MIND MAP

Hydrocarbon Alkane

Physical Properties

1. C_1 to C_4 gases, Neopentane also gas but n-pentane and isopentane are low B.P. liquids.
2. Next members C_6 to C_{17} are Colourless liquids and above C_{17} are Waxy solids.
3. BOILING POINT

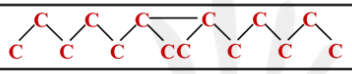
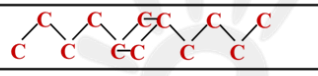
Boiling Point ∝ molecular weight (for n – alkanes) ∵ Vanderwaals force of attraction ∝ molecular weight ∝ surface area of molecule i.e. boiling point Pentane < hexane < heptane

$$\text{Boiling point} \propto \frac{1}{\text{number of side chain}}$$

For side chain containing compounds the shape approaches Spherical which results in decrease in Vanderwaal forces (as surface area decreases). Thus boiling point

n–Pentane > Isopentane > neopentane

4. MELTING POINT

Ineffective Packing Odd number of carbon	
Effective Packing Even number of carbon	

5. OXIDATION

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O \ (\Delta H = -ve)$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

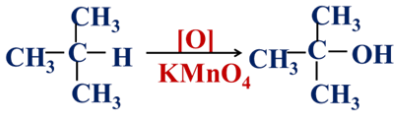
C–black (used in printing)

CATALYTIC OXIDATION (Red hot Cu or Fe tube)

i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation. $2CH_4 + O_2 \longrightarrow 2CH_3OH$ (High P and T)

ii) Alkanes on oxidation in presence of manganese acetate give fatty acids. $CH_3(CH_2)_nCH_3 \xrightarrow{(CH_3COO)_2Mn} CH_3(CH_2)_nCOOH$ (High Temp)

iii) Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.



The reactivity order for halogens is

$$F_2 > Cl_2 > Br_2 > I_2$$

$$X{:}X \xrightarrow[\text{Or } \Delta]{UV} X^{\bullet} + X^{\bullet}$$

Hydroforming or Dehydrogenation or Cyclisation or Catalytic Reforming or Aromatization

It provides an excellent method of passing from aliphatic to aromatic series.

$$n\text{-hexane} \xrightarrow[O_3\,500^0C]{Cr_2O_3/Al_2} \text{benzene} + 4H_2$$

$$CH_3(CH_2)_6-CH_3 \xrightarrow[500^0C]{Cr_2O_3/Al_2O_3} \text{o-xylene} + \text{benzene}$$

n-octane

Alkane(C_nH_{2n+2})

Alkanes do not react with chemical reagents such as dil. and conc. HCl, dil. & conc. H_2SO_4, dil. & conc. HNO_3, Caustic soda, acidic & basic $K_2Cr_2O_7$, $KMnO_4$ etc.

That is why alkanes are called paraffins. (Parum = little, affins = reactivity).

CATALYST is a substance that increases or decreases the rate of a chemical reaction without itself undergoing any permanent chemical change.

Mechanism for Halogenation

Step I Chain Initiation Step $Cl:Cl \xrightarrow[\text{Or } \Delta]{UV/\ h\nu} Cl^{\bullet} + Cl^{\bullet}$

Step II Chain Propagation Step

$Cl^{\bullet} + H:CH_3 \longrightarrow H:Cl + {}^{\bullet}CH_3$ (Carbon Free Radical Intermediate)

${}^{\bullet}CH_3 + Cl:Cl \longrightarrow CH_3Cl + Cl^{\bullet}$ (Methyl Free Radical)

Step III Chain Termination Step

$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$

$CH_3^{\bullet} + {}^{\bullet}Cl \longrightarrow CH_3Cl$

$CH_3^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$

Le Chatelier's Principle

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HIO_4, HNO_3, HgO etc. which destroy HI.

