Chapter 11
Hydroxy Compounds and Ethers

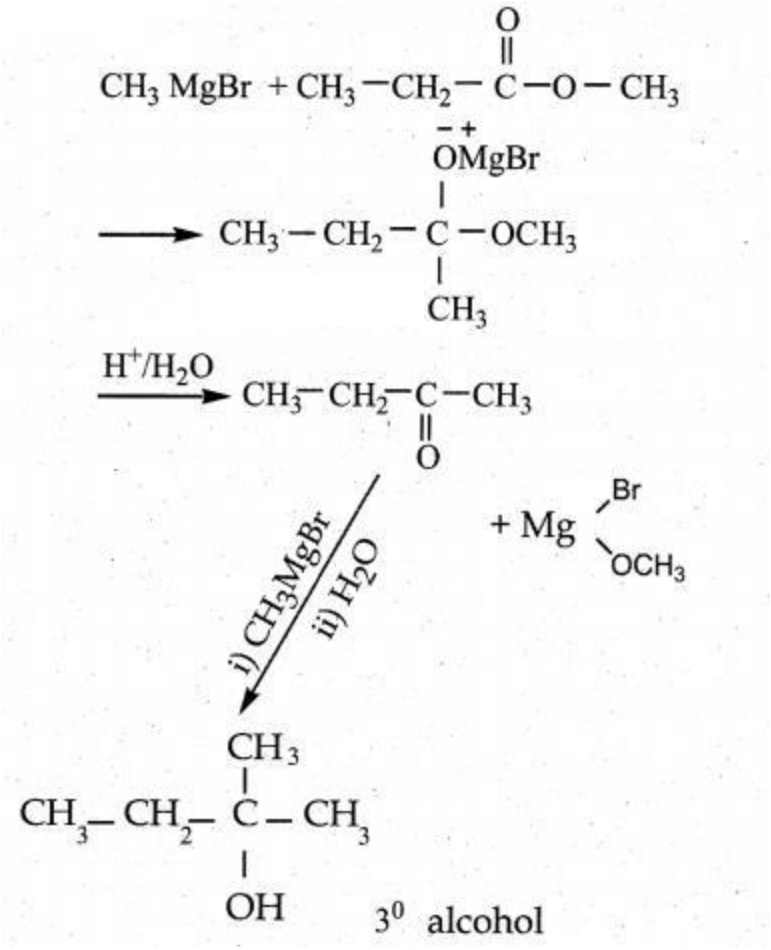
I. Choose the correct answer

Question 1.
An alcohol (x) gives blue colour in victormayer's test and 3.7g of X when treated with metallic sodium liberates 560 mL of hydrogen at 273 K and 1 atm pressure what will be the possible structure of X?
(a) CH_3 CH (OH) CH_2CH_3
(b) CH_3 – CH(OH) – CH_3
(c) CH_3 – C (OH) $(CH_3)_2$
(d) CH_3 – CH_2 – CH (OH) – CH_2 – CH_3
Answer:
(a) CH_3 CH (OH) CH_2CH_3
Hint:
$2R - OH + Na \rightarrow 2RONa + 2H_2 \uparrow$ 2 moles of alcohol gives 1 mole of H_2 which occupies 22.4L at 273K and 1 atm
number of moles of alcohol $= \frac{2\ moles\ of\ R-OH}{22.4L\ of\ H2}$ x 560 mL = 0.05 moles
number of moles $= \frac{mass}{\text{molar mass}}$
$= \text{molar mass} = \frac{3.7}{0.05} = 74\ g\ mol^{-1}$
General formula for
R – OH $C_n\ H_{2n+1}$ – OH
$n(12) + (2n+1)\ (1) + 16 + 1 = 74$
$14n = 74 - 18$
$14n = 56$
$n = \frac{56}{4} = 4$

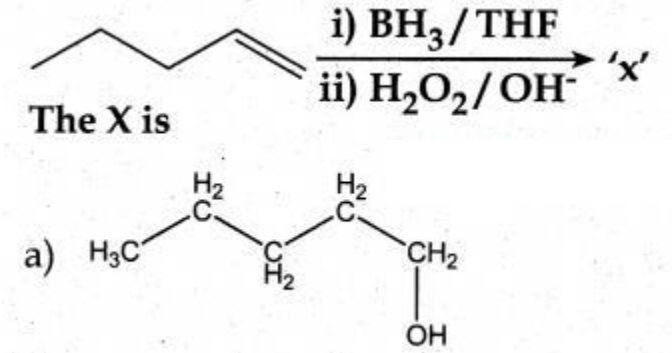
The 2° alcohol which contains 4 carbon is CH_n $CH(OH)CH_2$ CH_3

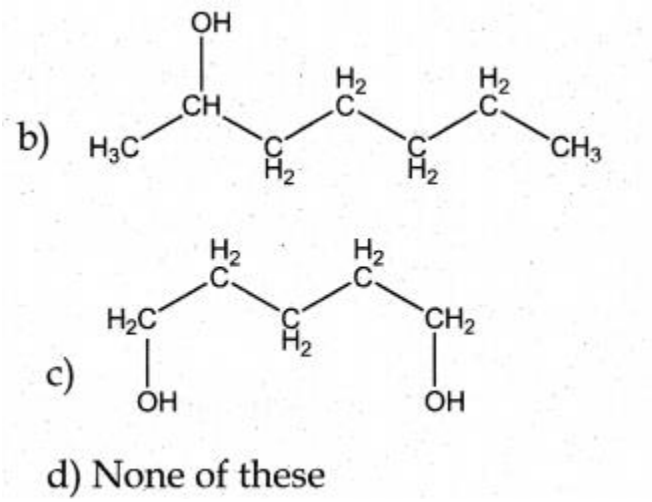
Question 2.
Which of the following compounds on reaction with methyl magnesium bromide will give tertiary alcohol.
(a) benzaldehyde
(b) propanoic acid
(c) methyl propanoate
(d) acetaldehyde
Answer:
(c) methyl propanoate

Solution:



Question 3.





Answer:

a

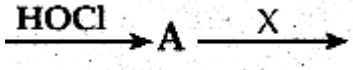
Solution:

hydro boration – Anti markownikoff product

i.e $CH_3 – CH_2 – CH – CH_2 – CH_2 – OH$

Question 4.

In the reaction sequence, Ethane



Ethan – 1, 2 – diol. A and X respectively are ……..

(a) Chioroethane and NaOH

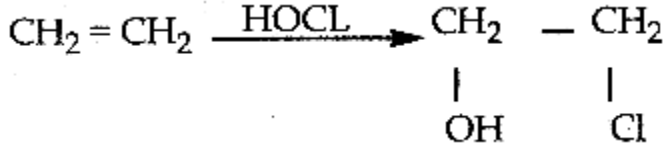
(b) ethanol and H_2SO_4

(c) 2 – chloroethan – 1 – ol and $NaHCO_3$

(d) ethanol and H_2O

Answer:

(c) 2 – chloroethan – 1 – ol and $NaHCO_3$\



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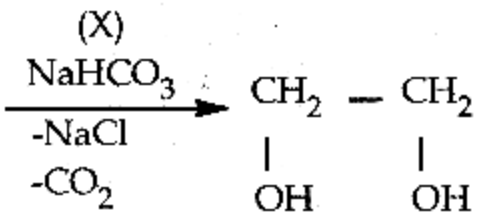
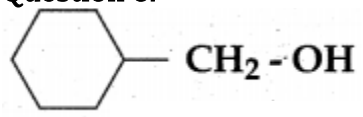
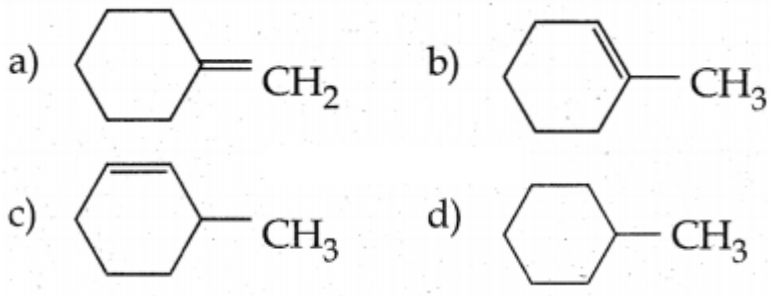


Question 5.
Which one of the following is the strongest acid …….
(a) 2 – nitrophenol
(b) 4 – chlorophenol
(c) 4 – nitrophenol
(d) 3 – nitrophenol
Answer:
(c) 4 – nitrophenol

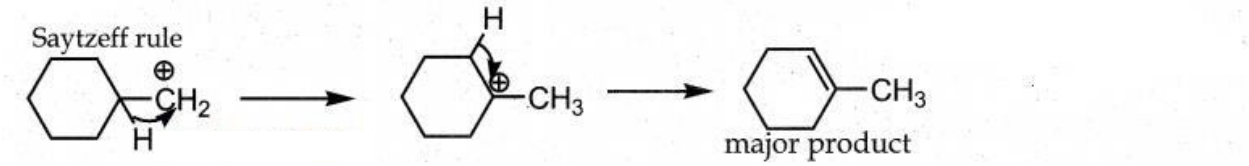
Question 6.



on treatment with Con. H_2SO_4, predominately gives ……..



