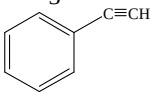
ALKYNES (ACETYLENES)

Alkynes are unsaturated hydro carbons which contain a triple bond in the carbon skeleton as their functional group.

They have a general formula C_nH_{2n-2} where $n \geq 2$.

NOMENCLATURE AND ISOMERISM OF ALKYNES

The name of alkyne is formed by replacing the end, from the corresponding "ane" with "yne" as shown below.

Alkyne	IUPAC name
$HC\equiv CH$	Ethyne
$CH_3C\equiv CH$	Propyne
$CH_3C\equiv CCH_3$	Butyne
	Phenyl ethyne
$HC\equiv CC\equiv CH$	Buta-1,3- diyne
$CH_3CHC\equiv CH$ (with CH_3 branch)	3-methylbut-1-yne
$CH_3CHC\equiv CCHCH_3$ (with CH_3 branches)	2,5-dimethylhex-3-yne

Note:

Alkynes show chain, functional and position isomerism.

Types of alkynes

Alkynes are classified according to the position of the triple bond.

1. Terminal
2. Symmetrical
3. Unsymmetrical

Examples:

Alkyne	Structure	Type
Propyne	$CH_3C\equiv CH$	Terminal/unsymmetrical
Butyne	$CH_3CH_2C\equiv CH$	Terminal/unsymmetrical
Buta-2-yne	$CH_3C\equiv CCH_3$	Symmetrical but not terminal
Penta-2-yne	$CH_3C\equiv CCH_2CH_3$	Unsymmetrical but non terminal
Hepta-2,5-diyne	$CH_3C\equiv CCH_2C\equiv CCH_3$	Unsymmetrical but terminal
Buta-1,3-diyne	$CH_3C\equiv CC\equiv CH$	Unsymmetrical but terminal

PREPARATION OF ALKYNE

a) Only ethyne can be prepared by the following methods:

1. Partial combustion of methane, yields ethyne.

$$4CH_4 + 3O_2 \longrightarrow 2HC\equiv CH + 6H_2O$$

2. Heating of methane in absence of air at 1500^oC also yields ethyne.

$$CH_4 \xrightarrow{1500^0C} HC\equiv CH$$

3. Hydrolysis of calcium carbide also yields ethyne.

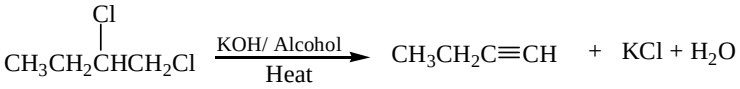
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

GENERAL METHODS FOR PREPARATION OF ALKYNES

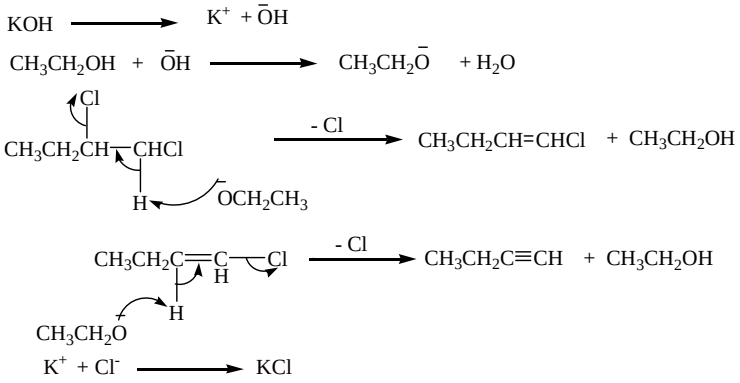
b) From dihalogeno alkanes

When dihalogeno alkanes are heated with excess alkali in the presence of an organic solvent like ethanol, dehydrohalogenation occurs giving an alkyne.It is an elimination reaction in which two moles of halogen acids (HX) are lost

