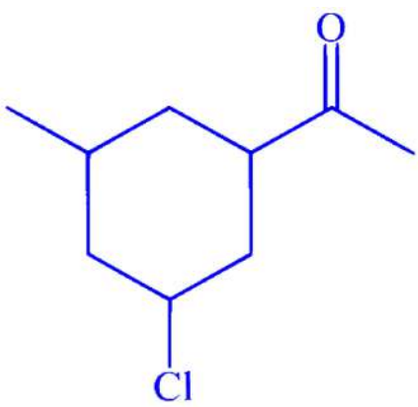
B.



C.



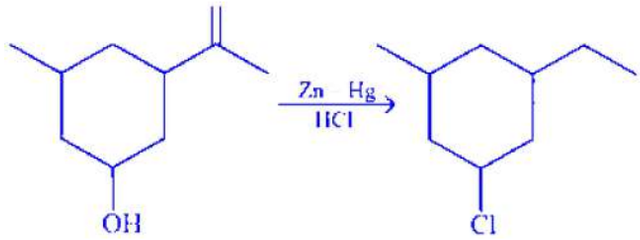
D.



Answer: C

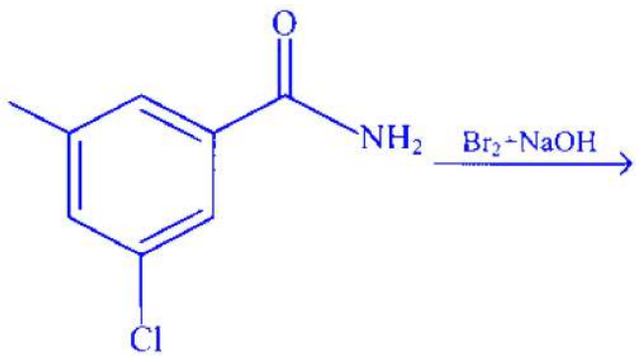
Solution:

Zn − Hg/HCl is used to reduce carbonyl compounds to alkane. This reaction is called Clemmenson reduction. But in presence of basic groups like −OH, $-NH_2$ etc. side reaction also takes place. In this case substitution of alcoholic group by $Cl^{\ominus}$ will take place.



Question34

Identify the major product of the following reaction,

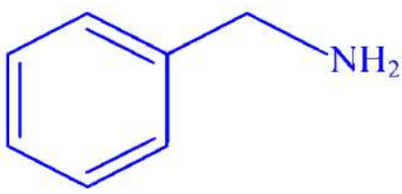


AP EAPCET 2022 - 4th July Evening Shift

Options:

A.

B.



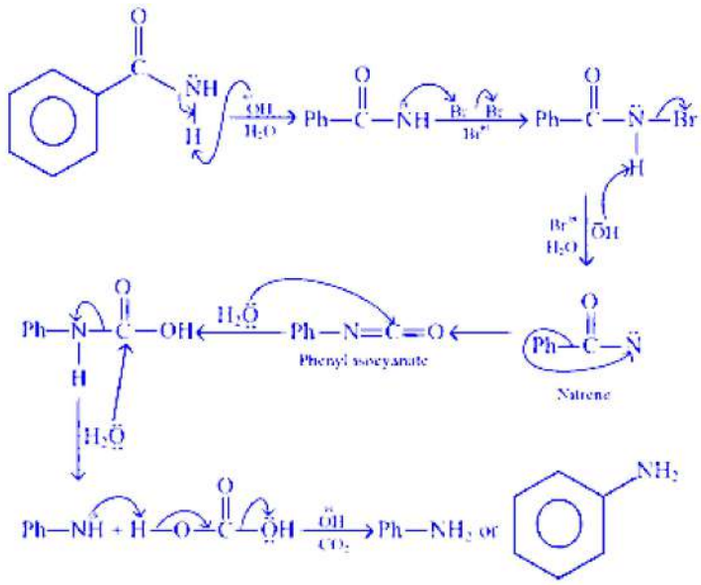
C.

D.

Answer: D

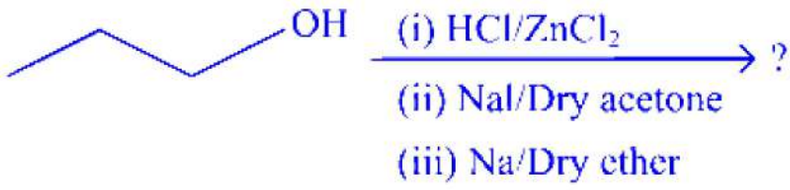
Solution:

Amides reacts with Br_2 in presence of an alkali base (KOH, NaOH) to form amine. This reaction is known as Hofmann bromamide reaction. This reaction proceeds via formation of nitrene intermediate.