Answer:
b
Solution:



Question 7.
Carbolic acid is ……..
(a) Phenol
(b) Picric acid
(c) benzoic acid
(d) phenylacetic acid
Answer:
(a) Phenol

Question 8.
Which one of the following will react with phenol to give salicyladehyde after hydrolysis ……..
(a) Dichioro methane
(b) trichioroethane
(c) trichloro methane

(d) CO_2

Answer:

(c) trichloro methane (Riemer Tiemann reaction)

Question 9.

$$(CH_3)_3 - C - CH(OH)\,CH_3 \xrightarrow{\text{Con } H_2SO_4} X \text{ (major product)}$$

(a) $(CH_3)_3\,CCH = CH_2$

(b) $(CH_3)_2\,C = C\,(CH_3)_2$

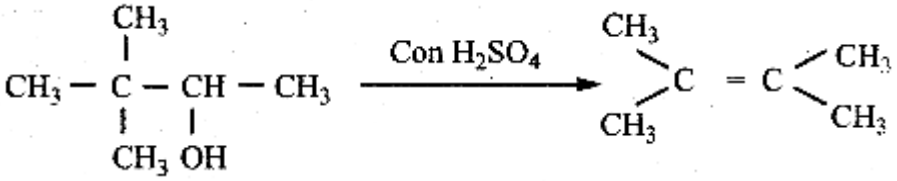
(c) $CH_2 = C(CH_3)CH_2 - CH_2 - CH_3$

(d) $CH_2 = C\,(CH_3) - CH_2 - CH_2 - CH_3$

Answer:

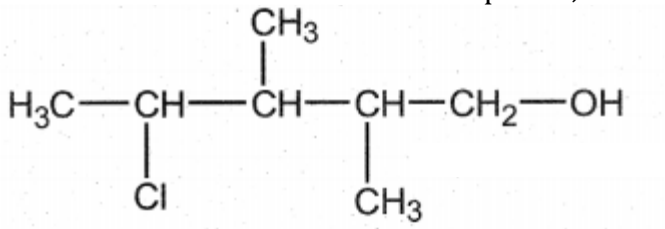
(b) $(CH_3)_2\,C = C\,(CH_3)_2$

Solution:



Question 10.

The correct IUPAC name of the compound,



(a) 4 – chloro – 2, 3 – dimethyl pentan – 1 – ol

(b) 2, 3 – dimethyl – 4 – chloropentan – 1 – ol

(c) 2, 3, 4 – trimethyl – 4 – chiorobutan – 1 – ol

(d) 4 – chioro – 2, 3, 4 – trimethyl pentan – 1 – ol

Answer:

(a) 4 – chloro – 2, 3 – dimethyl pentan – 1 – ol

Question 11.

Assertion: Phenol is more acidic than ethanol

Reason: Phenoxide ion is resonance stabilized

(a) if both assertion and reason are true and reason is the correct explanation of assertion.

(b) if both assertion and reason are true but reason is not the correct explanation of assertion.

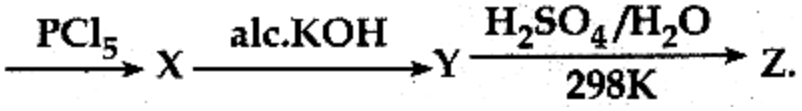
(c) assertion is true but reason is false

(d) both assertion and reason are false.

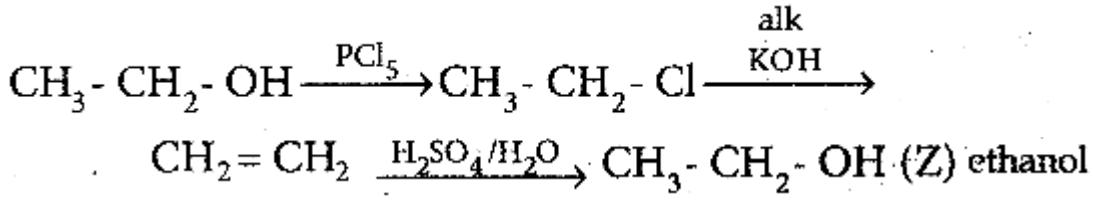
Answer:

if both assertion and reason are true and reason is the correct explanation of assertion.

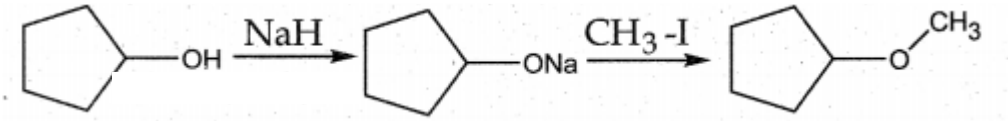
Question 12.
In the reaction Ethanol



is ……
(a) ethane
(b) ethoxyethane
(c) ethylbisuiphite
(d) ethanol
Answer:
(d) ethanol
Solution:



Question 13.
The reaction



can be classified as
(a) dehydration
(b) Williams on alcohol synthesis
(c) Williamson ether synthesis
(d) dehydrogenation of alcohol
Answer:
(c) Williamson ether synthesis
Solution:
Cyclic alcohol → sodium cyclic alkoxide → Williamson ether synthesis

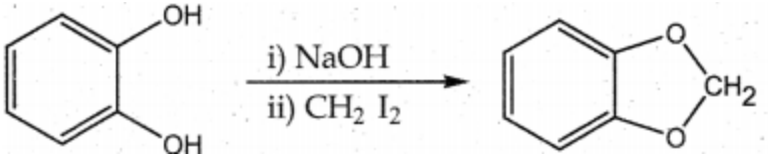
Question 14.
Isoprophylbcnzene on air oxidation in the presence of dilute acid gives ……
(a) C_6H_5COOH
(b) $C_6H_5COCH_3$
(c) $C_6H_5COC_6H_5$
(d) $C_6H_5 – OH$
Answer:
(a) $C_6H_5 – OH$ (phenol)

Question 15.
Assertion: Phenol is more reactive than benzene towards electrophilic substitution reaction
Reason: In the case of phenol. the intermediate arenium ion is more stabilized by resonance.
(a) if both assertion and reason are true and reason is the correct explanation of assertion.
(b) if both assertion and reason are true but reason is not the correct explanation of assertion.
(c) assertion is true but reason is false
(d) both assertion and reason are false,.
Answer:
(a) if both assertion and reason are true and reason is the correct explanation of assertion.

Question 16.
HO CH_2 CH_2 – OH on heating with periodic acid gives …….
(a) methanoic acid
(b) Glyoxal
(c) methanol
(d) CO_2
Answer:
(c) methanol

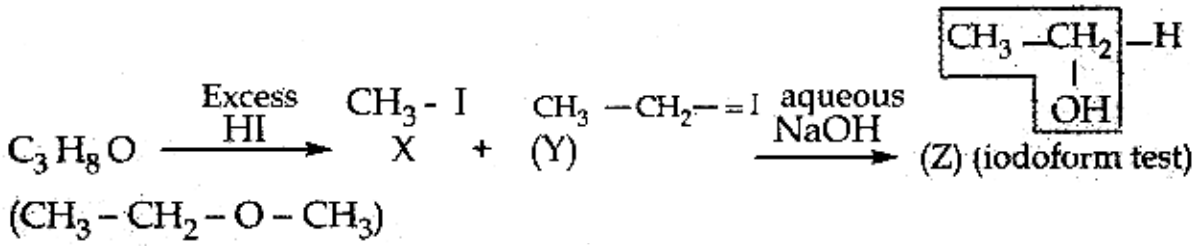
Question 17.
Which of the following compound can be used as artireeze in automobile radiators?
(a) methanol
(b) ethanol
(c) Neopentyl alcohol
(d) ethan -1, 2-diol
Answer:
(d) ethan -1, 2-diol

Question 18.
The reaction



is an example of ……..
(a) Wurtz reaction
(b) cyclic reaction
(c) Williamson reaction
(d) Kolbe reactions
Answer:
(c) Kolbe reactions

Question 19.
One mole of an organic compound (A) with the formula C_3H_8O reacts completely with two moles of HI to form X and Y. When Y is boiled with aqueous alkali it forms Z. Z answers the iodoform test. The compound (A) is ……
(a) propan – 2 – ol
(b) propan- 1- ol
(c) ethoxy ethane
(d) methoxy ethane
Answer:
(d) methoxy ethane
Solution:



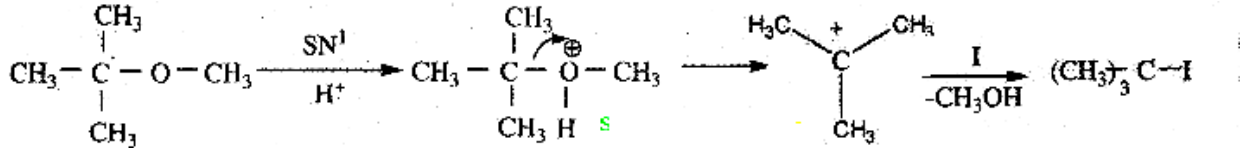
$(CH_3 - CH_2 - O - CH_3)$

Question 20.
Among the following ethers which one will produce methyl alcohol on treatment with hot HI?

