ALKENES:

These are unsaturated hydrocarbons with general molecular formulae C_nH_{2n}, n = 2, 3, 4, ...
Their functional group is carbon to carbon double bond.

Nomenclature of Alkenes.

They are named by replacing the ending letters of the corresponding alkanes with the suffix "ene". When the parent chain has more than three carbon atoms, the position of the carbon to carbon double bond must be specified.

Example:

$H_2C=CH_2$ - ethene
$CH_3CH=CH_2$ → propene
$CH_3CH=CHCH_3$ → but-2-ene
$CH_3CH_2CH=CH_2$ → but-1-ene
$CH_3CH_2CH_2CH=CH_2$ → pent-1-ene
CH_3

 - cyclohexene

ISOMERISM

The first two members in the homologous series have no isomers. The rest of the isomers exhibit structural and stereo isomerism.

Structural Isomerism.

- Chain isomerism

Molecular formula C_4H_8 represents the following chain is

$CH_3CH_2CH=CH_2$ → but-1-ene
$CH_3C(CH_3)=CH_2$ → 2-methylpropene
CH_3

- Position Isomerism

MF C_4H_8 represents the following position isomers

$CH_3CH_2CH=CH_2$ → but-1-ene
$CH_3CH=CHCH_3$ → but-2-ene

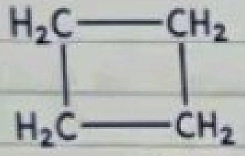
ALKENES (2)

Functional group Isomerism

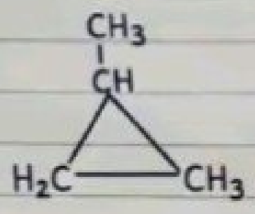
Alkenes are isomers with cycloalkanes.

e.g., M.F. C_4H_8 represents the following functional group isomers:

$CH_3CH_2CH=CH_2$ but-1-ene.



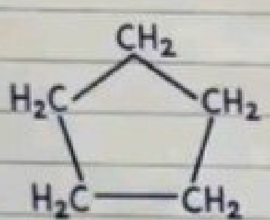
Cyclobutane.



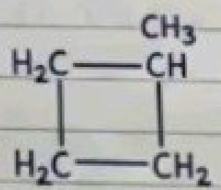
methylcyclopropane

MF: C_5H_{10}

$CH_3CH_2CH_2CH=CH_2$ pent-1-ene.



Cyclopentane.



methylcyclobutane.

STEREO ISOMERISM

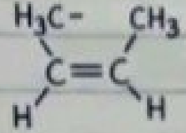
Alkenes exhibit geometrical isomerism. This arises due to restricted rotation of atoms around the carbon to carbon double bond.

Geometrical isomers have the same structural formula but differ in spatial arrangement of atoms around the carbon to carbon double bond. There are two types of geometrical isomerism:

- ✓ Cis-Isomers
- ✓ Trans-Isomers

CIS-ISOMERS:

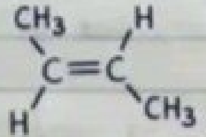
In this case, identical ahms or groups of ahms are ~~on the~~ same side of the carbon to carbon double bond. Froxumple. Consider a compuind with molecular formula C_6H_8



Cis-but-2-ene

TRANS-ISOMERS:

In this case, identical ahms or groups of ahms occupy opposite directions around the carbon to carbon double bond ey:



Trans-but-2-ene

PREPARATION OF ALKENES:

a) Dehydration of Alcohols

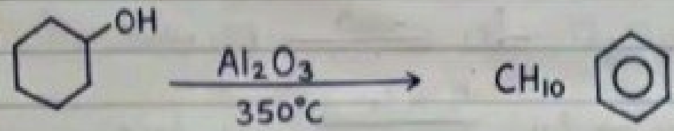
Alcohuls in He vapour phase;

These are dehydrated using aluminum oxide at a temperator 300 – 350°C

Example:

$$CH_3CH_2OH \xrightarrow[350°C]{Al_2O_3} H_3C=CH_2 + H_2O.$$

$$CH_3CH_2CH_2OH \xrightarrow[350°C]{Al_2O_3} CH_3CH=CH_3$$



b) Alcohols in the liquid phase.