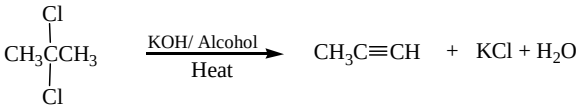
Example I



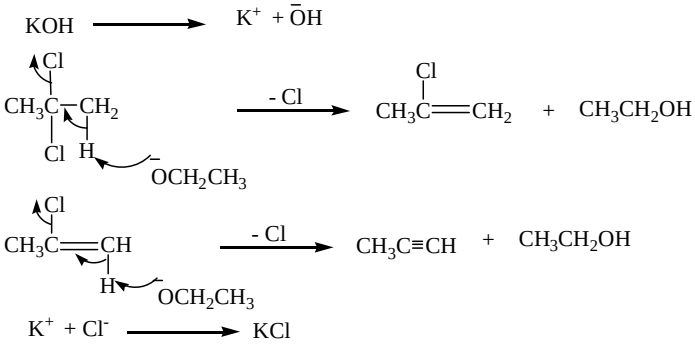
Mechanism



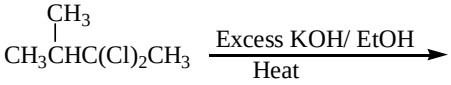
Example II



Mechanism



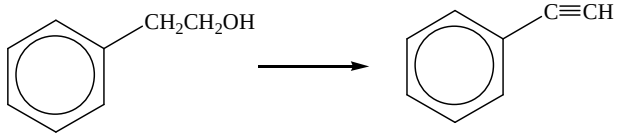
Complete and suggest a suitable mechanism



Organic synthesis

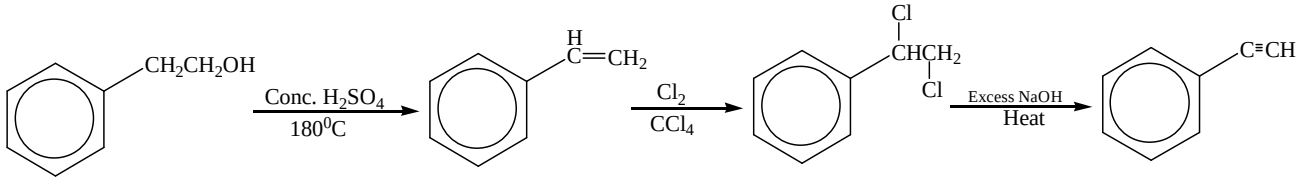
Sample question

Convert



Phenyl ethanol Phenyl ethyne

Solution



c) From CaO

This method is specifically for ethyne.

$CaO\ (s) + 3C\ (s) \xrightarrow[2000^0C]{} CaC_2\ (s) + CO\ (g)$

$CaC_2\ (s) + H_2O\ (l) \longrightarrow C_2H_2 + Ca(OH)_2\ (aq)$

Organic synthesis

Sample question

Convert

$C\ (s) \longrightarrow CH_3CH_2OH$

$C\ (s) + CaO\ (s) \xrightarrow[2000\ ^0C]{} CaC_2 \xrightarrow{H_2O} HC{\equiv}CH \xrightarrow[Ni/\ 150\ ^0C]{Limited\ H_2} H_2C{=}CH_2 \xrightarrow{H_2O/\ H^+(aq)} CH_3CH_2OH$

d) From alkanes

(i) **partial oxidation of alkanes**

$CH_4 + ½O_2 \longrightarrow HC{\equiv}CH + H_2O$

(ii) **Thermal cracking**

$2CH_4 \xrightarrow[15000\ ^0C]{} HC{\equiv}CH + 3\ H_2$

Physical properties

Physical properties of alkynes are similar to alkanes and alkenes. However boil to at higher temperatures than alkanes and alkenes with the same number of carbon atoms.

REACTIONS OF ALKYNES

1. Electrophilic addition

This is where an **electron seeking species** is added across a triple bond. Alkynes are very reactive because of the presence of π electrons in a triple bond. This reaction is essentially like that of alkenes however, 2moles of the electrophile are required to saturate an alkyne.

2. Addition of halogens (X_2)

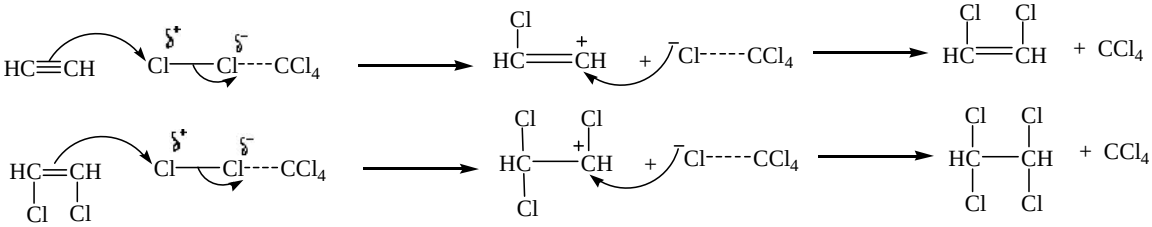
$HC{\equiv}CH + Cl_2 \xrightarrow{CCl_4} ClCH{=}CHCl \xrightarrow{Cl_2/CCl_4} Cl_2HCCHCl_2$

