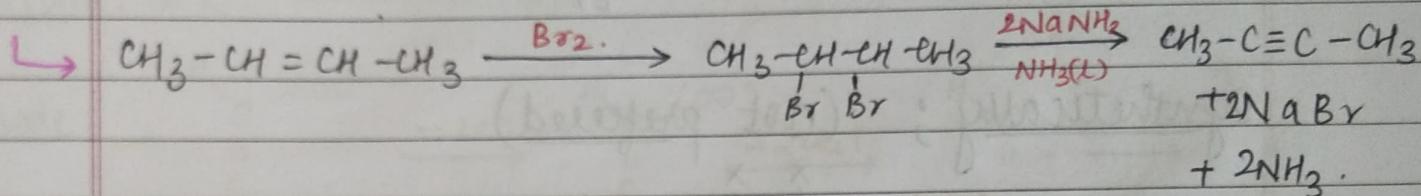
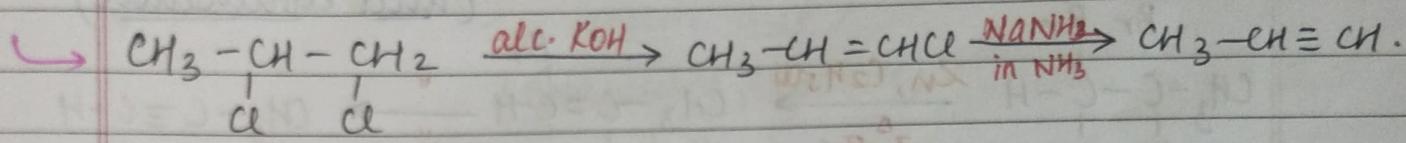


ALKYNES

Preparation of alkynes

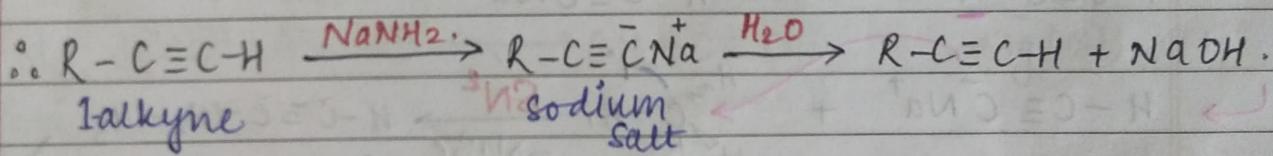
① Dehydrohalogenation of vicinal dihalides



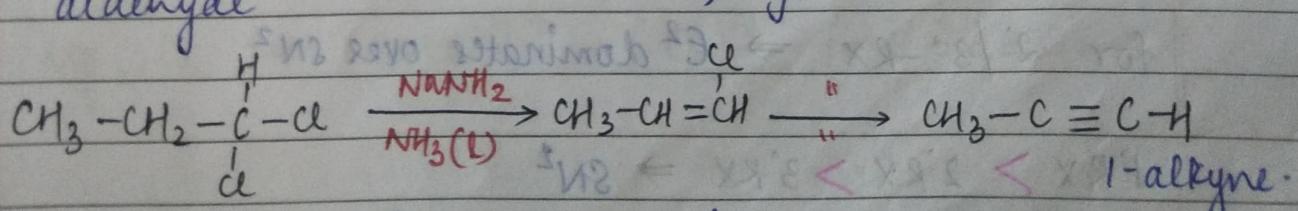
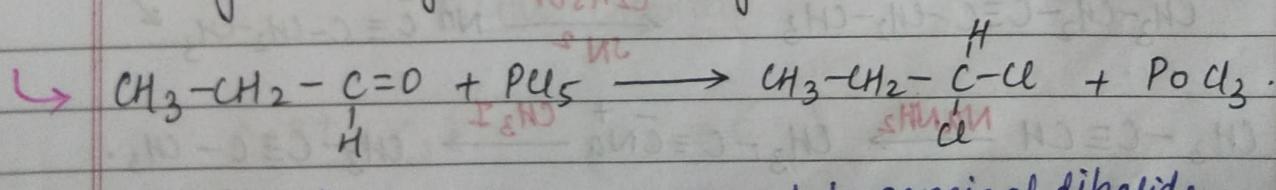
* NaNH_2 as a base for 1-alkyne product \Rightarrow sodium salt.
alkynes.

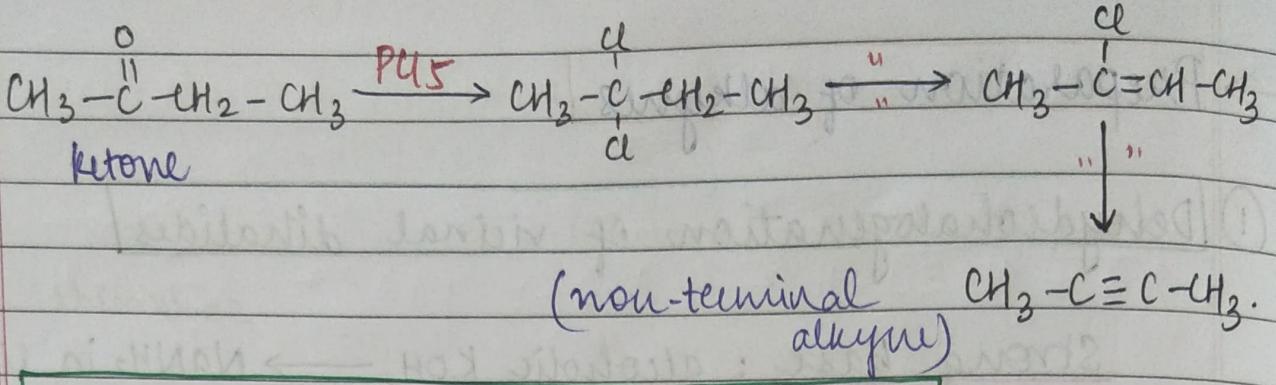
Terminal

Non-terminal
 $R-C\equiv C-R$ (xacidic)