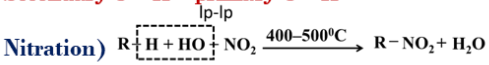
$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

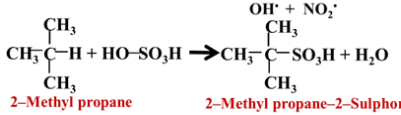
Reactivity order of hydrogen atom in alkane is

Tertiary C – H > Secondary C – H > primary C – H

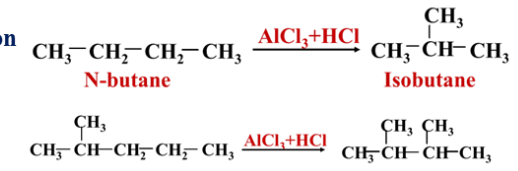
Nitration (Vapour Phase Nitration)



Sulphonation



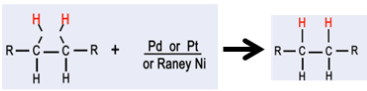
Isomerization



MIND MAP

Hydrocarbon Alkane

Methods of Preparation of Alkane

1) From alkenes and alkynes (Catalytic Hydrogenation)	$R-CH=CH-R + H_2 \xrightarrow{\text{Catalyst}} R-CH_2-CH_2-R$ Alkene → Alkane	
	Catalytic Hydrogenation a) Pd/Pt at ordinary T&P. b) Ni, 200–300° C (Sabatier & Sandren's reaction) c) Raney Nickel at room temp.	Catalyst is taken in powdered form. Methane can not be prepared by this method (From unsaturated hydrocarbon).
2) From Alkyl Halides	$R-X + H_2 \longrightarrow R-H + HX$ i) Zn + HCl ii) $Zn + CH_3COOH$	Reduction is due to the electron transfer from the metal to the substrate (R- X)
3) From alkyl halide (By Wurtz reaction	$R-X + 2Na + X-R \xrightarrow[\text{Ether}]{\text{Dry}} R-R + 2NaX$ $CH_3X + C_2H_5X \longrightarrow CH_3-CH_3$, $C_2H_5-C_2H_5$, $CH_3-CH_2-CH_3$ (Mixture) Separation Not Possible	1. Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken. 2. Two different alkyl halides, on Wurtz reaction give all possible alkanes. 3. The separation of mixture into individual members is not easy because their B.P. are near to each other and thus Wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.
4) From Frankland Reagent	$R\text{-}X + 2Zn + RX \longrightarrow R_2Zn + ZnX_2$ Frankland Reagent $R_2Zn + R\text{-}X \longrightarrow R\text{-}R + RZnX$	
5) From Carboxylic Acid (By Decarboxylation)	$RCOONa + NaOH \xrightarrow[CaO]{\Delta} R\text{-}H + Na_2CO_3$	Reactivity of decarboxylation ∝ stability of carbanion $HCOONa + NaOH\ (CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3$ If in a compound two carboxylic groups are present and they are attached to same carbon atom then also decarboxylation of one of the carboxylic groups takes place simply on heating
6) From carboxylic acid (By Kolbe's process) Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.	Electrolysis $2RCOONa + 2H_2O \longrightarrow \underbrace{R-R + 2CO_2}_{\text{At Anode}} + \underbrace{2NaOH + H_2}_{\text{At cathode}}$	Kolbe's Electrolysis $2CH_3COONa \longrightarrow CH_3-CH_3$ Kolbe's Electrolysis $CH_3COONa + C_2H_5COONa \longrightarrow CH_3-CH_3$, $CH_3-CH_2-CH_2-CH_3$, $CH_3-CH_2-CH_3$

MIND MAP

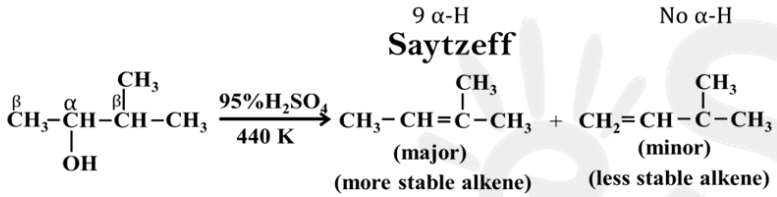
Hydrocarbon Alkene

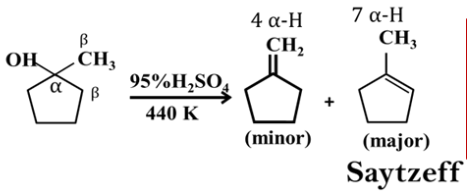
Introduction

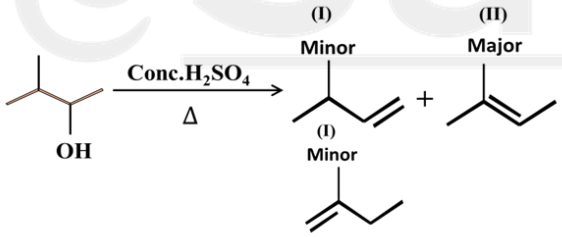
Alkenes are hydrocarbons with carbon-carbon double bonds. Alkenes are sometimes called olefins, a term derived from olefiant gas, meaning 'oil forming gas'.