Overall

$HC{\equiv}CH + 2Cl_2 \xrightarrow{CCl_4} Cl_2HCCHCl_2$

1,1,2,2- tetrachloroethane

Mechanism



Complete and suggest a suitable mechanism

$CH_3C{\equiv}CH + Br_2 \xrightarrow{CCl_4}$

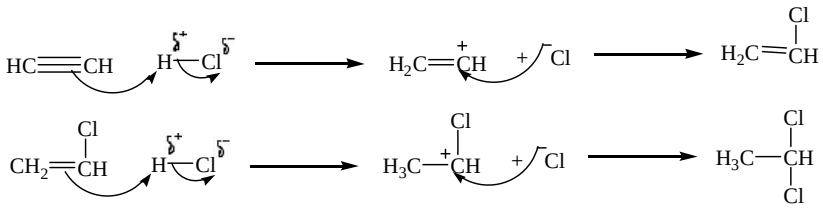
3. Reaction with Halogen acids (HX)

Alkynes react with halolgen acids to give dihalides depending on the structure of an alkyne, the dihalide can either be a gem or vicinal due to Makwonikov's rule.

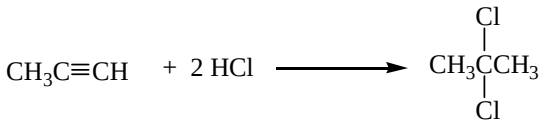
Example I

$HC{\equiv}CH + 2\ HBr \longrightarrow CH_3CHBr_2$

Mechanism

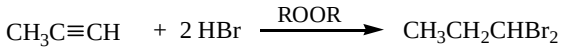


Example II

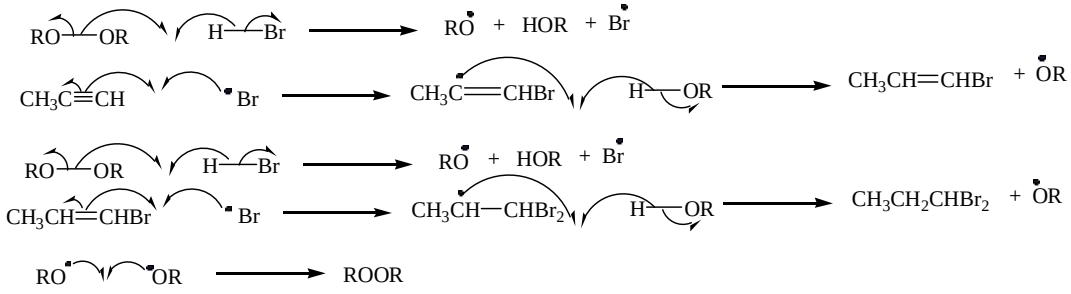


Suggest a suitable mechanism

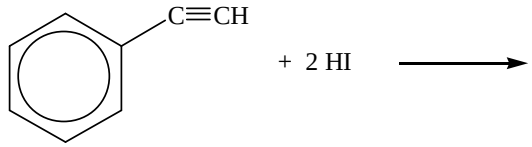
Example III



Mechanism



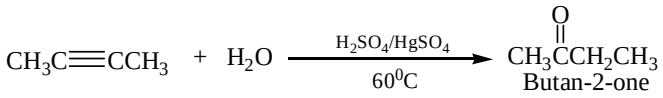
Complete and suggest a suitable mechanism



4. Reaction with H_2O

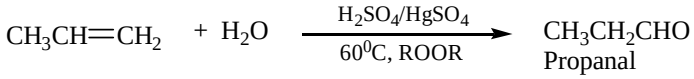
Alkynes react with $_{H2}O$ in the presence of $_{H2}S_{O4}$ acid and HgS_{O4} with a temperature of about $6^{0o}C$ to form carbonyl compounds. A symmetrical alkyne forms a ketone.

Example I



Suggest a suitable mechanism

Example II

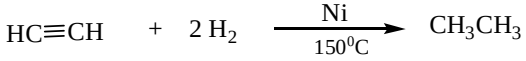


Suggest a suitable mechanism

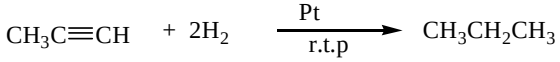
5. Reaction with H_2

Alkynes just like alkenes react with H_2 when passed over a suitable catalyst like Ni/150^{o}C, pt/r.t.p to form an alkane.

Example I

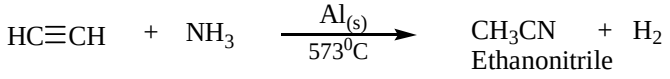


Example II



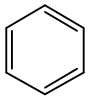
6. Nitrile formation

When little NH_3 is passed over an alkyne heated over an Al catalyst at 573^{o}C, a nitrile is formed.