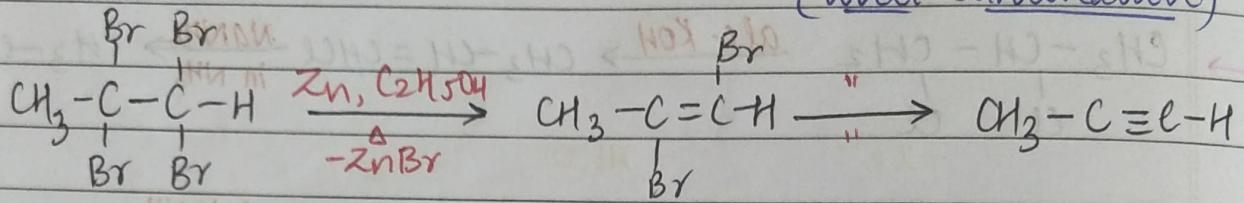


② Dehydrohalogenation of geminal dihalides /

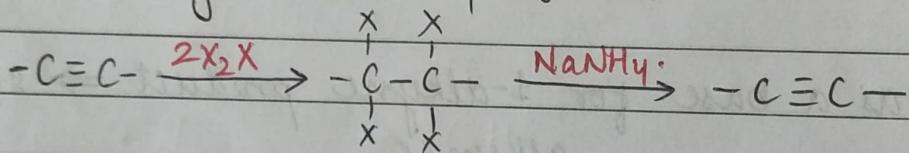




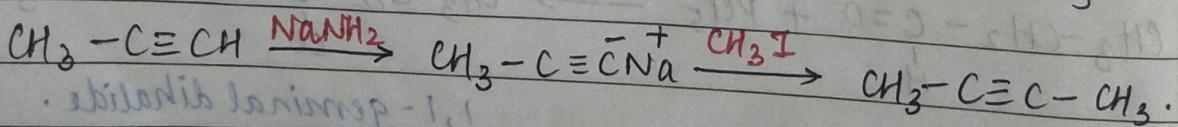
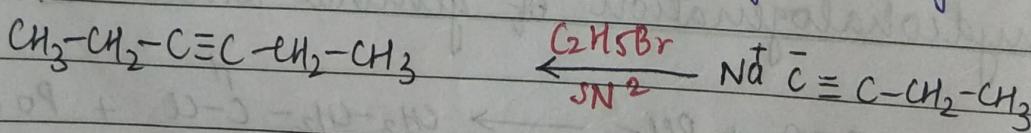
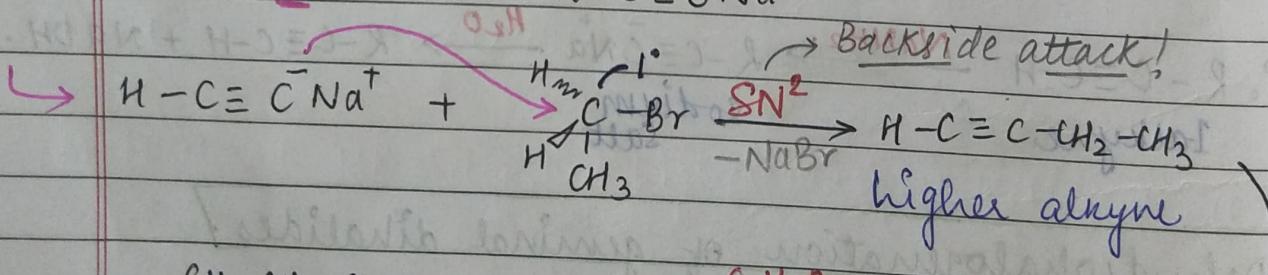
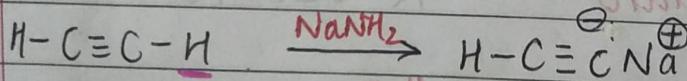
(3) Dehalogenation of vicinal tetrachloride (anti elimination)



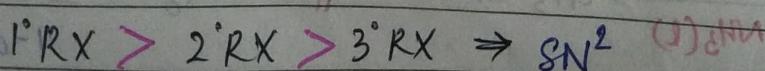
synthetically; (not preferred)



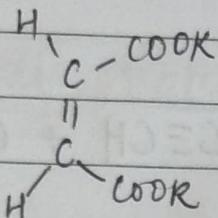
(4) Synthesis of higher alkynes from 1-alkyne



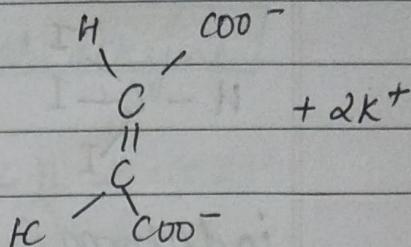
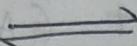
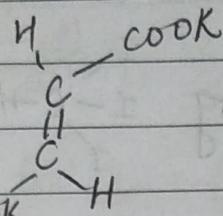
for $2^\circ/3^\circ-\text{RX} \Rightarrow \text{E}^2$ dominates over SN^2



(5) Kolbe's electrolytic method



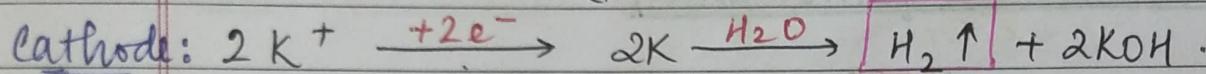
or



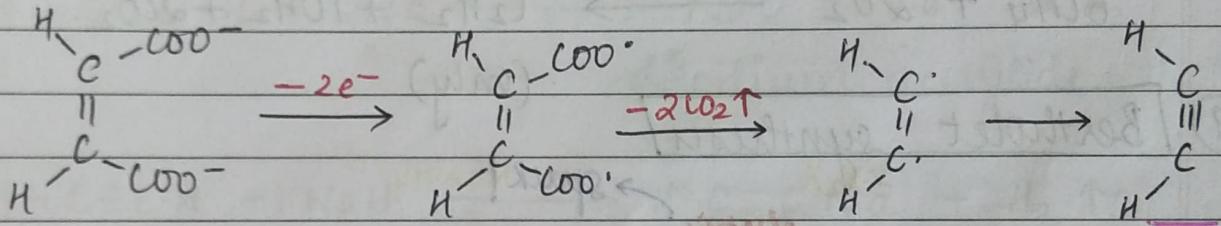
(salt of malic acid)
(potassium malate)

(salt of
formic acid)