a) $(H_3C)_3—C—O—CH_3$ b) $(CH_3)_2—CH—CH_2—O—CH_3$

c) $CH_3—(CH_2)_3—O—CH_3$ d) $CH_3—CH_2—CH(CH_3)—O—CH_3$

Answer:
a
Solution:

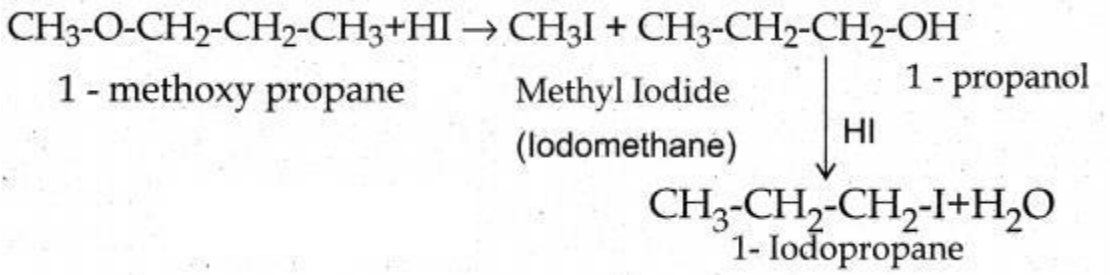


Question 21.
Williamson synthesis of preparing dimethyl ether is a / an
(a) SN^1 reactions
(b) SN^2 reaction
(c) electrophilic addition
(d) electrophilic substitution
Answer:
(b) SN^2 reaction

Question 22.
On reacting with neutral ferric chloride, phenol gives
(a) red colour
(b) violet colour
(c) dark green colour
(d) no colouration
Answer:
(b) violet colour

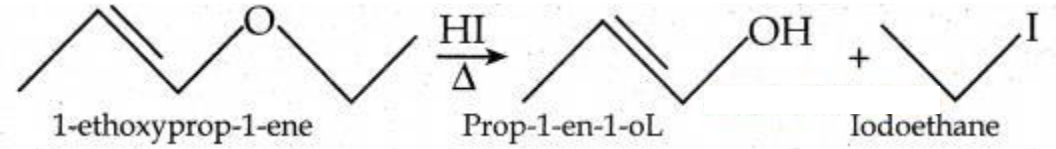
II. Short Answer

Question 1.
IdentIfy the product (s) is/are formed when 1 – methoxy propane is heated with excess HI. Name the mechanism involved in the reaction.
Answer:

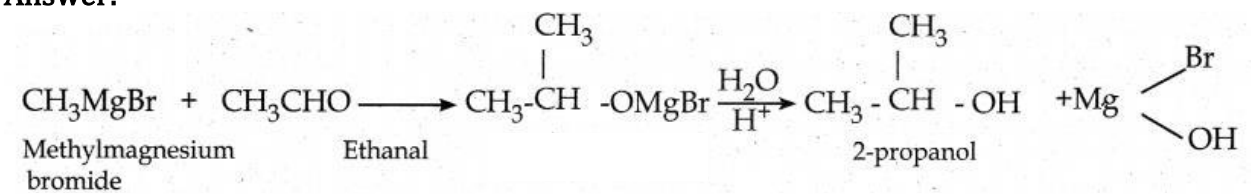


Ethers having primary alkyl group undergo S2N reaction

Question 2.
Draw the major product formed when 1 – ethoxyprop – 1 – ene is heated with one equivalent of HI
Answer:

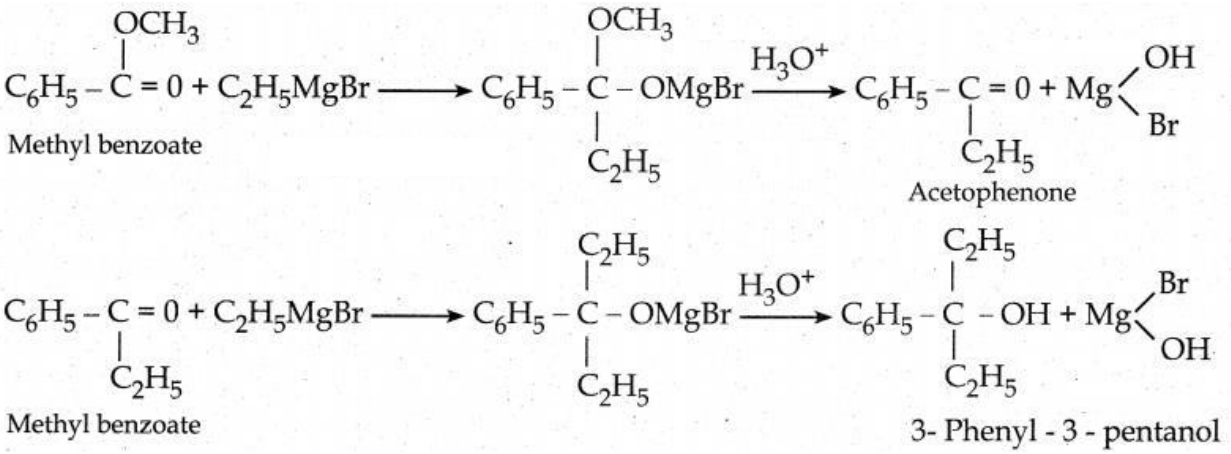


Question 3.
Suggest a suitable reagent to prepare secondary alcohol with an identical groups using a Grignard reagent.
Answer:



Question 4.
What is the major product obtained when two moles of ethyl magnesium bromide is treated with methyl benzoate followed by acid hydrolysis

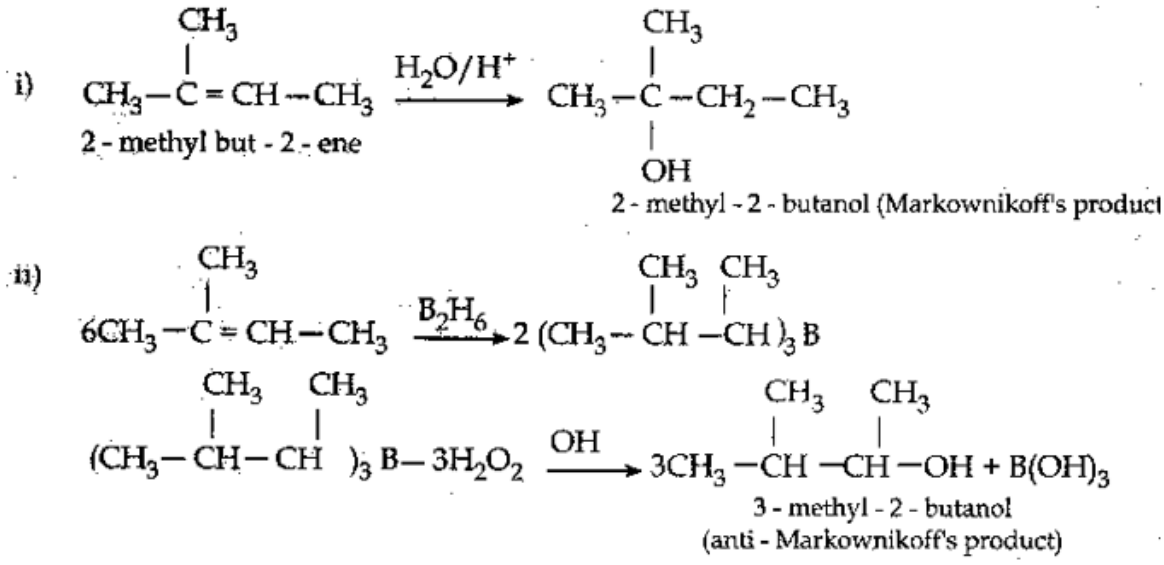
Answer:

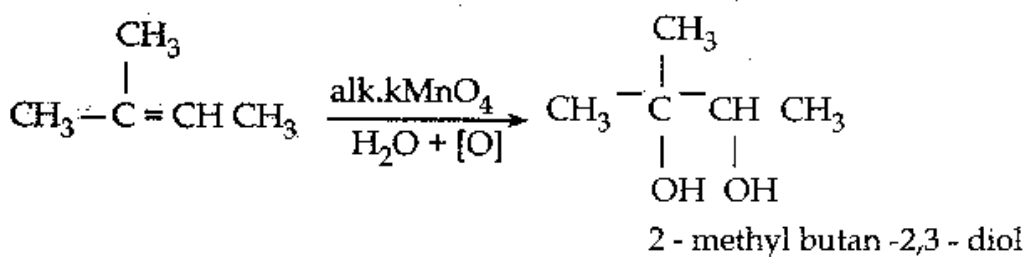


Question 5.
Predict the major product, when 2-methyl but – 2 – ene is converted into alcohol in each of the following methods.