7. Polymerisation

Due to the presence of a triple bond, alkynes polymerise to form cyclic or aromatic compounds. This occurs when an alkyne is heated in a glass tube containing Fe catalyst (4000^oC).

$$HC{\equiv}CH \xrightarrow[4000^0C]{Fe}$$ 

When two molecules of ethyne combine by passing them through a saturated solution of copper(I) chloride in ammonium chloride, vinyl ethyne is formed.Vinyl ethyne is a good starting material for linear polymers.

$$2\,HC{\equiv}CH \xrightarrow[NH_4Cl]{CuCl} \underset{\text{Vinyl ethyne}}{H_2C{=}CHC{\equiv}CH}$$

$$H_2C{=}CHC{\equiv}CH + HC{\equiv}CH \longrightarrow H_2C{=}CHCH{=}CHC{\equiv}CH$$

A terminal proton of an alkyne can be substituted by other electropositive metals. This indicates that, such alkynes are acidic.

NOTE: Only terminal alkynes behave this way. Non terminal do not.

$$HC{\equiv}CH \xrightarrow{\text{Liquid } NH_3} Na^+C^-{\equiv}C^-Na^+ + H_2$$

$$2CH_3C{\equiv}CH \xrightarrow{\text{Liquid } NH_3} 2\,CH_3C{\equiv}C^-Na^+ + H_2$$

8. With Ammoniacal copper(I)chloride solution

Similary, H_2 in alkynes can be substituted when its passed in solution of $CuCl/NH_3$ giving a red precipitate of Cu^+ alkyne derivative. This reagent is called ammoniacal copper(I)chloride solution, $CuCl/NH_{3(aq)}$.

$$HC{\equiv}CH \xrightarrow{CuCl/NH_3} \underset{\substack{\text{Red ppt.}\\ \text{Copper(I) ethyne (or Copper acetylide)}}}{CuC{\equiv}CCu} + 2HCl$$

9. With ammoniacal silver nitrate solution

When a terminal alkyne is bubbled through a solution of ammonial $AgNO_3$, a white precipitate of silver dicarbide is formed.

$$HC{\equiv}CH + 2AgNO_3 + 2NH_3 \longrightarrow \underset{\text{White ppt}}{AgC{\equiv}CAg} + 2NH_4NO_3$$

Differentiate between $CH_3\,C \equiv CH$ and $CH_3\,C \equiv CCH_3$

Reagent: Ammoniacalcopper (I) chloride solution.

Observation

With $CH_3C \equiv CH$: No observable change.

With $CH_3C \equiv CCH_3$: A red precipitate is observed.

The above reactions are used for distinguishing between terminal alkynes and non terminal

SYNTHESIS OF HIGHER ALKYNES

When an alkyne is passed through liquid NH_3 in presence of Na metal and the derivative formed is reacted with an alkyl halide, the chain is increased giving a higher alkyne.

$$HC{\equiv}CH \xrightarrow{\text{liquid } NH_3/Na} Na^+C^-{\equiv}C^-Na^+$$

$$Na^+C^-{\equiv}C^-Na^+ + 2CH_3Cl \longrightarrow CH_3C{\equiv}CCH_3 + 2NaCl$$

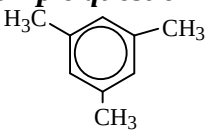
$$CH_3C{\equiv}CH + Na \xrightarrow{NaNH_2} CH_3C{\equiv}C^-Na^+$$

$$CH_3C{\equiv}C^-Na^+ + CH_3CH_2Cl \longrightarrow CH_3C{\equiv}CCH_2CH_3 + NaCl$$

Physical properties of alkynes

- They are insoluble in H_2O.
- They are very soluble in organic solvents like benzene, CCl_4.
- They are less dense than H_2O.
- Their boiling points increase with increase in number of carbon atoms. E.g. Ethyne boils at -75, propane -43, butyne at 91.
- They have got almost the same boiling points as those of corresponding alkenes because they have got the same vanderwaal's forces of attraction.

Organic synthesis sample question

Convert $HC\equiv CH$ to 

Solution

$2HC\equiv CH + Na \xrightarrow{NaNH_2} 2HC\equiv C^-Na^+ + H_2$

$HC\equiv C^-Na^+ + CH_3Cl \longrightarrow CH_3C\equiv CH + NaCl$

$CH_3C\equiv CH \xrightarrow[4000^0C]{Fe}$