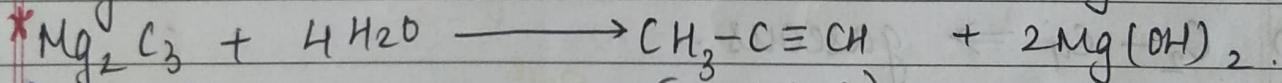
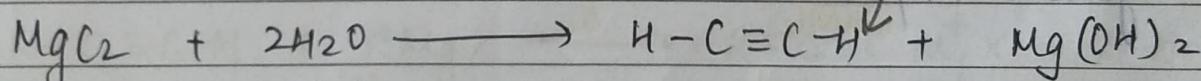
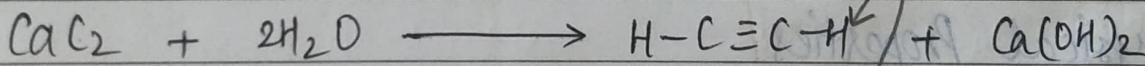
(potassium formate)



Anode:

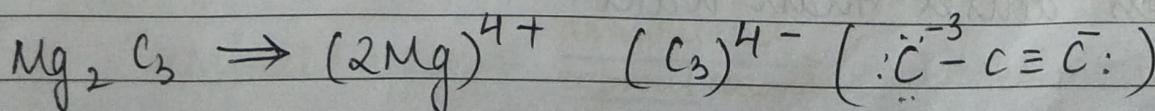
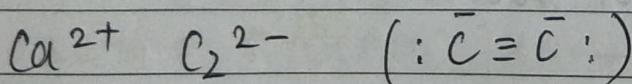


(6) Hydrolysis of carbides. (Only give acetylenes)



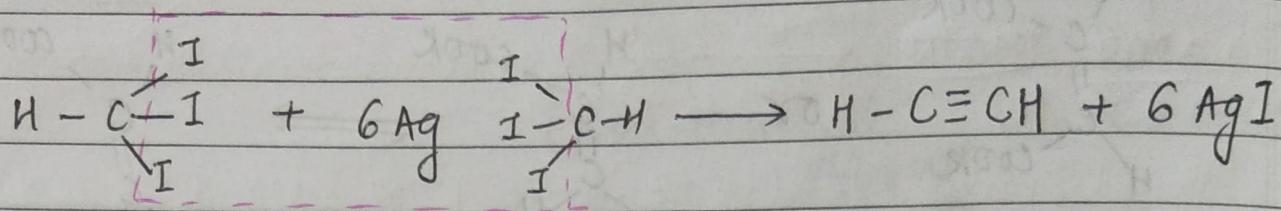
(magnesium
allylide)

Alkaline earth metal carbides (Mc_2) \Rightarrow Acetylides.



* Pupaeation of Acetylene *

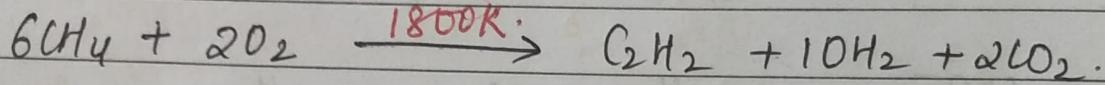
⑦ From Haloform (CHX_3) [trihalogen derivative of CH_4]



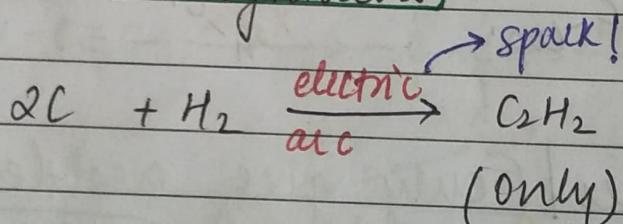
iodoform/chloroform.

(forms only
acetylene)

⑧ Partial oxidation of methane



⑨ Bertholet synthesis



(only)

spark!

Physical Properties

(1) $\text{C}_2 - \text{C}_4 \Rightarrow$ gaseous.

(2) BP and MP slightly higher than alkanes & alkenes.

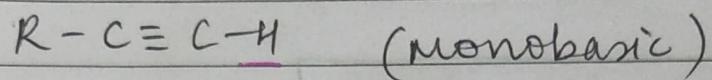
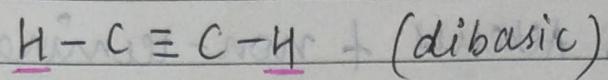
(3) Insoluble in water.

Soluble in organic solvents.

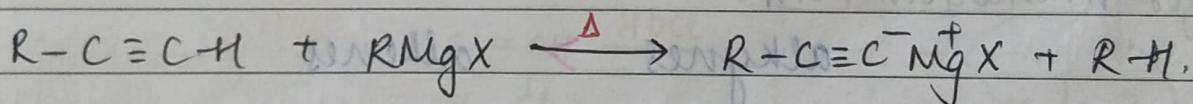
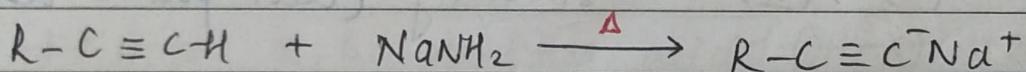
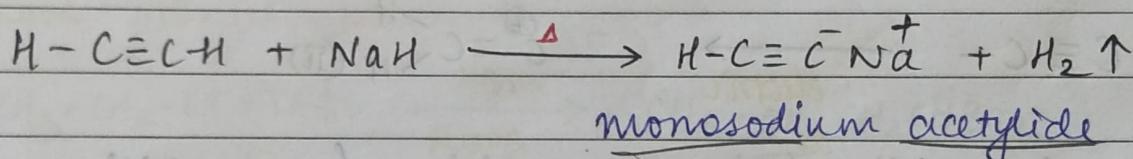
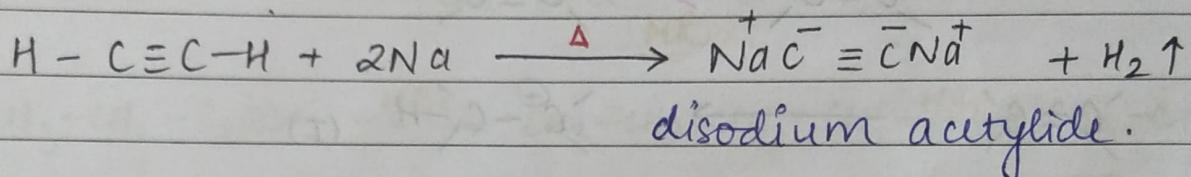
(4) Less dense than water.