Saytzeff Rule

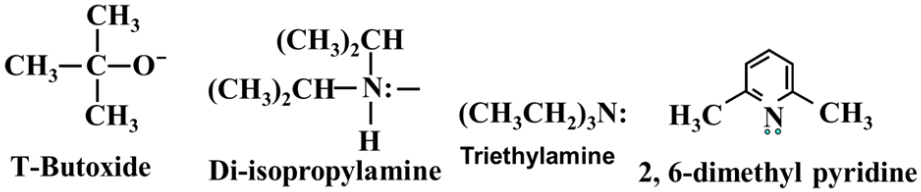
The product with the most highly substituted (more alkylated) double bond will predominate. This rule is called the Saytzeff or Zaitsev rule. More alkylated product is called the Saytzeff Product.



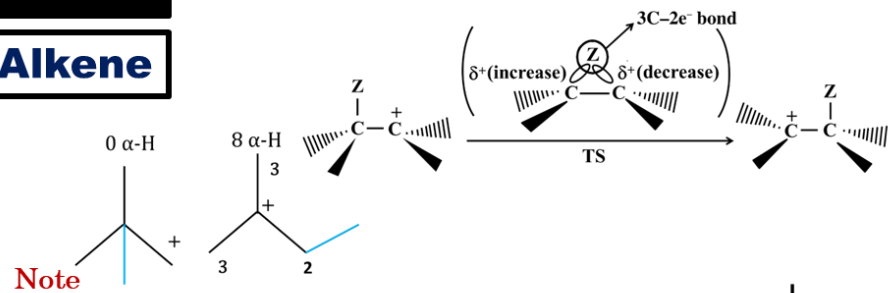




Bulky Base

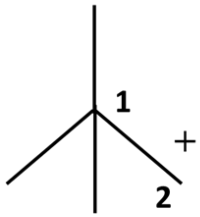


Carbocation Rearrangement

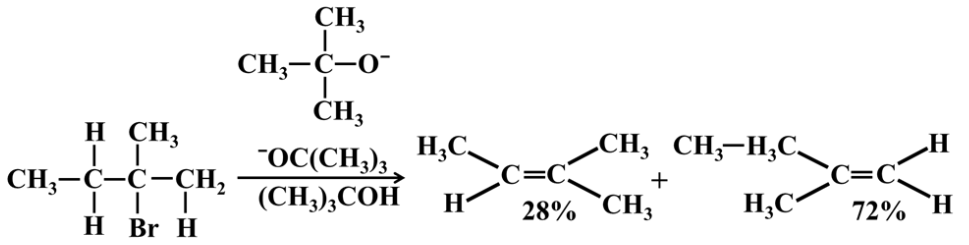


Note

1. It's an example of 1, 2 shift.
2. 3-MCTS (3 membered cyclic transition state) involved
3. Migration takes place according to stability of Carbocation. That group migrates which leads to increased stability of C+



Formation of The Hoffmann Product

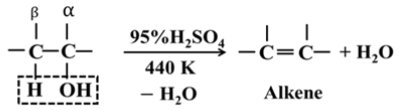


MIND MAP Hydrocarbon Alkene

Method Of Preparation of Alkene

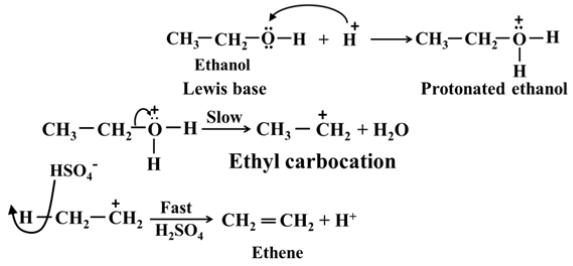
(1) From Alcohols (Dehydration)

1. For dehydration following catalyst can be used Conc. H_2SO_4, H_3PO_4, $KHSO_4$ etc.
2. Endothermic Reaction
3. Higher temperature is required for dehydration.