There are dehydrated using conc-Sulphuric acid or conc phosphoric anid (Corthophorphoric acid).

The temperature at which he reachion occurs depends on the class of the alcohol.

Classes of alcohols: primary, secondary and tertiary.

1) Primary alcohols

These ore dehydrated at a temperature of 170°-180°c

teg. $CH_3CH_2OH \xrightarrow[150°c]{Cinc.\ H_2SO_3} H_2C\text{-}CH_3 + H_2O.$

Mechanism:

(2)

Step 1.

Parhial iomisation of the acid

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

Step 2.

Protonation of the alcohol.

$$CH_3CH_2\ddot{O}H \quad H^+ \longrightarrow CH_3CH_2-\bar{O}H_2$$

Step III

Loss of water

$$CH_3CH_2-\bar{O}H_2 \xrightarrow{-H_2O} CH_3\overset{+}{C}H_2$$

Step IV

Abstraction of a proton from the carbenium ion

$$H_2C-\overset{+}{C}H_2 \xrightarrow{-H^+} H_2C=CH_2$$

$$H \quad [\ddot{O}-SO_3H]^-$$

(2)

Example 2.

$$CH_3CH_2CH_2OH \xrightarrow[180°c.]{Conc.\ H_2SO_4} CH_3CH=CH_2 + H_2O$$

mechanium

$$H_2SO_4 \rightleftharpoons H^+ + O^- HSO_4^-$$

$$CH_3CH_2CH_2\ddot{O}H \quad H^+ \longrightarrow CH_3CH_2CH_2-\overset{+}{O}H_2$$

$$CH_3CH_2CH_2-\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2\overset{+}{C}H_2$$

$$CH_3CH_2\overset{+}{C}H_2 \underset{shift}{\overset{hydride}{\rightleftharpoons}} CH_3\overset{+}{C}HCH_3$$

$$CH_3\overset{+}{\underset{H}{C}}-CH_2 \xrightarrow{-H^+} CH_3CH=CH_2.$$

$$H \quad \ddot{O}SO_3H$$

Example 3.

$$CH_3CH_2CH_2CH_2OH \xrightarrow[heat]{Cunc.\ H_2PO_4} CH_3CH=CHCH_3$$

Mechanism:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4$$

Dehydration and rearrangement of secondary alcohols

$$CH_3CH_2CH_2CH_2\ddot{O}H \xrightarrow{H^+} CH_3CH_3CH_2CH_2-\overset{+}{O}H_2$$

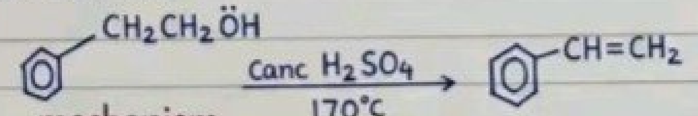
$$CH_3CH_2CH_2CH_2-\overset{+}{\ddot{O}}H_2 \xrightarrow{-H_2O} CH_3CH_2CH_2\overset{+}{C}H_2$$

$$CH_3CH_2CH_2\overset{+}{C}H_2 \underset{shift}{\overset{hydride}{\rightleftharpoons}} CH_3CH_2\overset{+}{C}HCH_3$$

$$CH_3\underset{H}{\overset{H}{C}}-\ddot{C}(H)CH_3 \quad :\ddot{O}PO_3H_2 \xrightarrow{-H^+} CH_3CH=CHCH_3$$