→ Chemical properties

- Acidic nature of acetylene & terminal alkyne

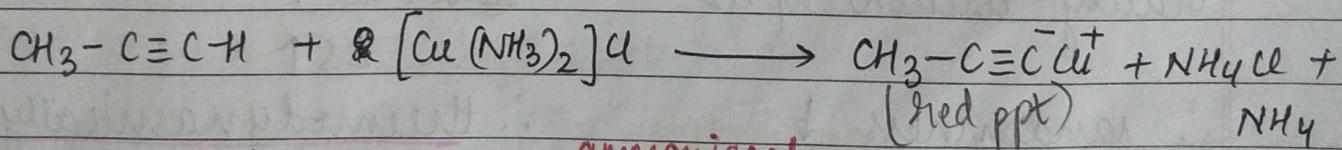
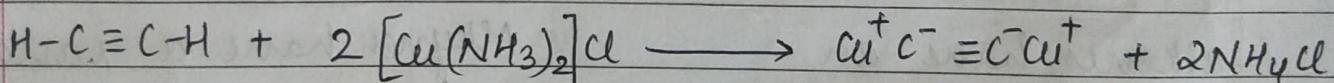


- Salt formation w/ light metals:

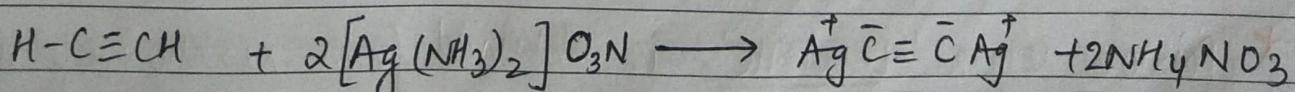


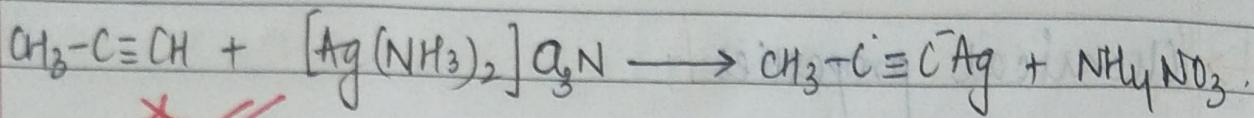
- Salt formation w/ heavy metals:

* [Test for Terminal alkyne]



→ Terminal alkyne ammoniacal cuprous chloride → red precipitate

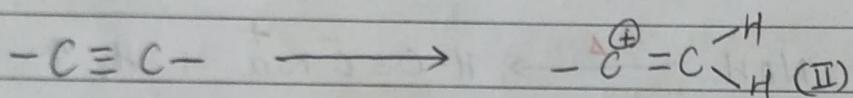
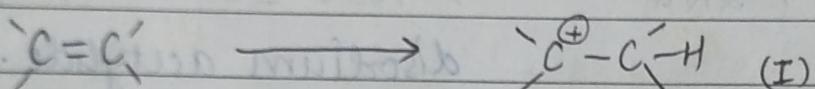
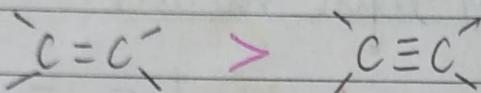




~~* Terminal alkyne~~ $\xrightarrow[\text{silver nitrate}]{\text{ammonia soln}}$ white ppt.

* Alkanes & Alkenes + non-terminal alkynes don't give this test.

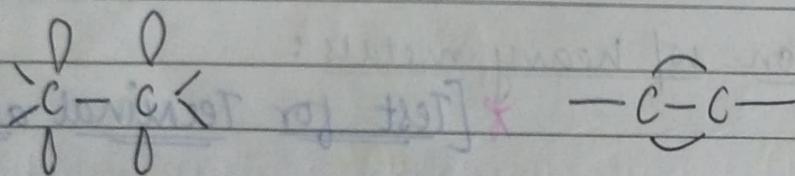
Reactivity of alkynes



\therefore (I) $>$ (II) \Rightarrow stability. (electrophilic addⁿ)

for HYDROGENATION :-

alkynes $>$ alkenes (reactivity)



alkenes have an orderly reaction w/ H₂.

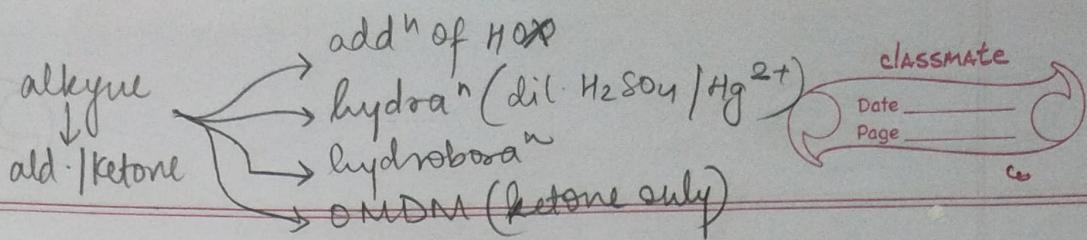
Alkynes have a random addition.

\therefore randomness \downarrow

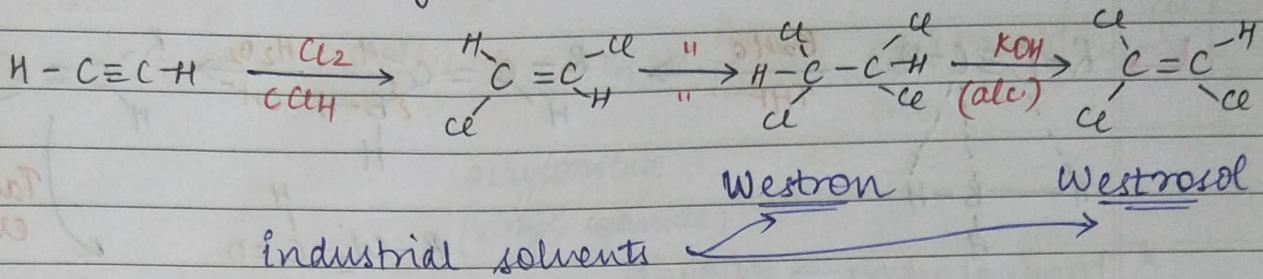
\therefore thermodynamically \uparrow favoured.