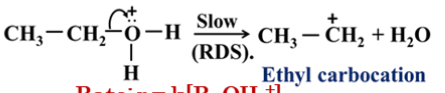
β–elimination or α, β–elimination

Mechanism of Reaction



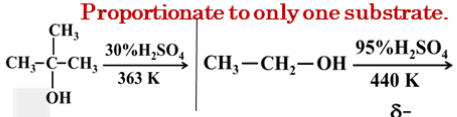
E1 Mechanism

Reaction involves E1(unimolecular elimination) mechanism

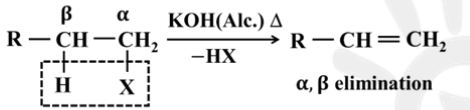


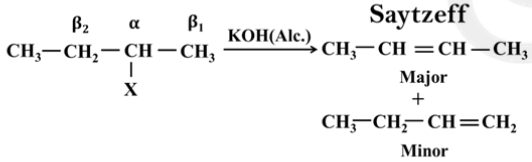
Rate: $r = k[R–OH_2^+]$

Proportionate to only one substrate.

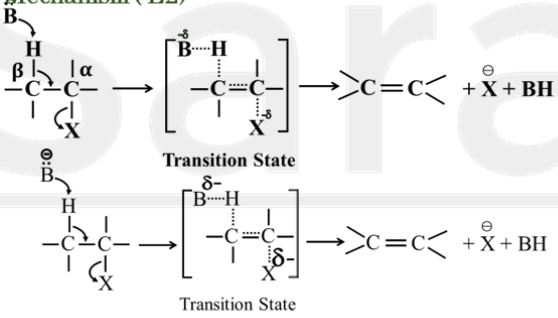


2) From Alkyl halide (By dehydrohalogenation)





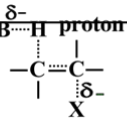
Mechanism (E2)



This is a single step, bimolecular reaction

Rate = k [R – X] [B^-]

Characteristics of E2 Reaction



(i) Rearrangement is not possible, since carbocation is not formed.

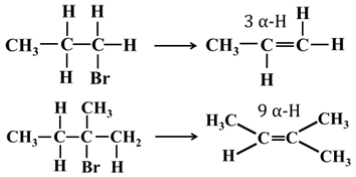
(ii) The proton & leaving group should be anti to each other or at an angle of 180 to each other.

(iii) Reactivity order for alkyl halide towards E2 reaction is given as R – I > R – Br > R – Cl > R – F

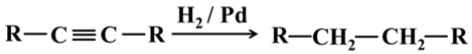
(R – X bond breaking involved)

(iv) Reactivity order for alkyl group towards E2 reaction is given as

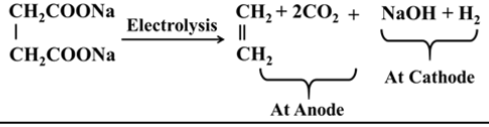
Tertiary > secondary > primary



3) Hydrogenation of Alkyne



4) Kolbe's Method



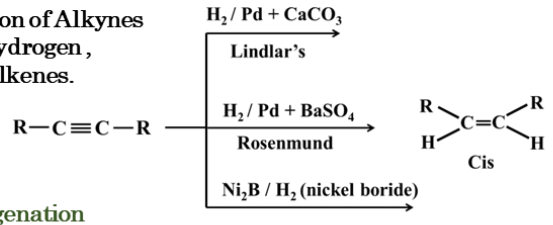
Method of Preparation of Alkene

MIND MAP

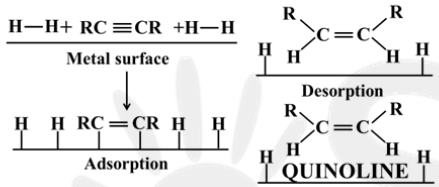
Hydrocarbon Alkene

5) Catalytic Hydrogenation of Alkynes in presence of Poisoned Catalyst

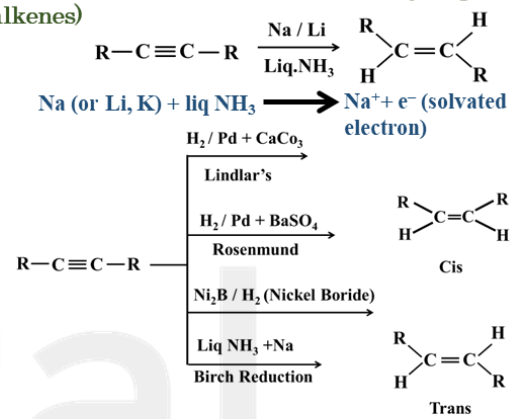
(a) By partial reduction of Alkynes
Syn addition of hydrogen,
Synthesis of cis-alkenes.