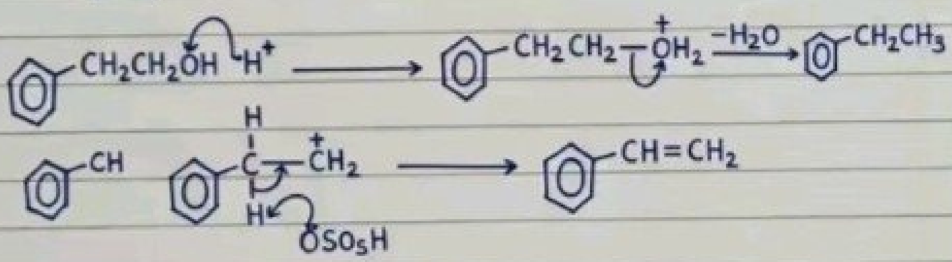
Exercise

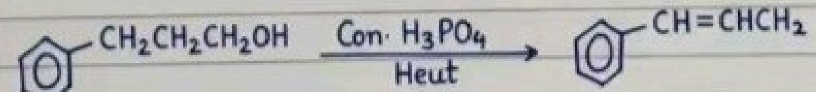
Complete by writing the major product ; Suggest the mechanism in each case:

(i) 

mechanism

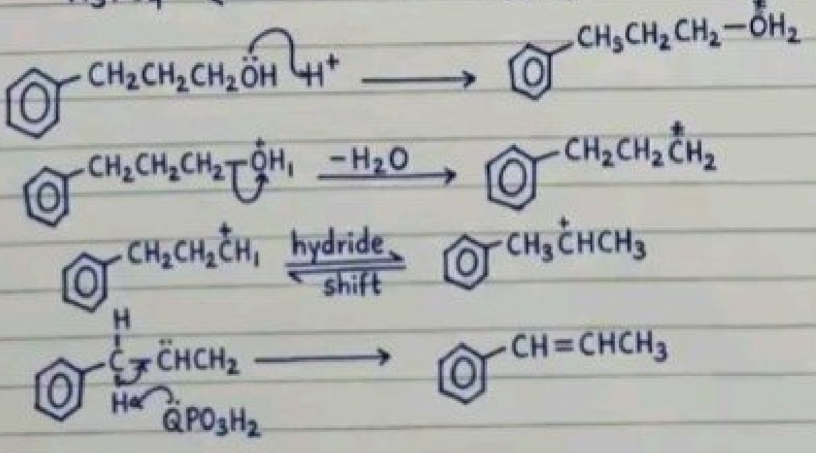
$$H_3SO_4 \rightleftharpoons H^+ + HSO_4^-$$



(ii) 

Mechanism

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$



Dehydration of Secondary Alcohols

These are dehydrated at a temperature ~~of~~ 120°C - 180°C.

Example 1 (Propan-2-ol):

$$CH_3CH(OH)CH_3 \xrightarrow[180°C]{Conc.\ H_2SO_4} CH_3CH{=}CH_2 + H_2O$$

Propan-2-ol

General mechanism for Example 1

1. $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

2. $CH_3CH(OH)CH_3 \xrightarrow{H^+} [CH_3CH(OH_2^+)CH_3] \longrightarrow CH_3CH^+CH_3 + H_2O$

3. $CH_3CH(H)CH_2^+H \xrightarrow{-HSO_4^-} CH_3CH{=}CH_2 + H_2SO_4$ ($^-OSO_3H$)

Example 2

$$CH_3CH(OH)CH_2CH_3 \xrightarrow[heat]{Conc.\ H_3PO_4} CH_3CH{=}CHCH_2 + H_2O$$

(major, Zaitsev's) (minor)

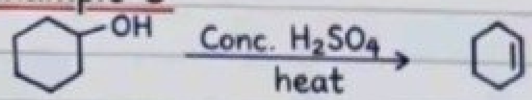
General mechanism for Example 2

1. $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

2. $CH_3CH(OH)CH_2CH_3 \xrightarrow{H^+} CH_3CH(OH_2^+)CH_2CH_3 \xrightarrow{-H_2O} CH_3CH^+CH_2CH_3$