$\Delta S \downarrow$

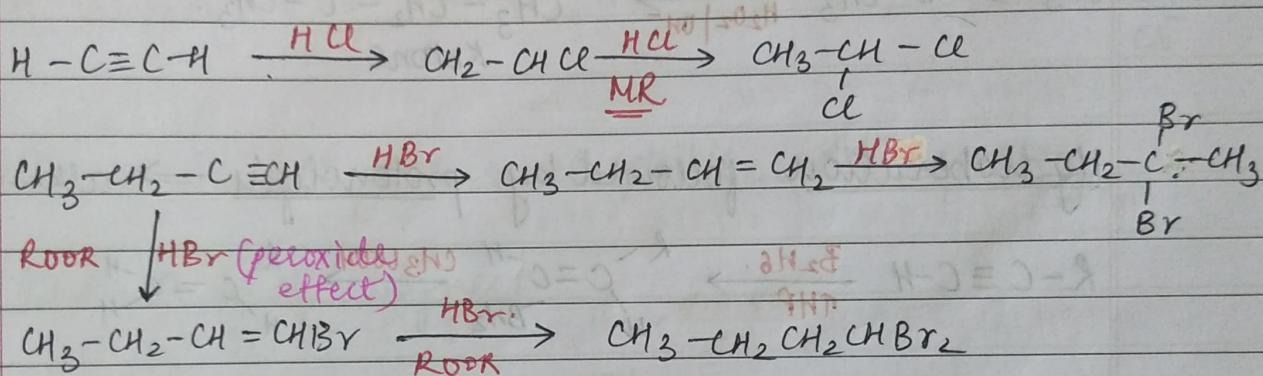
* Poisonous gas 'Lewisite' is obtained from reaction of acetylene and AsCl₃ (arsenic chloride)



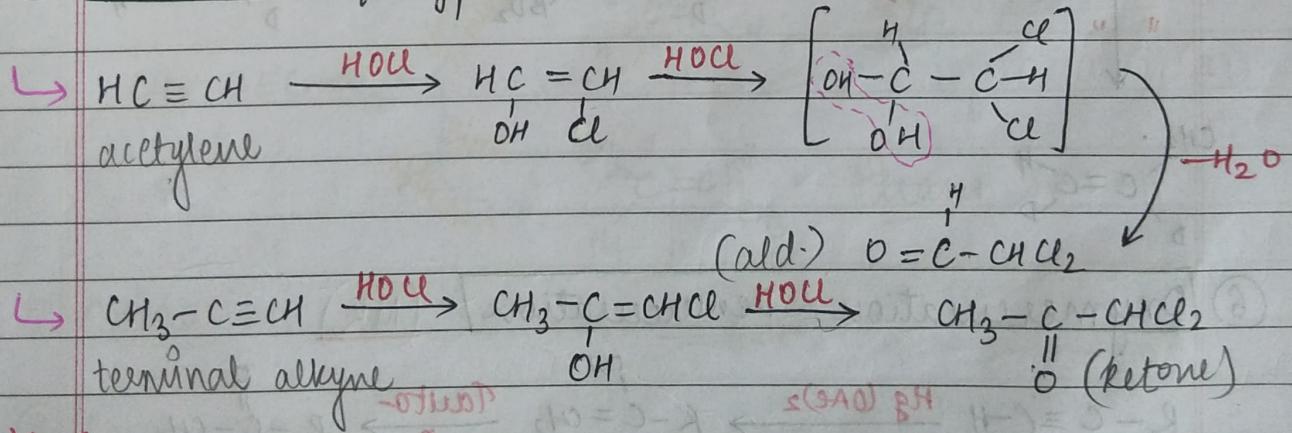
① Addition of Halogen :-



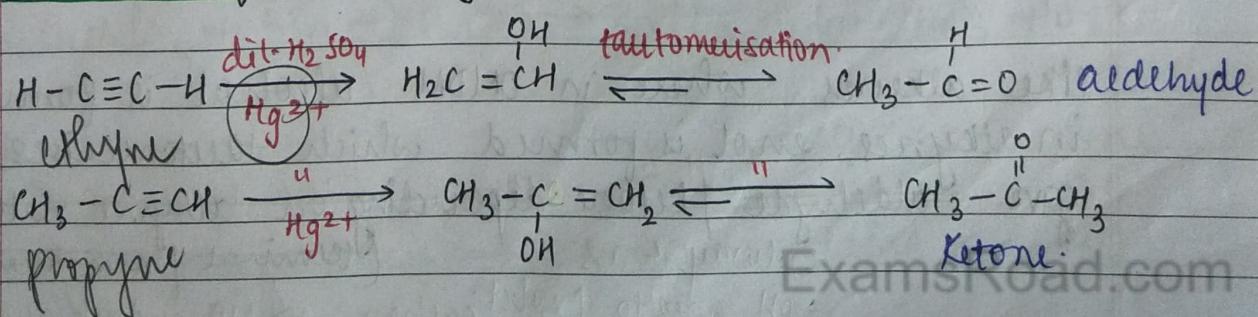
(2) Addition of hydrogen halide :-



(3) Addition of hypohalous acid. $(OH-X)$

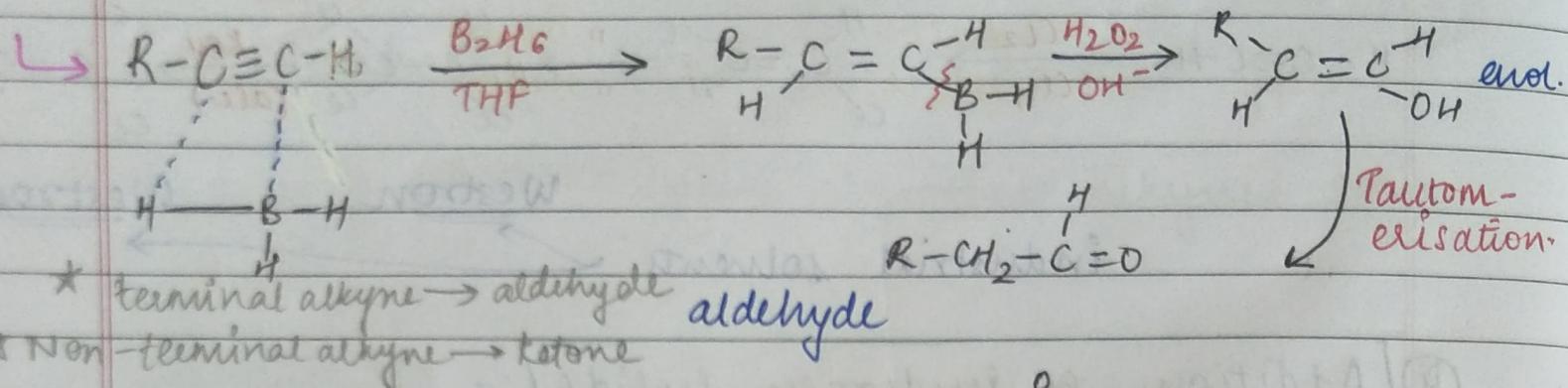


* (4) Addition of water (hydration)