Question35

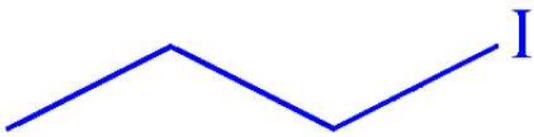
Identify the major product formed from the following.



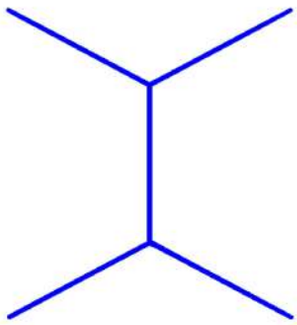
AP EAPCET 2022 - 4th July Morning Shift

Options:

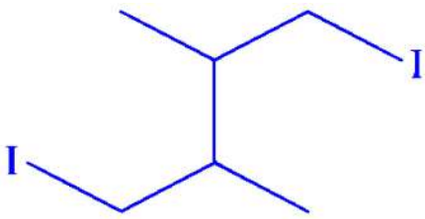
A.



B.



C.

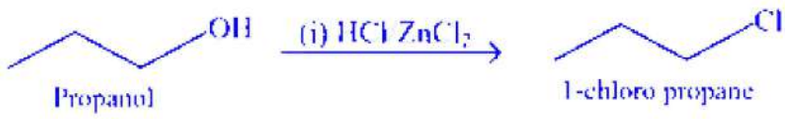


D.

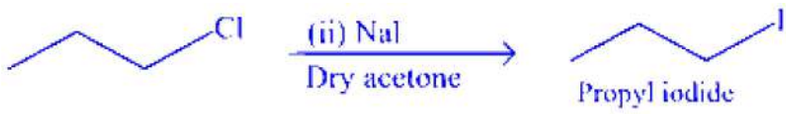
Answer: D

Solution:

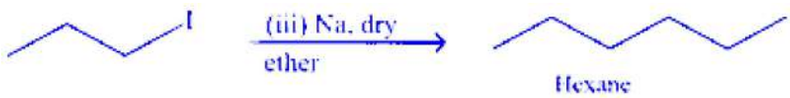
First step in the given reaction is "Lucas test" in which alcohols react with $HCl/ZnCl_2$ to give alkyl halides.



Second step proceed via nucleophilic substitution bimolecular (S_N2) mechanism. Here, I^- replaces Cl to form alkyl iodide.



Third step is "Wurtz reaction" in which two alkyl iodide reacts with Na in presence of dry ether to form alkane with even number of carbon atoms.



Question36

When 1-chlorobutane is treated with aqueous KOH it gives P. However, when it is treated with alcoholic KOH it gives Q. Identify the products P and Q respectively

AP EAPCET 2022 - 4th July Morning Shift

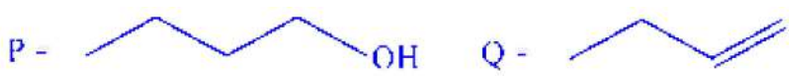
Options:

A.

B.

C.

D.

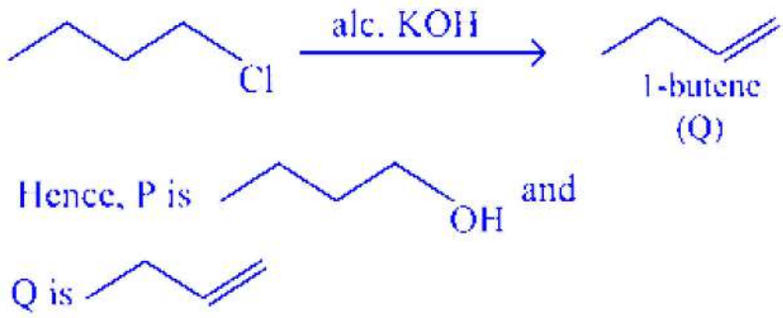


Answer: D

Solution:

1-chlorobutane reacts with aq. KOH to give 1-butanol by S_N2 reaction.

However, 1-chlorobutane reacts with alc. KOH to give 1-butene by elimination reaction.



Question37

An organic compound of molecular formula$C_6H_6Br_2$ has six carbon atoms in a ringsystem, two non-conjugate double bonds andtwo bromo groups at 1, 4-positions. Then thecompound is

AP EAPCET 2021 - 20th August Morning Shift

Options:

A. aromatic but non-homo-cyclic

B. aromatic and hetero-cyclic

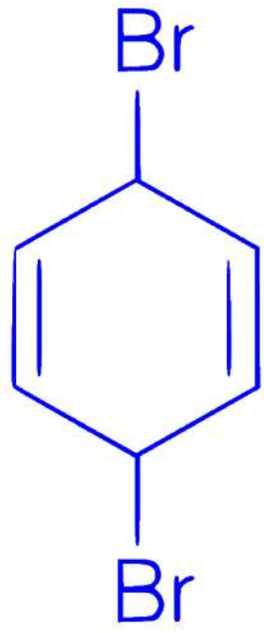
C. homo-cyclic but not aromatic

D. neither homo-cyclic nor hetero-cyclic

Answer: C

Solution:

For a compound to be aromatic, it must have (4n + 12) π-electrons.