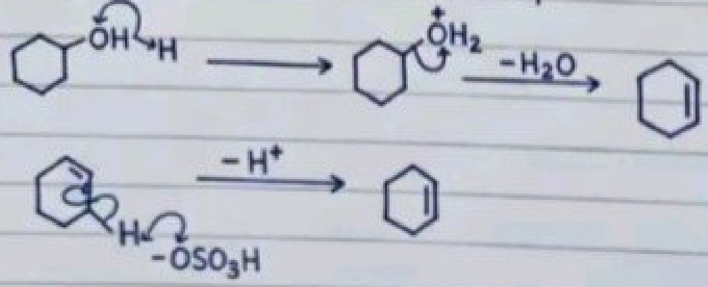
3. $CH_3CH(H)^+CH(H)CHCH_3 \xrightarrow{-H_2PO_4^-} CH_3CH{=}CHCH_2 + H_3PO_4$ ($^-OSO_3H$)

Example 3

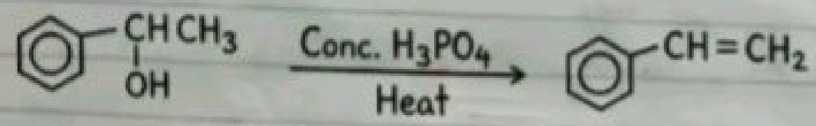


General mechanism for Example 3

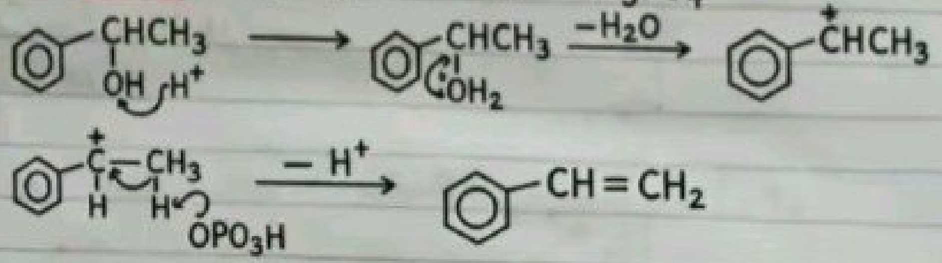
$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$



Complete the following equations by writing the major organic products. In each case suggest an acceptable mechanism.

i) 

mechanism: $H_3PO_4 \rightleftharpoons H^+ + H_3PO_4^-$



ii) $CH_3CH_2CH(OH)CH_2CH_3 \xrightarrow[180^\circ C]{Conc.\ H_2SO_4} CH_3CH_2CH{=}CHCH_3$

mechanism: $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

$CH_3CH_2CH(OH)CH_2CH_3 + H^+ \longrightarrow CH_3CH_2CH(\overset{+}{O}H_2)CH_2CH_3$

$CH_3CH_2CH(\overset{+}{O}H_2)CH_2CH_3 \xrightarrow{-H_2O} CH_3CH_2\overset{+}{C}HCH_2CH_3$

$CH_3CH_2\overset{+}{C}(H){-}CH(H)CH_3 \xrightarrow{-H^+} CH_3CH_2CH{=}CHCH_3$ ($\bar{O}SO_3H^-$)

3.iii) TERTIARY ALCOHOLS:

These are dehydruted at a temperature of 85–180°C

eg. 2-methylpropan-2-ol → 2-methylpropene

b) $(CH_3)_3\,C{-}OH \xrightarrow[180^\circ C]{Conc.\ H_2SO_4} (CH_3)_2\,C{=}CH_2$

mechanism:

$H_2SO_4 \rightleftharpoons H^+ + HSO_3^-$

3.iii)

$(CH_3)_3\,C{-}\ddot{O}H + H^+ \longrightarrow (CH_3)_3\overset{+}{C}{-}\overset{+}{C}H_2 \xrightarrow{-H_2O} (CH_3)_3\overset{+}{C}$