1. Acid-catalyzed hydration
2. Hydroboration
3. Hydroxylation using bayers reagent

Answer:



iii) 

2 - methyl butan -2,3 - diol

Question 6.
Arrange the following in the increasing order of their boiling point and give a reason for your ordering

1. Butan – 2 – ol, Butan – 1 – SI, 2 – methylpropan – 2 – ol
2. Propan – 1 – ol, propan – 1, 2, 3 – triol, propan – 1, 3 – diol, propan – 2 – ol

Answer:
1. Boiling points increases regularly as the molecular mass increases due to a corresponding increase in their Van der Waal's force of attraction. Among isomeric alcohols, 2° – alcohols have lower boiling points than 1° – alcohols due to a corresponding decrease in the extent

of H-bonding because of steric hindrance. Thus the boiling point of Butan – 2 – ol is lower than that of Butan – 1 – ol. Overall increasing order of boiling points is, 2 – methyl propane – 2 – ol < Butan – 2 – ol < Butan – 1 – ol

2. 2°-alcohols have lower boiling points than 1° – alcohols due to a corresponding decrease in the extent of H – bonding because of steric hindrance. Therefore Propan – 1 – ol has higher boiling point than Propan – 2 – ol. The hydrogen group increases, boiling point also increases. Overall increasing order of boiling points is, propan – 2 – ol < Propan – 1 – ol < propan – 1, 3 – diol < propan -1, 2, 3 – triol

Question 7.
Can we use nucleophiles such as NH_3, CH_3O for the Nucleophilic substitution of alcohols
Answer:
1. Increasing order of nucleophilicity,
$NH_3 < – OH^{\oplus} < CH_3O^{\ominus}$-

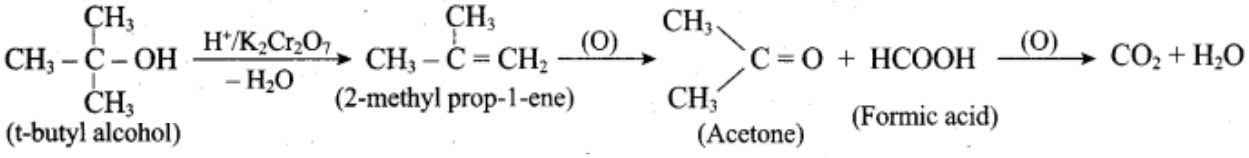
2. Higher electron density will increase the nucleophilicity.

3. Negatively charged species are almost always more nucleophiles than neutral species.

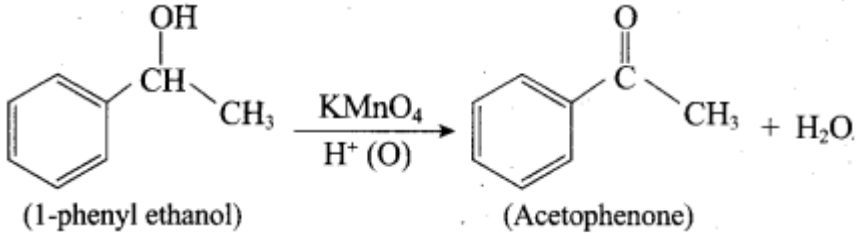
4. $RO^{\ominus}$ has an alkyl group attached, allowing a greater amount of polarizability. This means oxygen's lone pairs will be more readily available to reach in $RO^{\ominus}$ than in $OH^{\ominus}$. Hence CH_3O – is the better nucleophile for the nucleophilic substitution of alcohols. NH_3 cannot act as nucleophiles for the nucleophilic substitution of alcohols.

Question 8.
Is it possible to oxidise t – butyl alcohol using acidified dichromate to form a carbonyic compound.
Answer:
3° – alcohols do not undergo oxidation reaction under normal conditions, but at elevated temperature, under strong oxidising agent cleavage of C – C bond takes place to give a mixture of carboxylic acid.

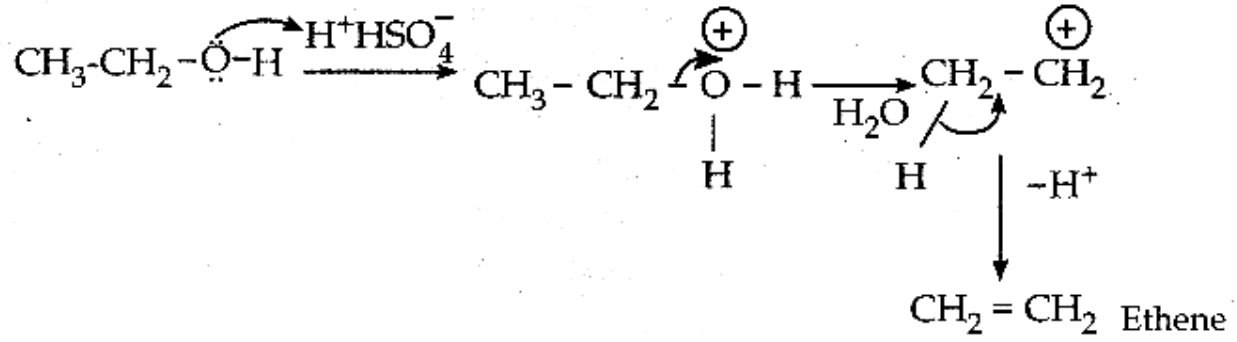
Yes, it is possible. t – butyl alcohol is readily oxidsing in acidic solution ($K_2Cr_2O_7$ / H_2SO_4) to a mixture of a ketone and an acid each containing lesser number of carbon atoms than the original alcohol. The oxidation presumably occur via alkenes formed through dehydration of alcohols under acidic conditions.



Question 9.
What happens when 1 – phenyl ethanol is treated with acidified $KMnO_4$.
Answer:
1 – phenyl ethanol reacts with acidified $KMnO_4$ to give Acetophenone.



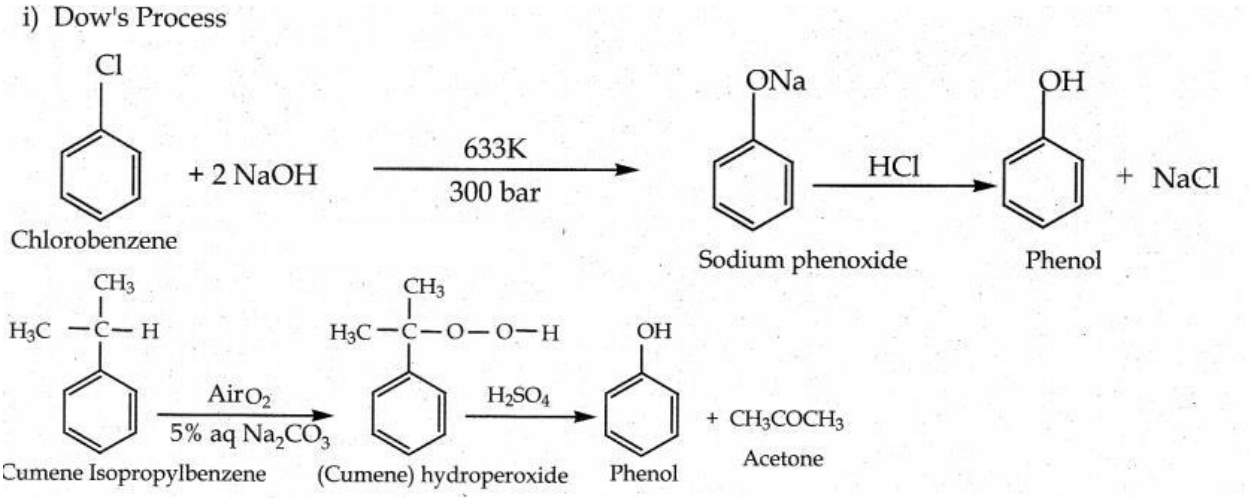
Question 10.
Write the mechanism of acid catalysed dehydration of ethanol to give ethene.
Answer:



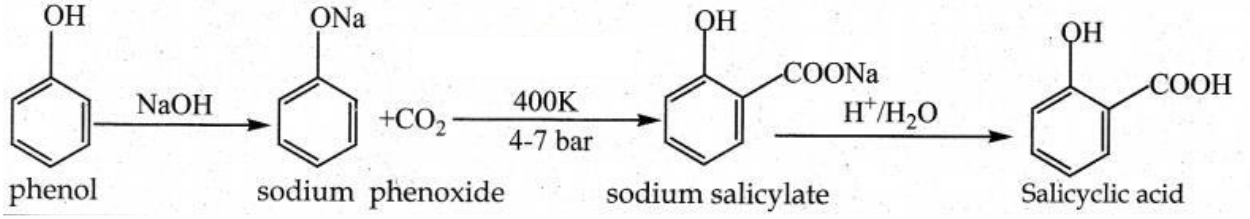
Question 11.
How is phenol prepared form

1. chloro benzene
2. isopropyl benzene

Answer:

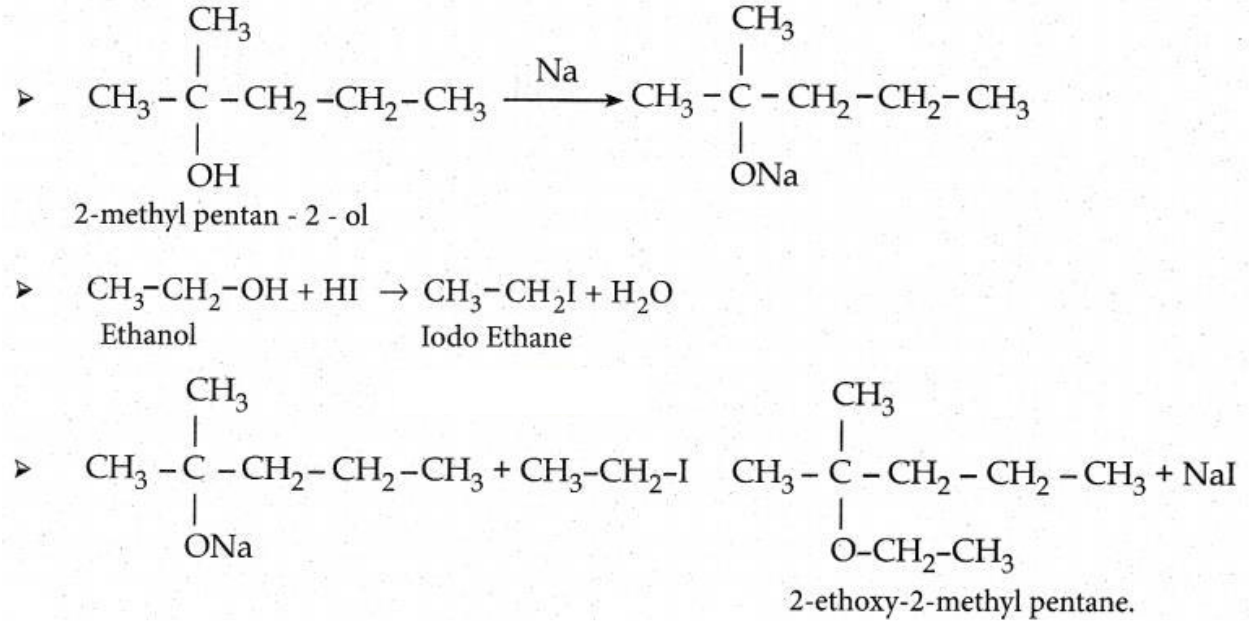


Question 12.
Explain Kolbe's reaction
Answer:
Kolbe's (or) Kolbe's Schmitt reaction:
In this reaction, phenol is first converted into sodium phenoxide which is more reactive than phenol towards electrophilic substitution reaction with CO_2. Treatment of sodium phenoxide with CO_2 at 400K, 4 -7 bar pressure followed by acid hydrolysis gives salicylic acid.



Question 13.
Writes the chemical equation for Williamson synthesis of 2 – ethoxy – 2 – methyl pentane starting from ethanol and 2 – methyl pentan – 2 – ol
Answer:

A tertiary alkoxide and primary alkyl halide easily undergo williamson ether synthesis

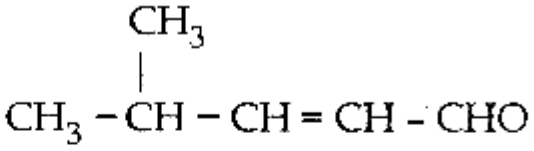


Question 14.

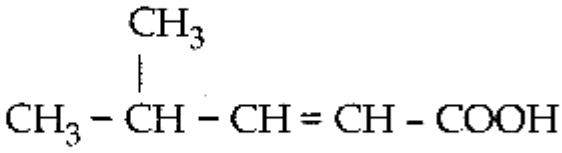
Write the structure of the aldehyde, carboxylic acid and ester that yield 4 – methylpent – 2 – en – 1 – ol.

Answer:

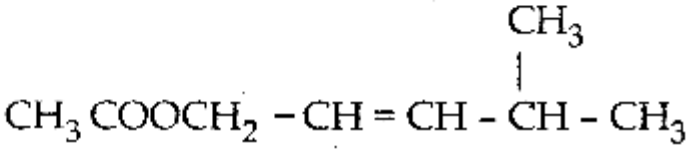
Aldehyde



Carboxylic acid



Ester



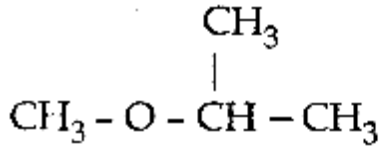
Question 15.

What is metamerism? Give the structure and IUPAC name of metamers of 2 – methoxy propane

Answer:

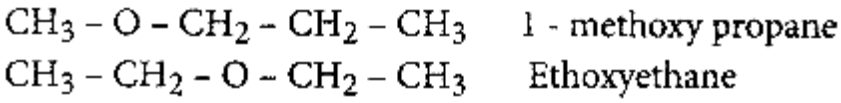
Metamerism:

It is a special type of isomerism in which molecules with same formula, same functional group, but different only in the nature of the alkyl group attached to oxygen.



2 - methoxy propane

Metamers :



1 - methoxy propane

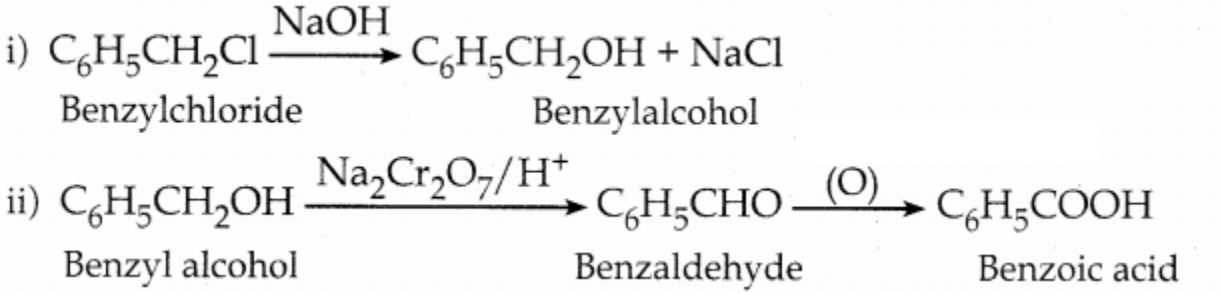
Ethoxyethane

Question 16.

How are the following conversions effected

1. benzyl chlorjde to benzyl alcohol
2. benzyl alcohol to benzoic acid

Answer:

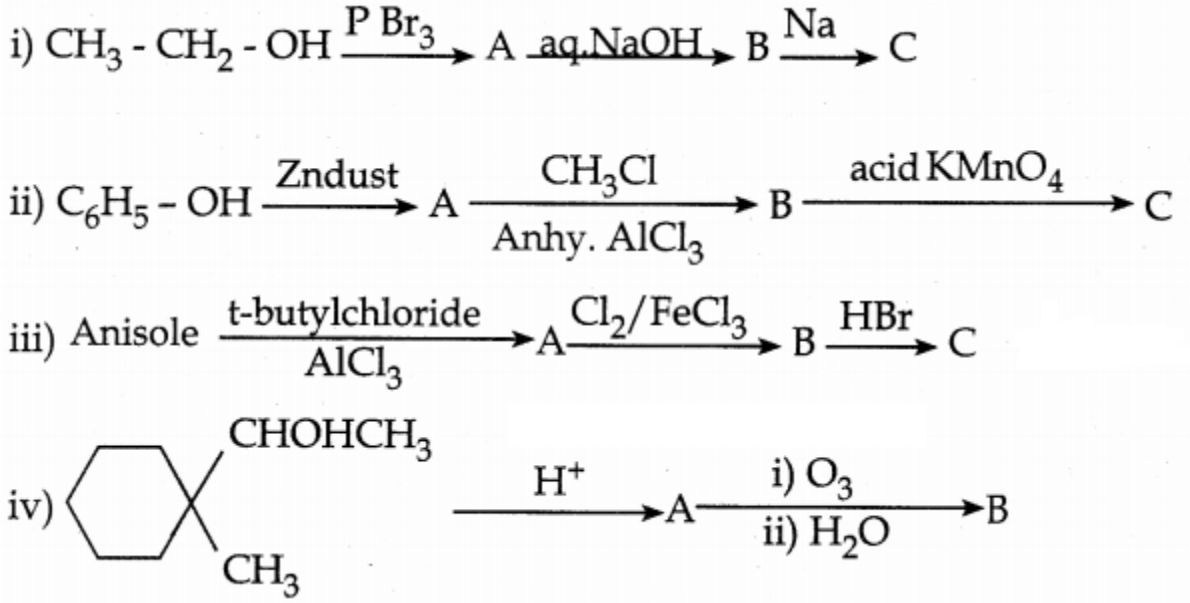


Benzylchloride — Benzylalcohol

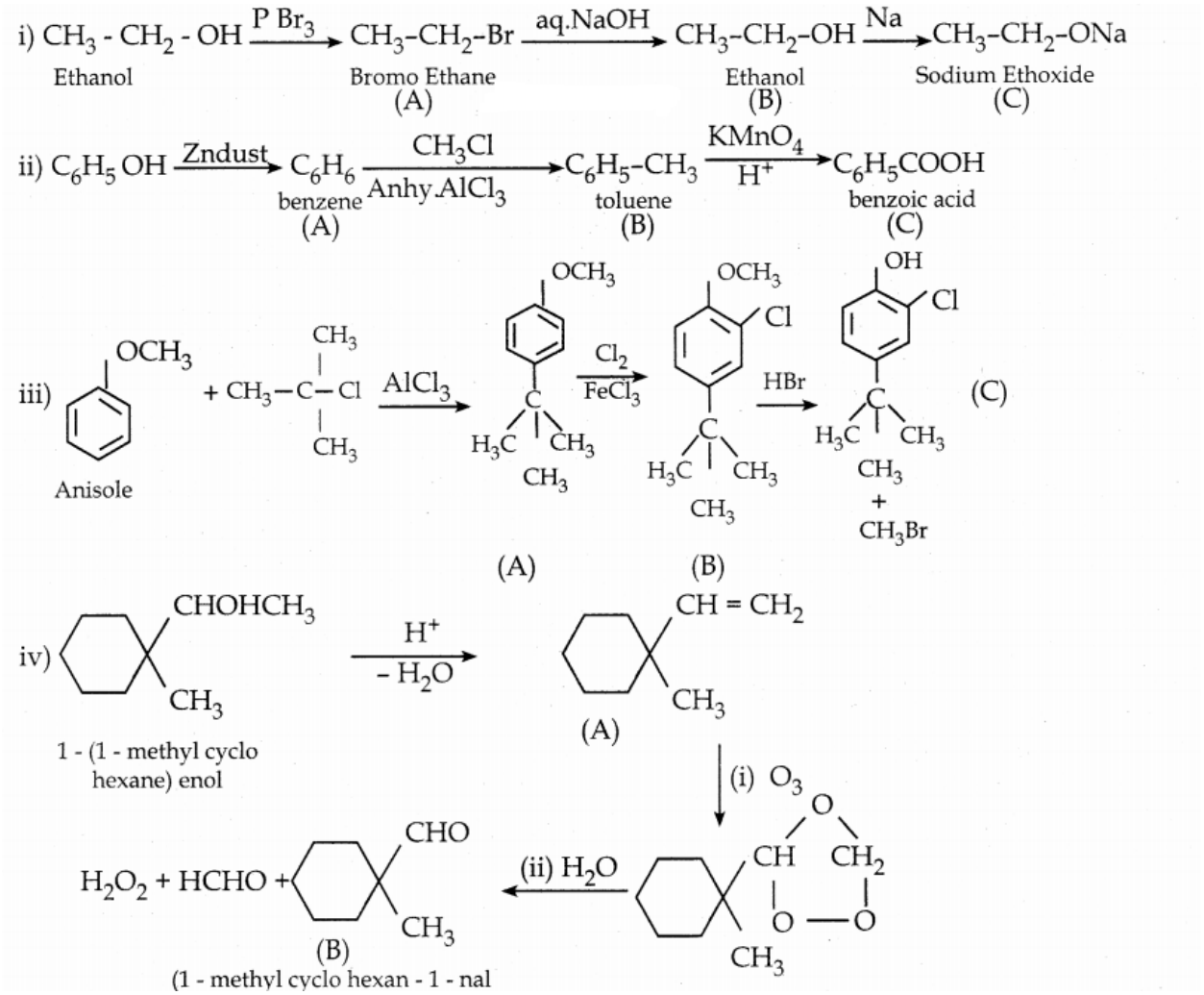
Benzyl alcohol — Benzaldehyde — Benzoic acid

Question 17.

Complete the following reactions

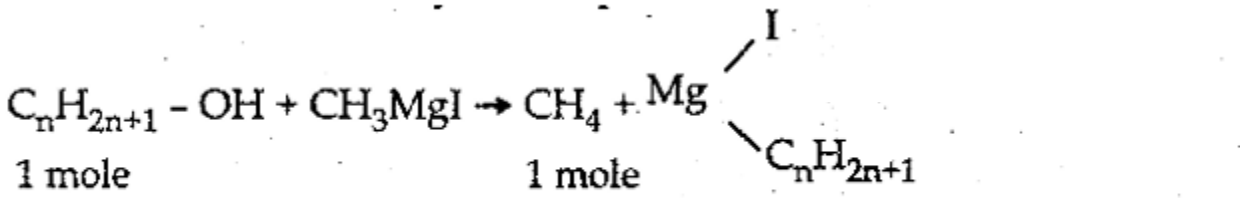


Answer:



Question 18.

0.44g of a monohydric alcohol when added to methyl magnesium iodide in ether liberates at STP 112 cm^3 of methane with PCC the same alcohol form a carbonyl compound that answers silver mirror test. Identify the compound.



(1 mole) 22400 cm^3 of Methane can be produced from 1 mole of alcohol

$\therefore 112 \frac{Cm^2}{Cm^3}$ of methane is liberated from $\frac{1}{22400} \times 112$ mole of alcohol

= 0.005 mole of alcohol

$$n = \frac{W}{M}; \quad M = \frac{W}{n} = \frac{0.44}{0.005} = 88$$

∴ Molar mass of alcohol in 88 g mol^{-1}

$C_nH_{2n+1}+OH$

$\Rightarrow n \times 12 + (2n + 1) \times 1 + 1 \times 16 + 1 \times 1 = 88$

$12n + 2n + 1 + 16 + 1 = 88$

$14n + 18 = 88$

$14n = 88 - 18$

$14n = 70$

$n = 70/14 = 5$

Answer:

: ie n - pentyl alcohol. or $CH_3 - CH_2 - \underset{\underset{CH_3}{|}}{CH} - CH_2OH$

2 methyl 1 - butanol.

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OH \xrightarrow{PCC} CH_3 - CH_2 - CH_2 - CH_2 - CHO$$

1 - pentanol

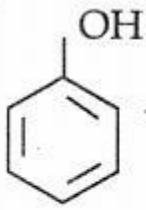
Pentanal

$\downarrow Ag_2O$

$2Ag + CH_3 - CH_2 - CH_2 - CH_2 - COOH$

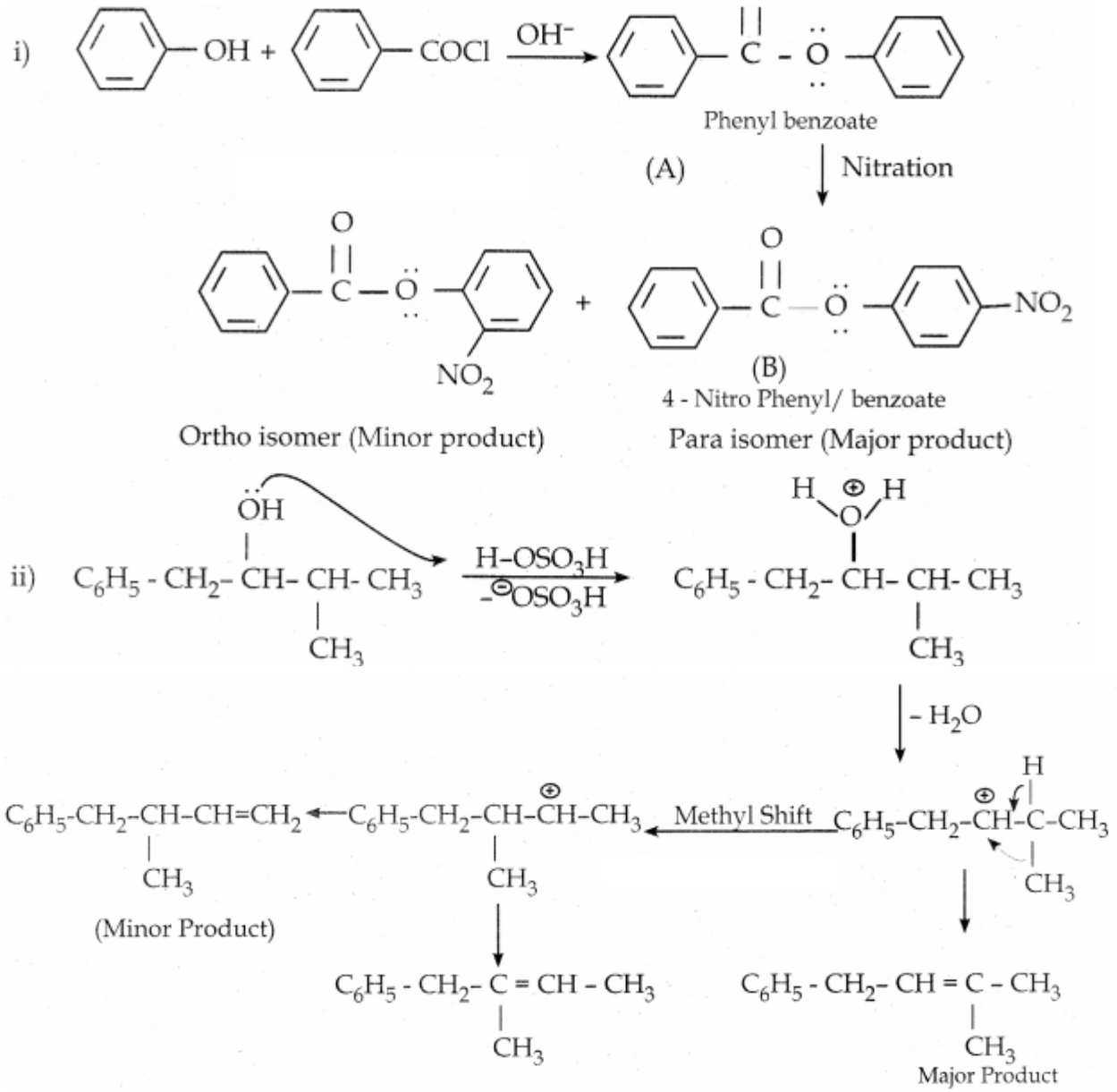
Question 19.