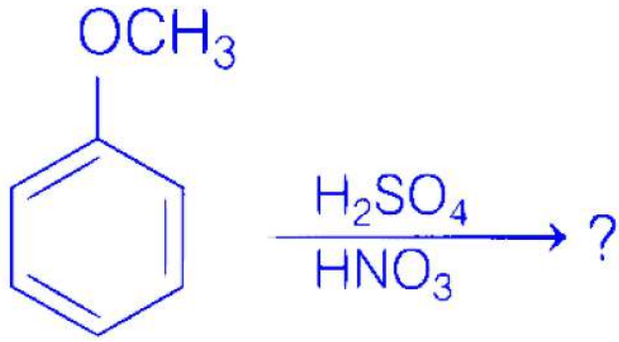
Here, two double bonds and 4π-electrons are present in the compound. Therefore, it is anti-aromatic.

Homocyclic compounds are ring structures that consist only of carbon atoms with in the ring. Bromo group is attached to ring system as substituent, so $C_6H_6Br_2$ is homocyclic but not aromatic.

Hence, option (c) is correct.

Question38

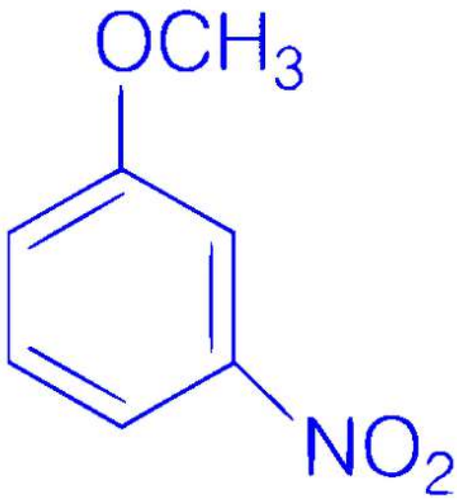
Identify the major product of the following reaction.



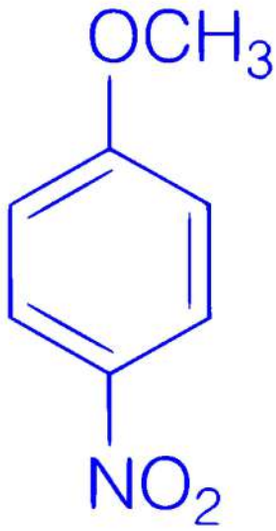
AP EAPCET 2021 - 20th August Morning Shift

Options:

A.

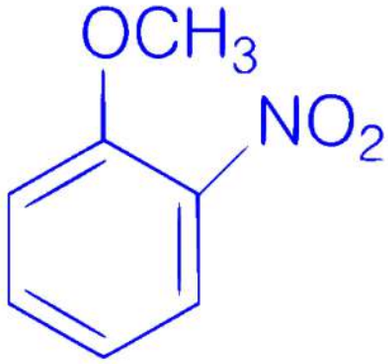


B.



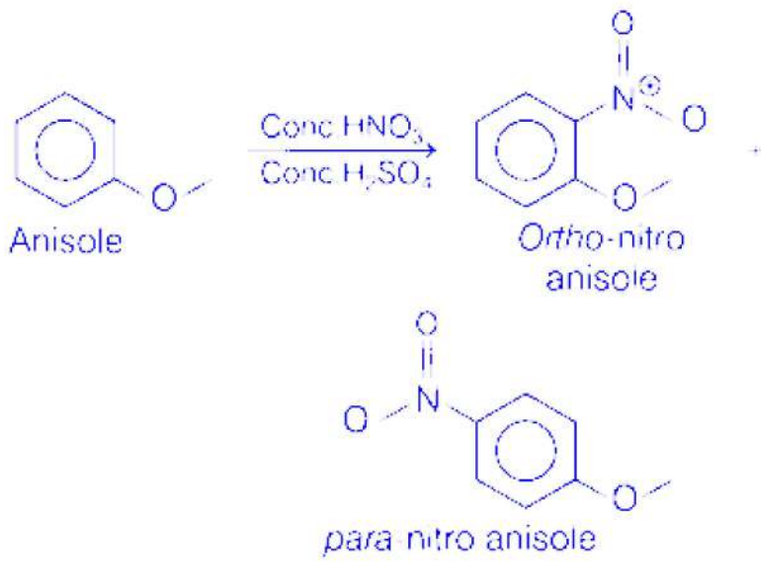
C.

D.



Answer: B

Solution:



With mixture of conc. HNO_3 and conc. H_2SO_4, anisole gives ortho and para-nitro anisole.

Methoxy group is activating and ortho-para directing group.