$CH_3\overset{+}{C}(CH_3){-}CH_2(H) \xrightarrow{-H^+} (CH_3)_2\,C{=}CH_2$ ($\bar{O}SO_3H$)

TERTIARY ALKYL HALIDE (E_1 & E_2)

E_1 Mechanism

Reaction:

$$(CH_3)_3C-Cl \xrightarrow[\text{Heat}]{\text{KOH/ethanol}} (CH_3)_2C=CH_2 + KCl + H_2O$$

Mechanism:

Step 1: $CH_3CH_2OH + KOH \longrightarrow CH_3CH_2O^-K^+ + H_2O$
(Potassium Ethoxide, corrected)

Step 2 (Carbocation Formation, Rate Determining Step)

$$(CH_3)_3C-Cl \rightleftharpoons (CH_3)_3C^+ + Cl^-$$
(t-butyl cation, corrected)

Step 3 (Elimination, corrected formula)

$$(CH_3)_2\underset{\underset{CH_3}{|}}{C^+}-CH_3 \xrightarrow{CH_3CH_2O^-} (CH_3)_2C=CH_2 + CH_3CH_2OH$$

E_2 Mechanism for $(CH_3)_2C(Br)CH_2CH_3$ (2-bromo-2-methylbutane)

Reaction:

$$(CH_3)_3C-CH_2Br \xrightarrow[\text{Heat}]{\text{KOH/ethanol}} (CH_3)_2C=CHCH_3 + (CH_3)_3CCH_2O^-K^+$$

Mechanism:

$CH_3CH_2O^-$ abstracts a H from CH_3 on C-2 (forming isobutylene unit) OR from C-3 (forming trimethylethylene).
Show the main trimethylethylene product:

$$CH_3CH_2O^- \; H-C \; C=C \longrightarrow (CH_3)_2C=CHCH_3$$
$$H \qquad Br^-$$

SECONDARY ALKYL HALIDE (E_1 & E_2)

These undergo either Unimolecular Elimination reaction (E_1) or Bimolecular Elimination reaction (E_2).

E_1 Mechanism

Reaction:

$$CH_3CH(Br)CH_3 \xrightarrow[\text{Heat}]{KOH/CH_3OH} CH_3CH=CH_2 + KCl + CH_3OH$$

Mechanism:

Step 1: Formation of $CH_3O^-K^+$

Step 2: $CH_3CH(Br)CH_3 \rightleftharpoons CH_3CH^+CH_3 + Br^-$

Step 3: $CH_3CH^+CH_3 + CH_3O^- \longrightarrow CH_3CH=CH_2 + CH_3OH$

2-chloro-2-methylpropane.

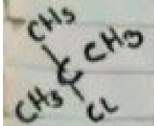
i) $(CH_3)_3C-Cl \xrightarrow[\text{heat}]{KOH/\text{ ethanol}} (CH_3)_2C=CH_2$

mechanism

Poluisium ethuvide

$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$

$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$



$(CH_3)_3C-Cl \rightleftharpoons (CH_3)_3\overset{+}{C} + \bar{Cl}$

$(CH_3)_2\overset{+}{C}-CH_2(H) \longrightarrow (CH_3)_2C=CH_2$

$\bar{O}CH_2CH_3$

ii) $CH_3CH_2C(CH_3)_2-Br \xrightarrow[\text{heaut}]{KOH/\text{ ethanol}} CH_3CH=C(CH_3)_2$

mechanism

$KOH + CH_3CH_2OH \longrightarrow CH_3CH_2\bar{O}K^+ + H_2O$

$CH_3CH_2\bar{O}K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$

$CH_3CH_2C(CH_3)_2-Br \rightleftharpoons CH_3CH_2\overset{+}{C}(CH_3)-CH_3 + \bar{Br}$

$CH_3CH(H)-\overset{+}{C}(CH_3)-CH_3 \xrightarrow{-H^+} CH_3CH=C(CH_3)_2$

$\bar{O}CH_2CH_3$

SECONDARY ALKYL HALIDE (E1)