Mechanism of Hydrogenation

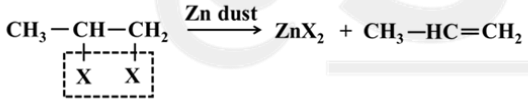


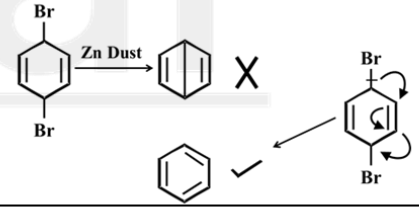
(b) Birch Reduction (Anti addition of hydrogen : synthesis of trans-alkenes)



6) Dehalogenation

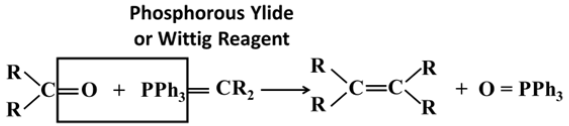
α, β elimination

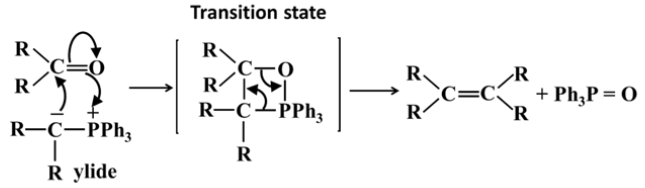




7) Wittig Reaction

The aldehydes and ketones are converted into alkenes by using a special class of compounds called phosphorus ylides, also called Wittig reagents.





Addition of Carbene

The addition of carbene to alkene is carried out by diazomethane CH_2N_2. Carbene group obtained from diazomethane is added to alkene and gives cycloalkanes.

$$CH_2 = CH_2 + CH_2N_2 \xrightarrow{\Delta} CH_2 - CH_2 + N_2$$
$$\qquad\qquad\qquad\qquad\quad \diagdown\!\diagup \; CH_2$$

Oxidation Reaction

Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

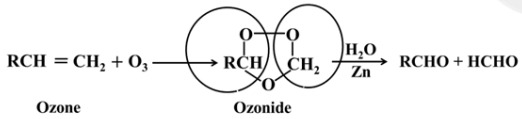
1. Alkene On Combustion Gives CO_2 And H_2O

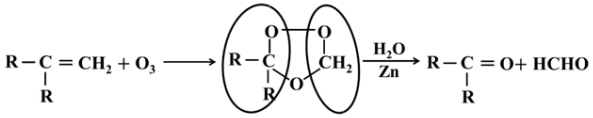
$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

One mole of alkene requires $\frac{3n}{2}$ moles of O_2 for complete combustion.

2. Ozonolysis (A Test For Unsaturation In Molecule)

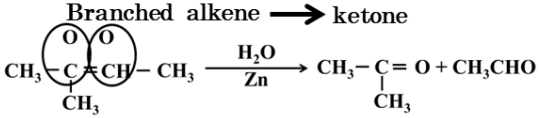
$$RCH = CH_2 + O_3 \xrightarrow[Zn]{H_2O} RCHO + HCHO$$





Unbranched alkene → aldehyde

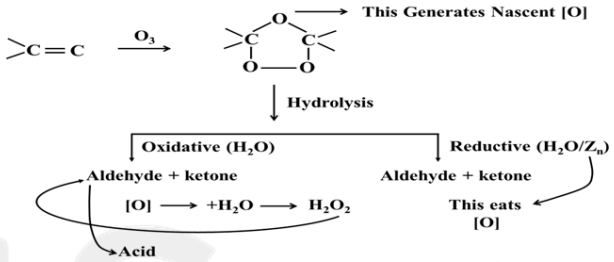
Branched alkene → ketone



This reaction is used to determine the position of double bond in alkene.