Complete the following reactions

i)  $\xrightarrow[OH^-]{C_6H_5COCl}$ A $\xrightarrow{\text{Nitration}}$ B (major product)

ii) $C_6H_5 - CHCH(OH)CH(CH_3)_2 \xrightarrow{\text{Con } H_2SO_4}$

Answer:

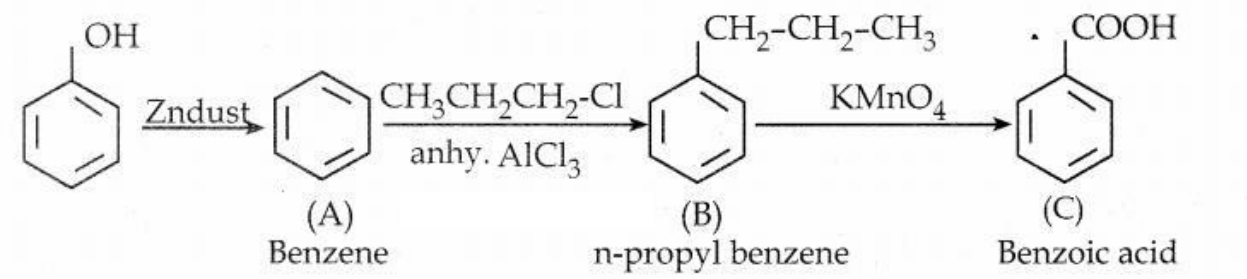


(According to Saytzeff s rule, during intramolecular dehydration, if there is a possibility to form C = C bond at different locations, the preferred location is the one that gives the more substituted alkene je, the stable alkene).

Question 20.

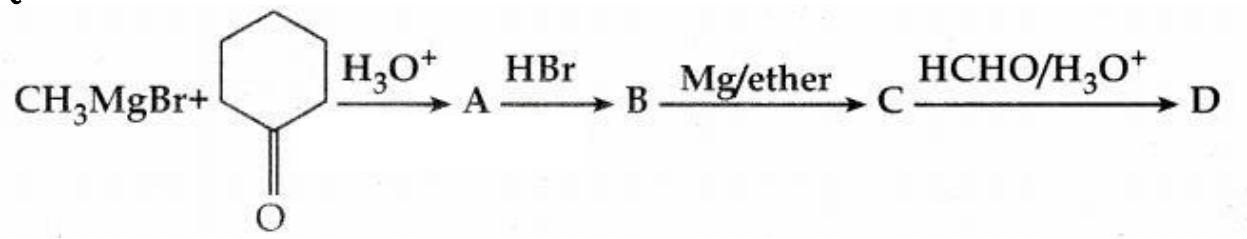
Phenol is distilled with Zn dust gives (A) followed by Friedel – crafts alkylation with propyl chloride to give a compound B, B on oxidation gives (C). Identify A,B and C.

Answer:



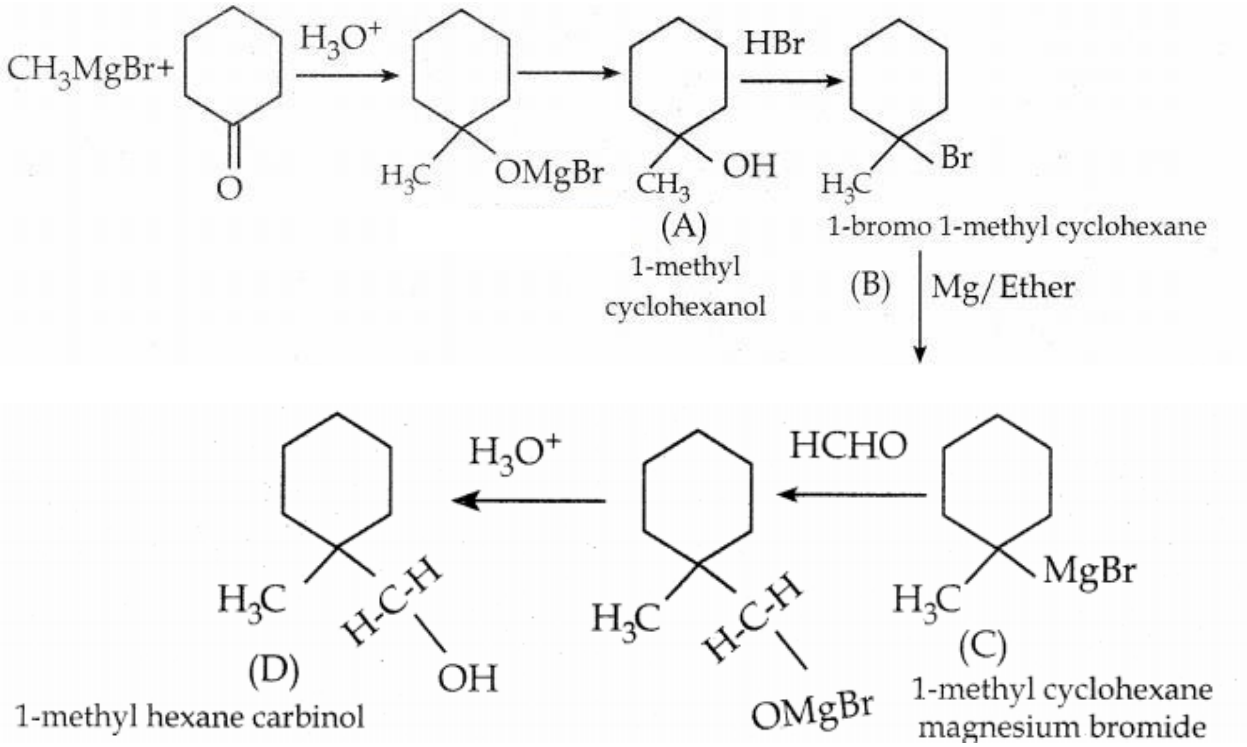
Note:
Carbon directly attached to the aromatic riñg is called benzylic carbon.
If there is hydrogen attached to benzylic carbon it will undergo oxidation.

Question 21.



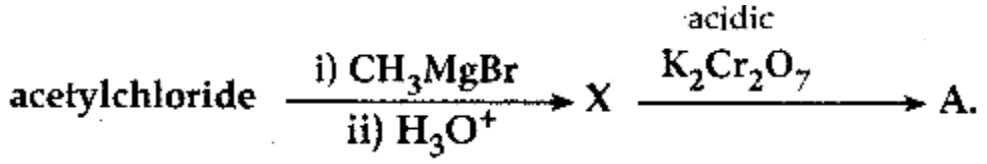
Identify A, B, C, D and write the complete equation.

Answer:

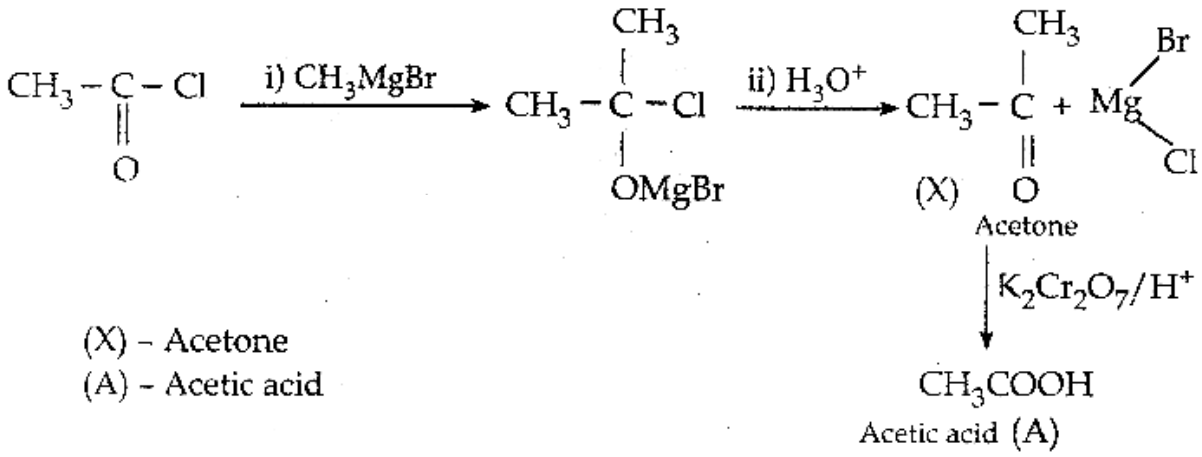


Question 22.