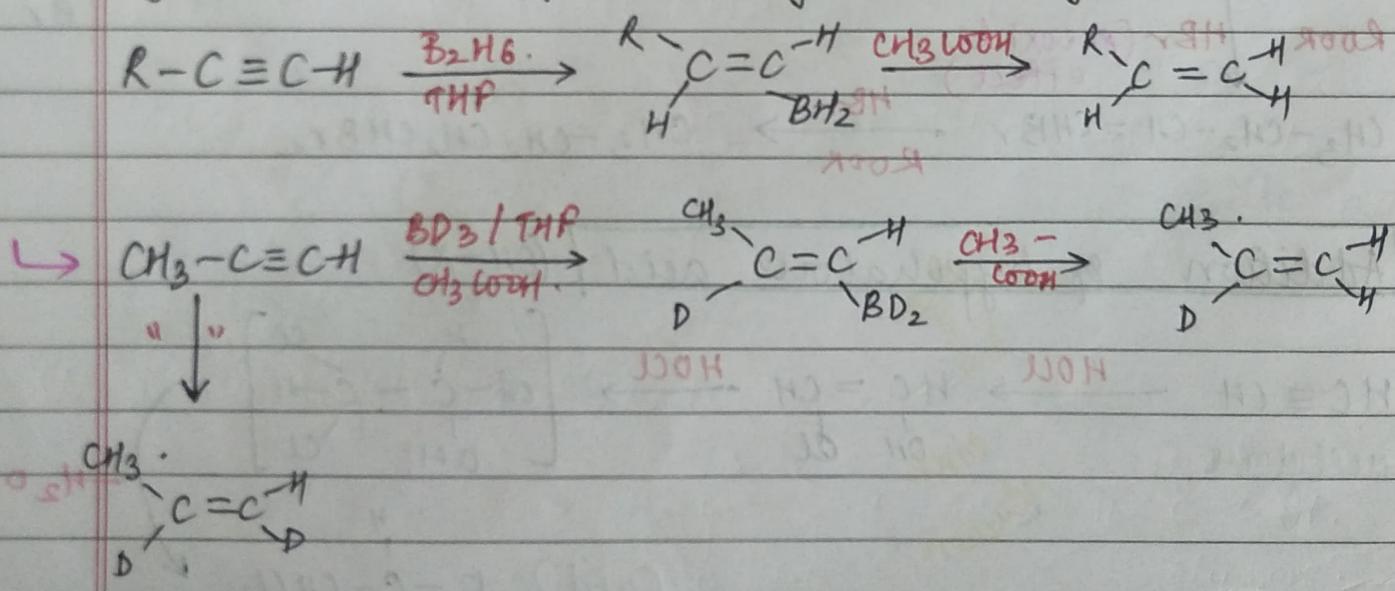
(5)

Hydroboration - oxidation

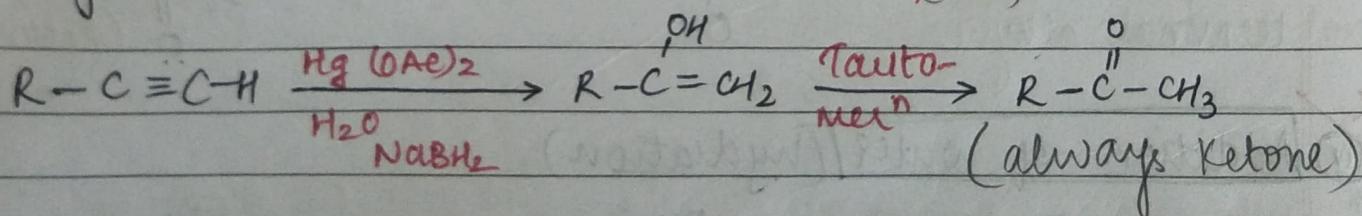
(FAN R)

Tautomerisation

Hydroboration followed by protonolysis \Rightarrow alkenes.



Oxymetallation - Demetallation (MR)

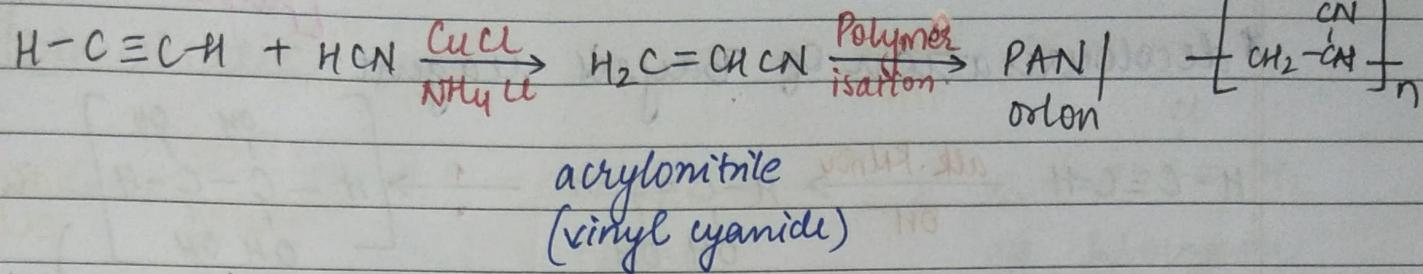


like alkenes where in OMDM alcohol is formed, in alkynes, enol is formed which tautomerises to give aldehyde / ketone depending on alkyne nature.