MIND MAP

Hydrocarbon Alkene

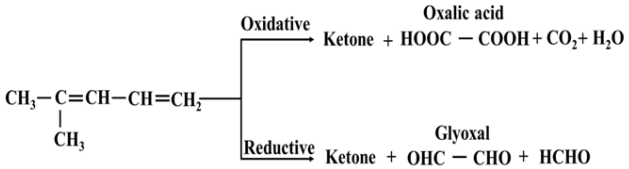


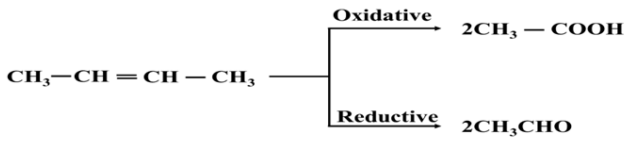
Note If aldehyde formed is formaldehyde (in Oxidative) then

$$HCHO \xrightarrow{H_2O_2} HCOOH \xrightarrow{[O]} OH - \underset{\underset{O}{\|}}{C} - OH \;(H_2CO_3)$$

Unstable

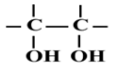
$$CO_2 + H_2O$$





3. Hydroxylation (Formation of Vicinal Alcohol)

Oxidation of carbon-carbon double bond to



is known as hydroxylation.

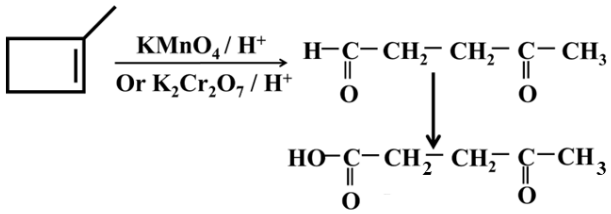
(a) Oxidation By Baeyer's Reagent (A Test For Unsaturation)

Alkenes on passing through dilute alkaline 1% cold $KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $KMnO_4$ and gives brown ppt of MnO_2 and glycol.

$$CH_3 - CH = CH_2 + H_2O + [O] \xrightarrow[273K]{\text{dil. } KMnO_4 \text{ (Bayer's Reagent)}} \underset{\text{Propane -1,2- diol}}{CH_3 - \overset{OH}{\overset{|}{C}}H - \overset{OH}{\overset{|}{C}}H_2}$$

Oxidation By Strong Oxidising Agent (Oxidative Cleavage)

The alkenes are readily oxidised to acid or ketone by means of acid permanganate ($KMnO_4/H^+$) or acid dichromate ($K_2Cr_2O_7/H^+$). If HCOOH is formed, it further oxidises to CO_2 and H_2O. No further oxidation of ketones will take place.



MIND MAP

Hydrocarbon Alkene

Substitution Reaction (Allylic and Benzylic Substitution)

Allylic

$CH_3-CH=CH_2$

Benzylic

CH_2-CH_3

$CH_3-CH=CH_2 + Cl_2 \xrightarrow{500°C} ClCH_2-CH=CH_2 + HCl$

Allyl chloride
(3-Chloro prop-1-ene)

$CH_2-CH_3 \xrightarrow[500^0C]{Cl_2} CH(Cl)-CH_3 + HCl$

Note N-Bromosuccinimide (NBS) is an important reagent used for allylic and benzylic bromination.

$CH_3-CH=CH_2 + CH_2(-C(=O)-N(-Br:)-C(=O)-)CH_2 \longrightarrow CH(-C(=O)-NH-C(=O)-)CH + Br-CH_2-CH=CH_2$

(NBS)

Substitution reaction is not given by ethene, because allylic or benzylic position is absent.

Polymerization

$n(CH_2=CH_2) \xrightarrow[\text{Catalyst}]{\text{High T/P}} +CH_2-CH_2+_n$

Monomer — Polythene — Polymer

Addition Reaction of Conjugated Diene

$CH_2=CH-CH=CH_2$

Electrophilic Addition Reactions

The electrophilic addition is illustrated by the attack of halogen acid on buta–1,3–diene, a conjugated diene.

$CH_2^1=CH^2-CH^3=CH_2^4 \xrightarrow{HBr}$ Buta–1, 3 diene

$CH_2^1(H)-CH^2(Br)-CH=CH_2$

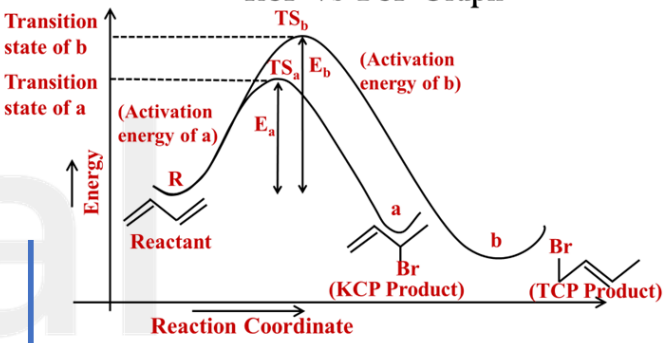
$CH_2^1(H)-CH^2=CH^3-CH_2^4(Br)$

KCP vs TCP

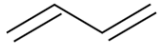
(i) KCP ⇒ Kinetically controlled product
⇒ Product which is quickly formed
⇒ Product formed by lowest activation energy