These undergo either Unimolecular elimination reaction or Bimolecular elimination reaction (E2)

d) Unimolecular elimination reachin (E1)

$CH_3CH(Br)CH_3 \xrightarrow[\text{heat}]{KOH/CH_3OH} CH_3CH=CH_2$

$\longrightarrow CH_3\bar{O} + K^+$

$KOH + CH_3OH \longrightarrow CH_3\bar{O}K^+ + H_2O$

$CH_3CH(Br)CH_3 \rightleftharpoons CH_3\overset{+}{C}HCH_3 + \bar{Br}$

$CH_3\overset{+}{C}(H)-CH_2(H) \xrightarrow{-H^+} CH_3CH=CH_2$

$\bar{O}CH_3$

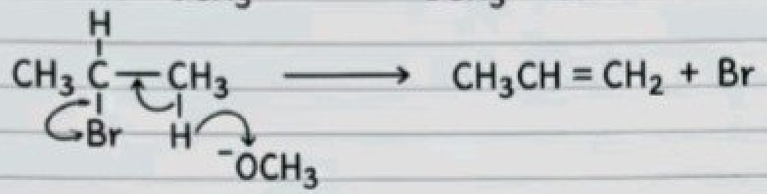
BIMOLECULAR ELIMINATION (E2)

The hydrogen atom and halogen atom of adjacent carbon atoms are lost at the same time.

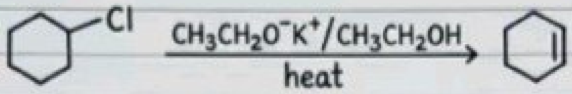
Example 1) $CH_3CH(Br)CH_3 \xrightarrow[\text{heat}]{CH_3OK/CH_3OH} CH_3CH{=}CH_2$

$KOH + CH_3OH \longrightarrow K^{+}\,{}^{-}OCH_3 + H_2O$

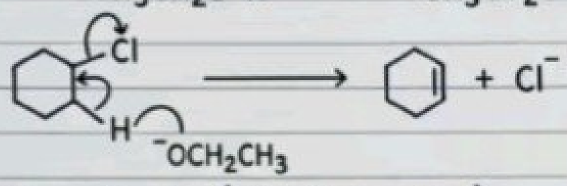
$K^{+}\,{}^{-}OCH_3 \longrightarrow {}^{-}OCH_3 + K^{+}$



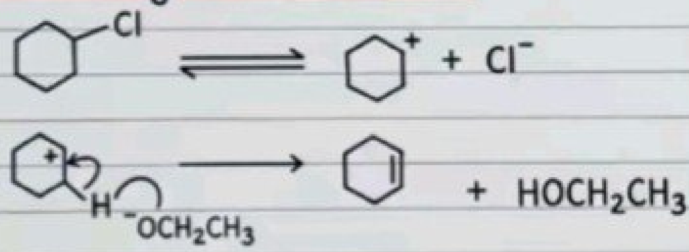
Example 2)



$CH_3CH_2O^{-}K^{+} \longrightarrow CH_3CH_2O^{-} + K^{+}$



Alternatively (E1 Mechanism)

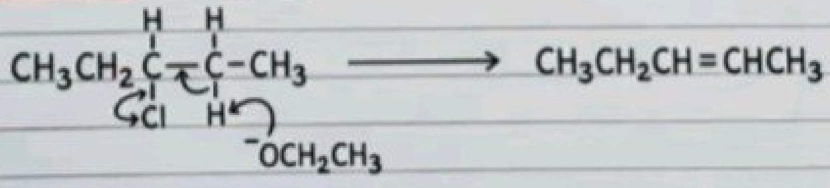


QUESTION

Complete the following reaction equations by writing the major organic products. In each case, suggest the accepted mechanism for the reaction.