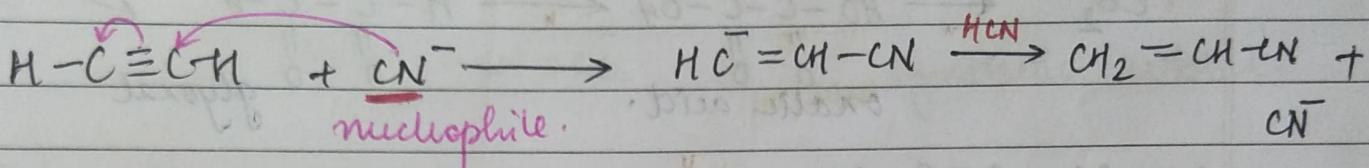
always as $\begin{cases} \text{Terminal} & \text{Non-terminal} \\ -OH \text{ goes to } \uparrow \text{subst. carbon} & \end{cases} \Rightarrow \text{MR product always is ketone}$

⑦ Addition of HCN

Nucleophilic addition:

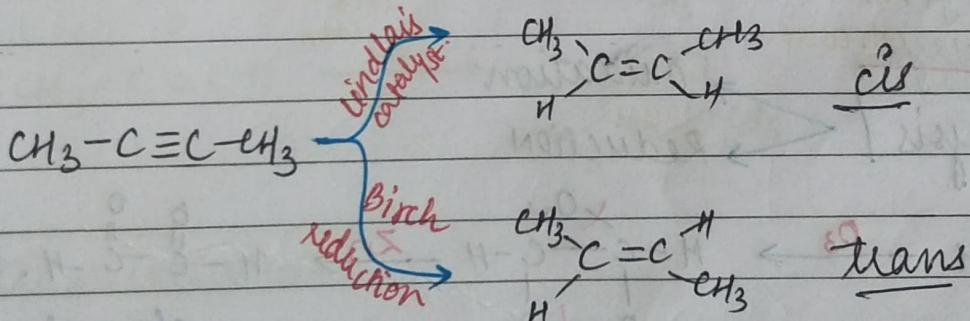
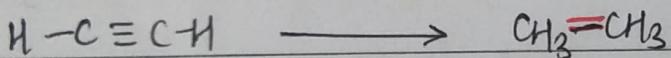


Mechanism :-



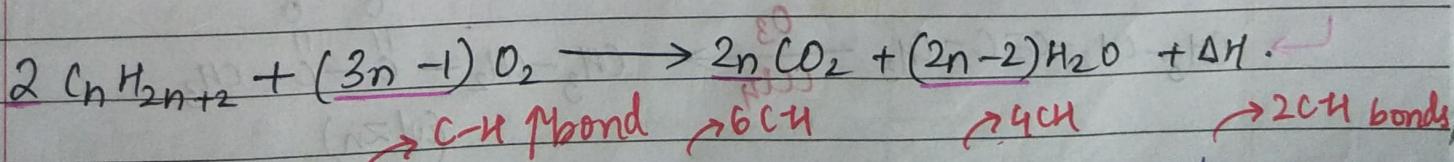
* Alkenes do not give nucleophilic addⁿ reaction.

⑧ Reduction of alkynes



* Oxidation reactions of alkynes:-

⑨ Combustion



heat of combustion \Rightarrow alkane $>$ alkene $>$ alkyne

\uparrow in temp \Rightarrow alkyne $>$ alkene $>$ alkane

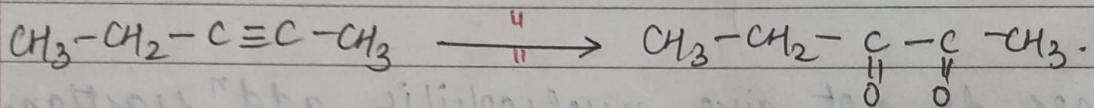
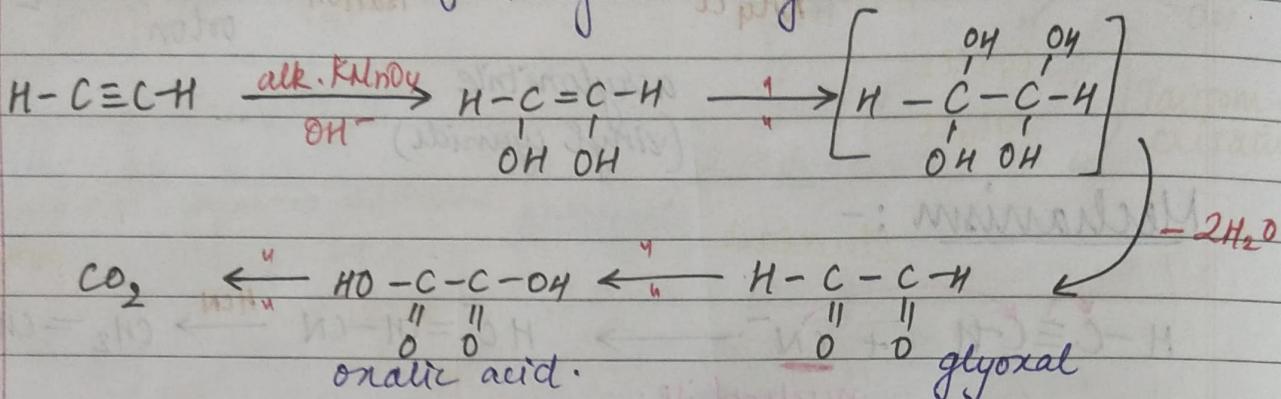
oxyacetylene flame \Rightarrow 3000°C \Rightarrow welding of metals.

test for
methane

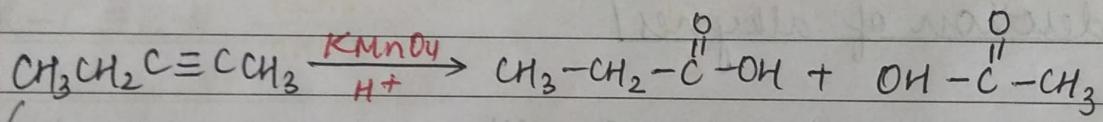
(10) Bayer's Reagent [alkaline KMnO_4]

[purple → brown]

* decolourisation of Baye's reagent.