(ii) TCP ⇒ Thermodynamically controlled product
⇒ Most stable

KCP Vs TCP Graph



Low Temprature :- KCP Product favoured
High Temprature :- TCP Product favoured



HBr

$-80°C \rightarrow CH_2=CH-CH(Br)-CH_3$

1,2–Addition product
(Major) KCP product

$35°C \rightarrow CH_2(Br)-CH=CH-CH_3$

1,4–Addition product
(Major) TCP product

MIND MAP

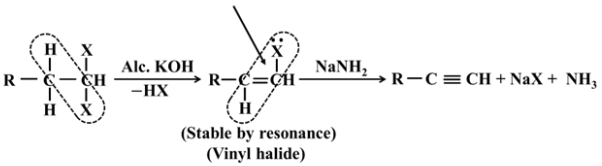
Hydrocarbon Alkene

Alkynes Methods of Preparation

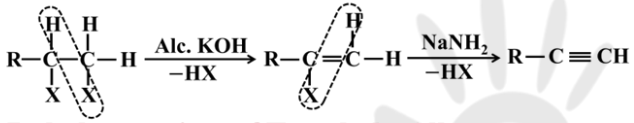
From Gem Dihalides (By Dehydrohalogenation)

Dehydrohalogenation agents are $NaNH_2$ (Sodamide) or Alc. KOH or ROH + RONa.

Resonance

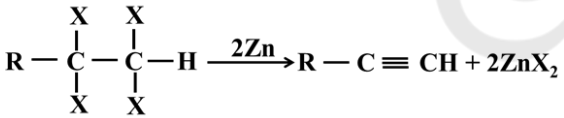


From Vicinal Dihalides (By Dehydrohalogenation)

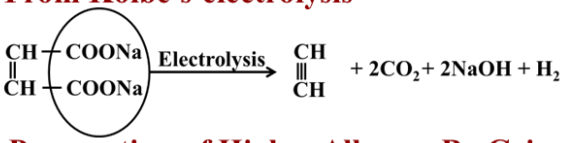


Dehalogenation of Tetrahalo Alkane

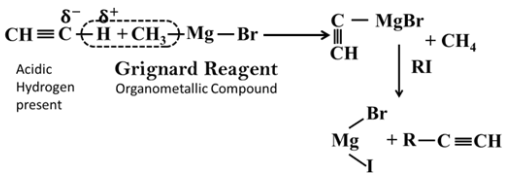
By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



From Kolbe's electrolysis



Preparation of Higher Alkynes By Grignard Reagent



Preparation of Ethyne or Acetylene

From Metal carbide [Laboratory method]

Acetylene is prepared in the laboratory by the action of water on calcium carbide.

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

From Haloform (CHI_3, $CHCl_3$)

Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder

$$CHI_3 + 6Ag + I_3CH \longrightarrow CH \equiv CH + 6AgI$$

(b) Presence of acidic hydrogen atom

Addition reaction

(a) Addition of hydrogen

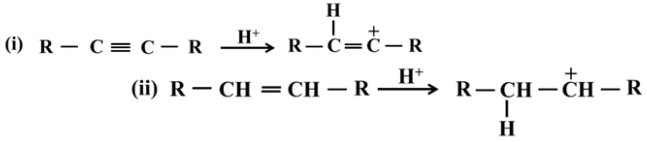
Alkynes react with hydrogen in presence of a catalyst. In presence of Pt, Pd or Ni alkynes give alkanes with H_2

Electrophilic Addition

The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes.

Reactivity order of hydrocarbons for electrophilic addition is Alkenes > Alkynes > Alkanes

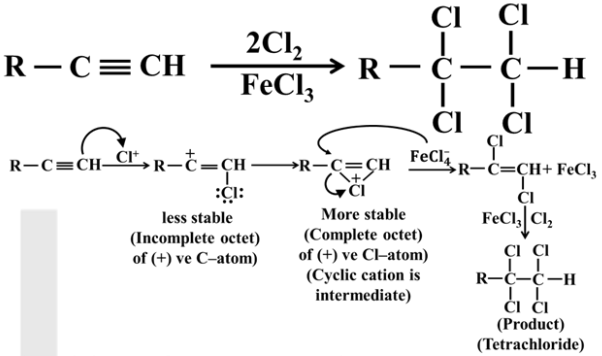
Reason is The intermediates when an electrophile attack on alkene and alkynes are



Addition of Halogens

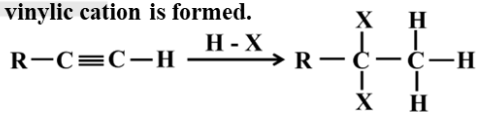
Reactivity order of Halogens $Cl_2 > Br_2 > I_2$

Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derivatives.