(a) $CH_3CH_2CH(Cl)CH_2CH_3 \xrightarrow[\text{heat}]{CH_3CH_2O^{-}Na^{+}} CH_3CH_2CH{=}CHCH_3$

MECHANISM $CH_3CH_2O^{-}Na^{+} \longrightarrow CH_3CH_2O^{-} + Na^{+}$



PRIMARY ALKYL HALIDES

They undergo bimolecular elimination reaction to form an alkene as a minor product.
The major product (ether) is formed through bimolecular nucleophilic substitution reaction, eg

(d) $CH_3CH_2Cl \xrightarrow[\text{heat}]{KOH \mid CH_3CH_2OH} CH_3CH_2OCH_2CH_3 + CH_2{=}CH_2$

Chloroethane → (ethoxyethane) [annotated: ethoxyethane]

Mechanism:

$$CH_3CH_2OH + KOH \longrightarrow CH_3CH_2O^-K^+ + H_2O$$

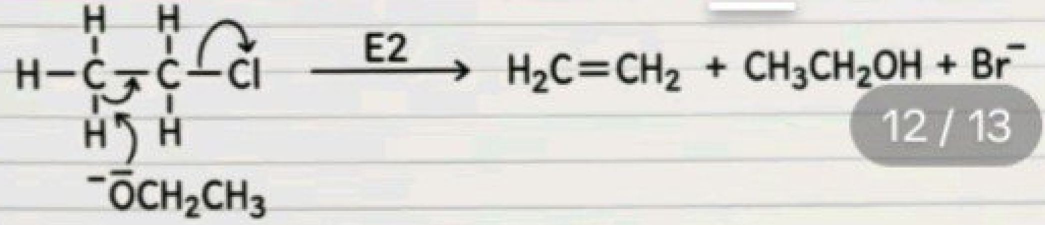
$$CH_3CH_2O^-K^+ \longrightarrow CH_3CH_2\bar{O} + K^+$$

$$CH_3CH_2{-}Cl \longrightarrow CH_3CH_2\bar{O}CH_2CH_3 + C\bar{l}$$

$^-OCH_2CH_3$

NOTE: If they give me a primary alkyl halide, I should write the major product as an ether (and not an alkene).

Mechanism for the formation of the minor product (ethene).



REACTION 2:

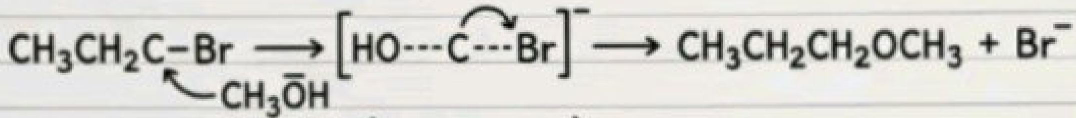
$$CH_3CH_2CH_2Br + \xrightarrow[\text{heat}]{KOH/CH_3OH} [\text{1-methoxypropane}] + [\text{Propene}]$$

Mechanism:

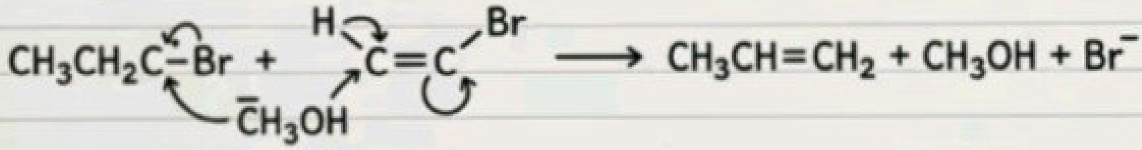
Formation of Nucleophile: $CH_3OH + KOH \rightleftharpoons CH_3\bar{O}\,K^+ + H_2O$

Dissociation: $CH_3\bar{O}\,K^+ \rightleftharpoons CH_3\bar{O} + K^+$

For Ether Product (Major - S_N2):