What will be the product for the following reaction



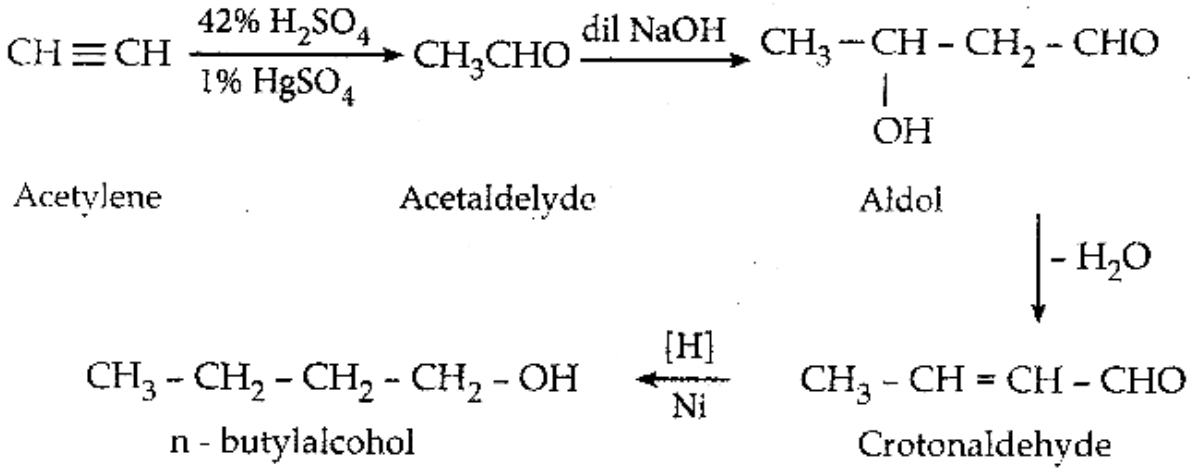
Answer:



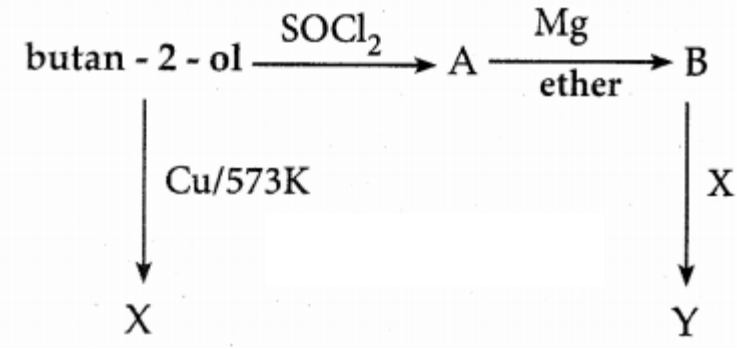
(X) – Acetone
(A) – Acetic acid

Question 23.
How will you convert acetylene into n – butyl alcohol.

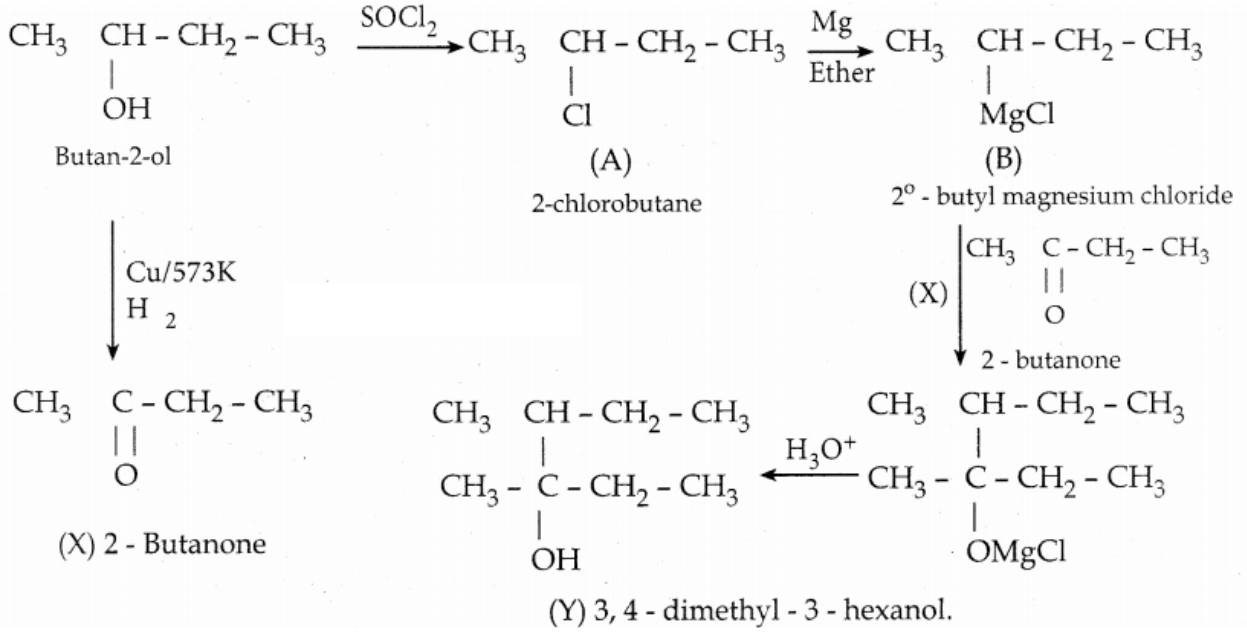
Answer:



Question 24.
Predict the product A, B, X and Y in the following sequence of reaction



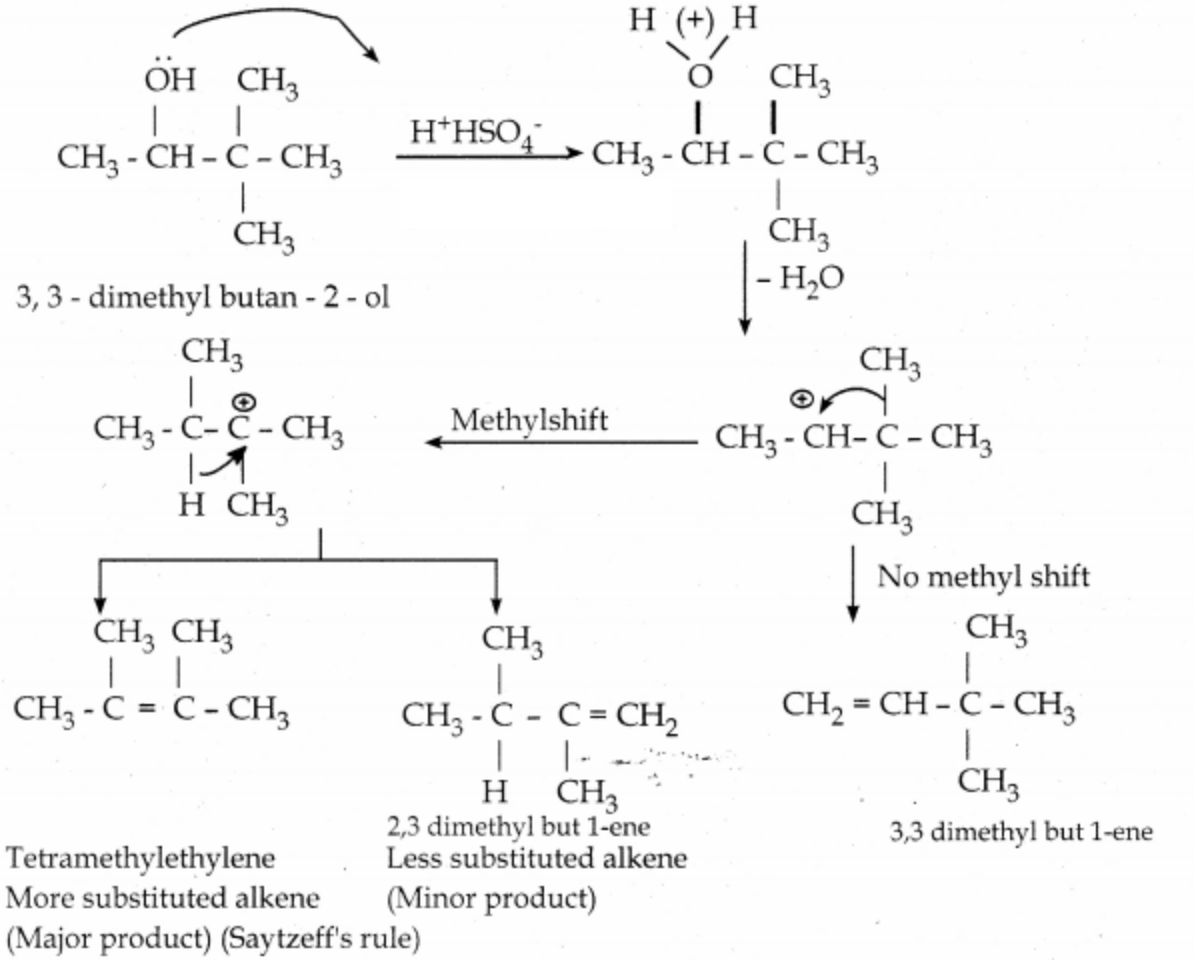
Answer:



Question 25.

3,3 – dimethyl butane – 2 – ol on treatment with conc. H_2SO_4 to give tetramethyl ethylene as a major product. Suggest suitable mechanisms.

Answer:


H (+) H
O
OH CH3
CH3 - CH - C - CH3
CH3
H+HSO4-
CH3 - CH - C - CH3
CH3
- H2O
3, 3 - dimethyl butan - 2 - ol
CH3
CH3 - C - C - CH3
H CH3
Methylshift
CH3
CH3 - CH - C - CH3
CH3
No methyl shift
CH3 CH3
CH3 - C = C - CH3
CH3
CH3 - C - C = CH2
H CH3
CH3
CH2 = CH - C - CH3
CH3
2,3 dimethyl but 1-ene
Less substituted alkene
(Minor product)
3,3 dimethyl but 1-ene
Tetramethylethylene
More substituted alkene
(Major product) (Saytzeff's rule)