(11) Oxidation w/ acidic KMnO_4 $\rightarrow \text{SO}_4^{2-}$



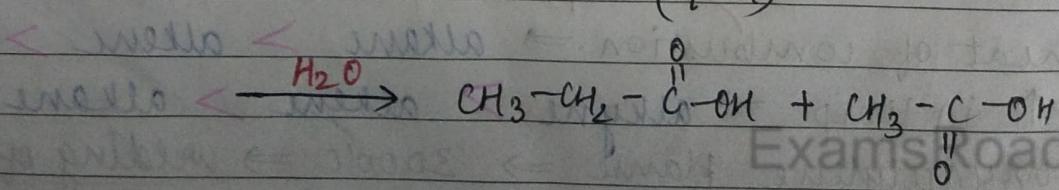
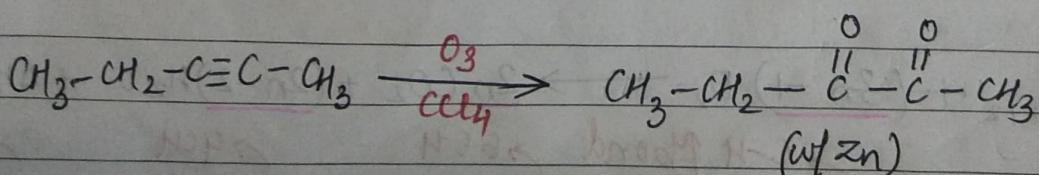
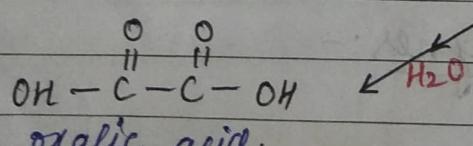
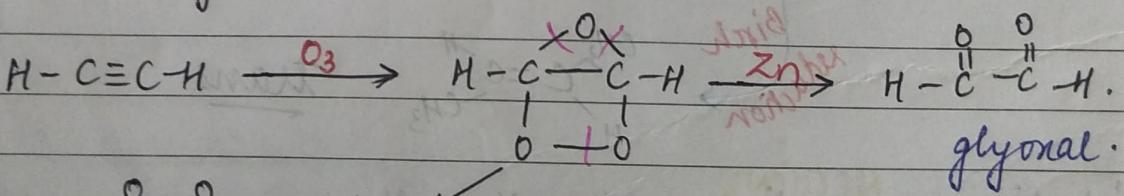
→ divides & gives

acid always:

(12) Ozonolysis

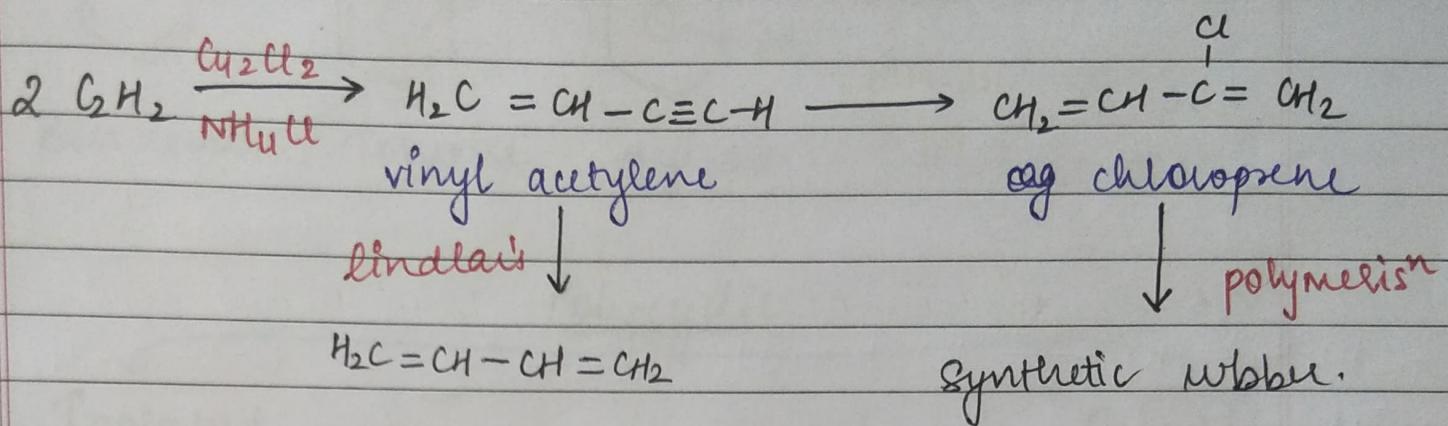
oxidation

→ Reduction



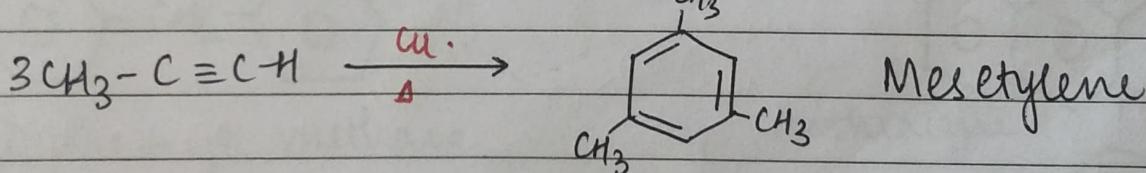
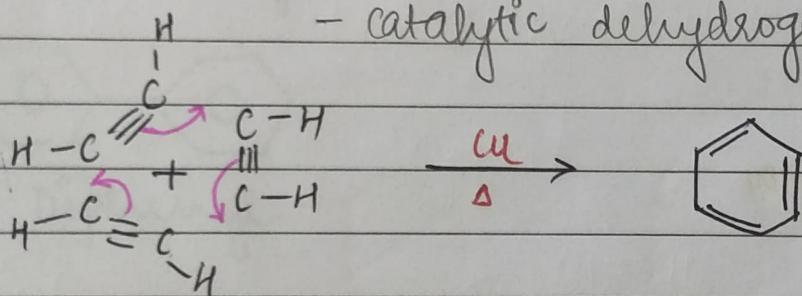
* Polymerisation of alkynes :-

(13) Dimerisation

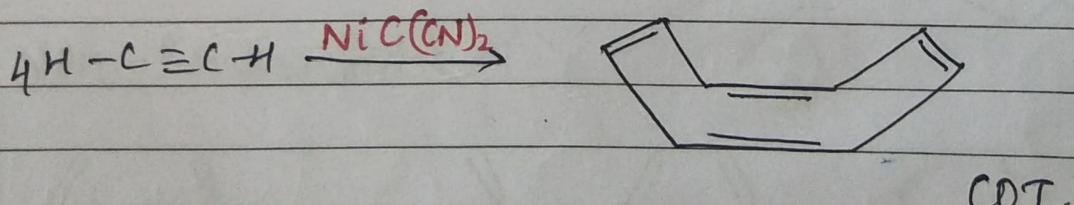


(14) Trimerisation

- catalytic dehydrogenation



(15) Tetramerisation



(16) Polymerisation