Addition of Halogen Acids (H – X)

Addition according to Markovnikov's Rule. Both the times Markovnikov's rule is applicable. Also no carbocation rearrangement will talke place here as vinylic cation is formed.



(Gem dihalides major product)

Reactivity order of H – X

HI > HBr > HCl > HF

Addition of HOX

Alkynes react with hypohalous acids according to Markovnikov's rule and form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.

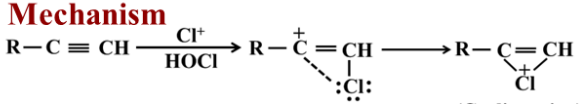
Reactivity order HOCl > HOBr > HOI

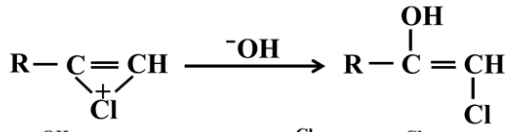
Hydrocarbon

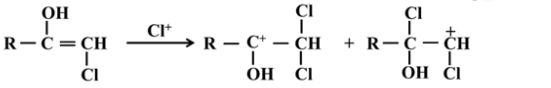
MIND MAP

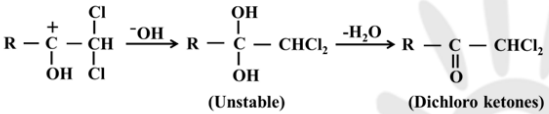
Hydrocarbon Alkynes

Mechanism



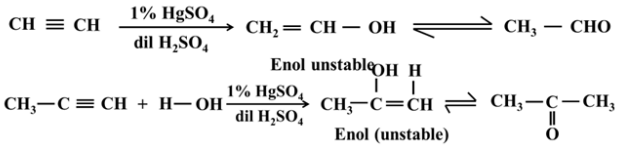






Nucleophilic addition reaction

In these reactions some heavy metal cation like Hg^{+2}, Pb^{+2}, Ba^{+2} are used. These cation attracts the π e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkyne.



Oxidation Reactions

(a) Combustion

$$C_nH_{2n-2} + \frac{3n-1}{2}O_2 \longrightarrow nCO_2 + (n-1)\,H_2O + \text{Heat}$$

$$2HC\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O + 312\ \text{K.cal}$$

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000^0C) is produced.

(b) Oxidation With Acidic $KMnO_4$ or $K_2Cr_2O_7$

In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$ alkynes are oxidized to monocarboxylic acids.

(c) Oxidation With Ozone (O_3)

In the ozonolysis both sp C-atoms are converted into $-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$ group.

Substitution Reaction

Formation of metallic derivatives

Only 1-alkynes give substitution reaction and show acidic characters $\equiv\overset{\delta^-}{C}-\overset{+\delta}{H}$

Cyclic Polymerisation

When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound.

Laboratory Test for alkynes(Test is used for presence of unsaturation in compound)

Functional Group	Reagent	Observation
$-C\equiv C-$	(1)Bayer's Reagent Alk.dil.Cold $KMnO_4$	Pink Colour disappears
	(2) Br_2/H_2O	Red Brown Colour decolourises
	O_3 (Ozone)	Acid Formed

Laboratory test of terminal alkynes(Test is used for distinguishing between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.)

Functional Group	Reagent	Observation	Reaction
$R-C\equiv C-H$	(1) Cuprous chloride $+NH_4OH$	Red ppt.	$R-C\equiv CH + CuCl \xrightarrow{NH_4OH} R-C\equiv C-Cu\downarrow$(red ppt)
	(2) $AgNO_3+NH_4OH$ Tollens reagent	White ppt. (silver mirror test)	$R-C\equiv CH + Ag \rightarrow R-C\equiv C\,Ag$ (white ppt)
	(3) Na in ether	Colourless gas	$HC\equiv CH + 2Na \rightarrow Na-C\equiv C-Na + H_2\uparrow$