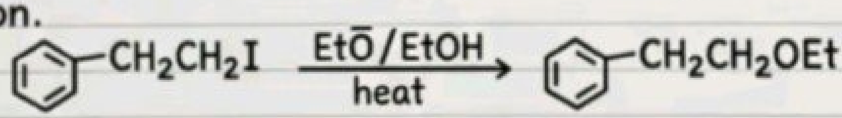


For Propene Product (Minor - E2):

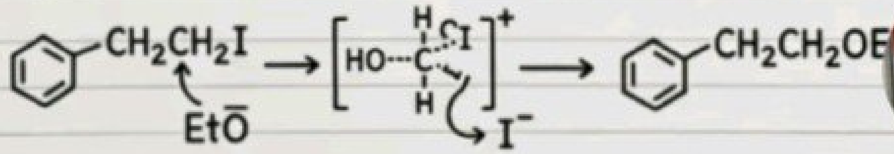


QUESTION: Complete the following equations by writing the major organic products. In each case, suggest the accepted mechanism of the reaction.

Question (a)



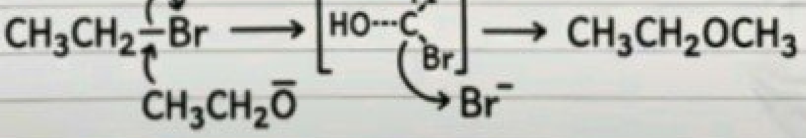
Mechanism



Question (b) $CH_3CH_2Br + \xrightarrow[CH_3CH_2OH,\ \text{heat}]{CH_3CH_2\bar{O}Na^+} CH_3CH_2OCH_2CH_3 + NaBr$

Mechanism

$$CH_3CH_2\bar{O}Na^+ \longrightarrow CH_3CH_2\bar{O} + Na^+$$



N.B. During organic synthesis, a primary alkyl halide cannot be **directly** converted to an **alkene**. The alkyl halide is first converted to an alcchol, which is then dehydrated to form the alkene, i.e.

$$CH_3CH_2Cl \xrightarrow[\Delta]{NaOH(aq)} CH_3CH_2OH \xrightarrow[180°C]{Conc.H_2SO_4} H_2C=CH_2$$

(3) PARTIAL REDUCTION OF ALKYNES

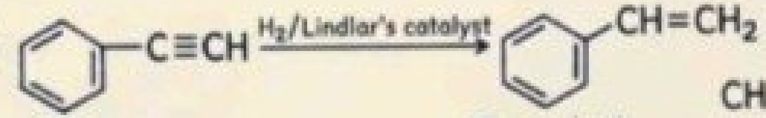
Alkynes react with hydrogen in the presence of **Lindlar's catalyst** to form **alkenes**, i.e. This reaction yields (Z)-alkenes (cis-alkenes) due to syn-addition.

$$RC \equiv CR' \xrightarrow{H_2/Lindlar's\ catalyst}$$ 

Examples:

1) $HC \equiv CH \xrightarrow{H_2/Lindlar's\ catalyst} H_2C=CH_2$
   Ethyne → Ethene

2) $CH_3C \equiv CH \xrightarrow{H_2/Lindlar's\ catalyst} CH_3CH=CH_2$
   Propyne → Propene

3) 

   Phenylethyne → Phenylethene (Styrene)

$CH_3CH_2CH=CH_2$

REACTIONS OF ALKENES

They are divided into two main categories, i.e.

- Oxidation reactions ↳ eg. $CCl_4/O_3,\ T<20°C$
- Electrophilic addition reactions

OXIDATION REACTIONS OF ALKENES

1 **REACTION WITH OZONE** (O_3)

Alkenes react with ozone in the presence of carbon tetrachloride at a **temperature** ... **20°C** to form **alkene ozonides**, i.e.

$$RCH=CHR' \xrightarrow[CCl_4,\ <20°C]{O_3}$$ 

$$\xrightarrow{Workup:\ Zn/H_2O} RCHO + R'CHO$$

Cleavage to Aldehyd...