Alkenes

→ Unsaturated hydrocarbon ($C=C$).

$C_n H_{2n}$, sp^2, planar, 120° (B.A)

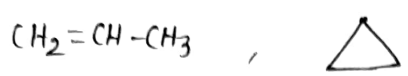C-C bond length – 1.34 Å (or) 134 pm, C-H bond length is 1.07 Å (or) 107 pm

Isomerism:

i) Chain → min. no of $C-4$

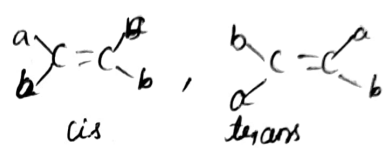ii) Position → exhibit positional isomerism

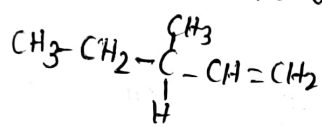Ex: $CH_2=CH-CH_2-CH_3$, $CH_3-CH=CH-CH_3$
      1-butene

iii) Functional isomerism:→ alkenes & cycloalkanes.

    $CH_2=CH-CH_3$ △
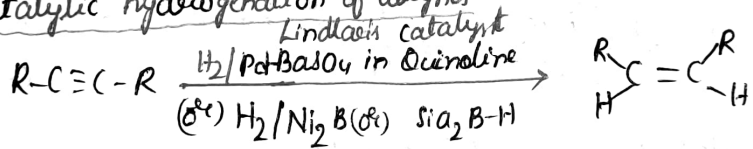
iv) Geometrical isomerism:

   $\overset{a}{\underset{b}{}}C=C\overset{b}{\underset{b}{}}$, $\overset{b}{\underset{a}{}}C=C\overset{a}{\underset{b}{}}$

     cis   trans

v) Optical isomerism – min. no of $C=6$

   $CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$

⇒ Preparation –

① Catalytic hydrogenation of alkynes –

Lindlar's catalyst

$R-C\equiv C-R \xrightarrow[\text{(or) } H_2/Ni_2 B \text{ (or) } Sia_2 B-H]{H_2/Pd+BaSO_4 \text{ in Quinoline}} \overset{R}{\underset{H}{}}C=C\overset{R}{\underset{H}{}}$

Birch reduction – $Na \mid liq \; NH_3$ (alc.) (or) $(PPh_3)_3 RhCl$ (wilkinson catalyst)

$R-C\equiv C-R \xrightarrow[(PPh_3)_3 RhCl]{Na/liq. NH_3} \overset{H}{\underset{R}{}}C=C\overset{R}{\underset{H}{}}$ $Na \rightarrow Na^+ + e^-$

                        trans alkene

ⓘ Kolbe's electrolysis:

at anode

$CH_2-\overset{\overset{O}{||}}{C}-OK$
$CH_2-\underset{\underset{O}{||}}{C}-OK$ $+ \; 2 H-OH \xrightarrow{electrolysis} CH_2=CH_2 + 2CO_2 + 2KOH + H_2\uparrow$

ⓘⓘⓘ cracking of alkanes

$CH_3-CH_2-CH_2-CH_3 \xrightarrow{773K-973K} CH_3-CH=CH_2 + CH_4 + CH_2=CH_2+H_2+H_6$

ⓘⓥ Wittig reaction:

Reagent → $PPh_3 = CH_2$

$R-\overset{\overset{O}{||}}{C}-H / R-\overset{\overset{O}{||}}{C}-R + PPh_3CH_2 \longrightarrow \overset{R}{\underset{R}{}}C=CH_2 + O=P-Ph_3$
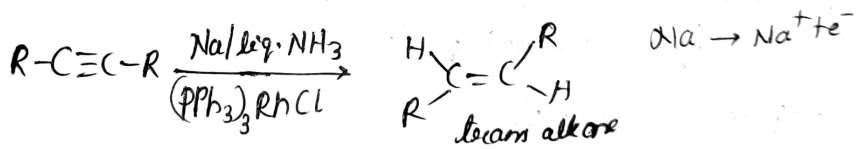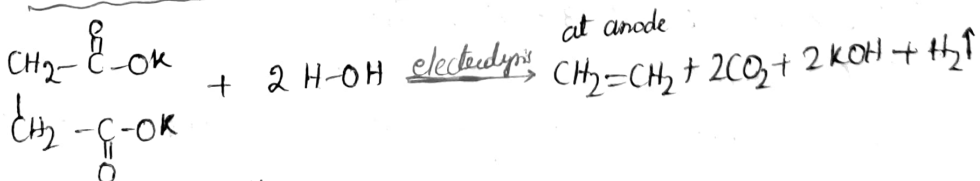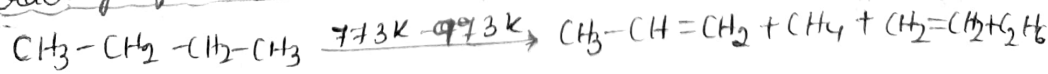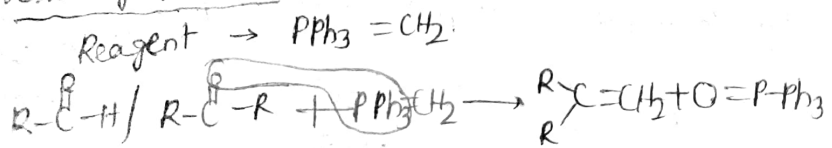
Elimination reactions

Types — E_1 - unimolecular elimination reaction
E_2 - bimolecular elimination reaction
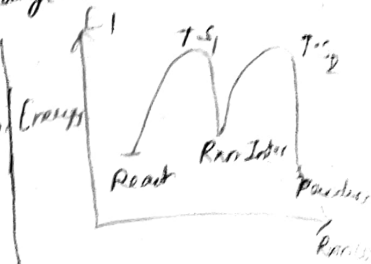E_{CB} - unimolecular conjugate base elimination reaction

$\underline{E_1} \rightarrow$ i) Rate α [alkyl halide], order is 1.
ii) non concerted reaction 2 step reactions proceeds thorough $C^{\oplus}$
iii) $C^{\oplus}$ may (or) may not undergo rearrangement based on structural rearrangement.
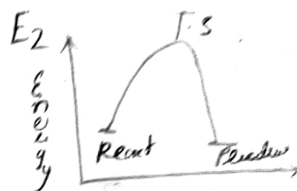iv) polar protic solvents favour E_1 e.g. n-[groups]
Ex: H_2O, H_2S, C_2H_5OH, NH_3, etc.

$\underline{E_2} \rightarrow$ i) Rate α [alkyl halide][Base]^1
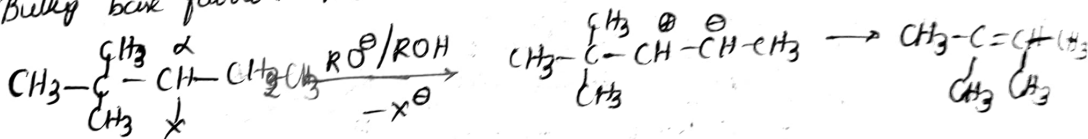ii) concerted reaction, only 1 step (T.S only).
iii) E_2 elimination, anti portions only.

Majorly following are used for E_2 reactions
$NaOH$, KOH, LiH, NaH, KH, $NaNH_2$, KNH_2, $RO^{\ominus}$, $CH_3O^{\ominus}$, $(CH_3)_2-CH-O^{\ominus}$ $(CH_3)_3-C$- [bulky base]

$\rightarrow$ Bulky base favours more rate of E_2 reaction

$$CH_3-\underset{\underset{CH_3}{\overset{|}{\underset{\times}{}}}}{\overset{\overset{CH_3}{\overset{\alpha}{|}}}{C}}-CH-CH_2CH_3 \xrightarrow[-x^{\ominus}]{RO^{\ominus}/ROH} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H-\overset{\ominus}{C}H-CH_3 \rightarrow CH_3-C=CH-CH_3$$

Saytzeff's rule: More substituted alkene is formed as major product. formed by removal of ($H^{\oplus}$) from β-carbon atom containing less no. of H.

Identification of E_1 & E_2

$\rightarrow$ All 3° R-X are E_1 molecule.
$\rightarrow$ 1°, 2° R-X when β-C is 3° & 4° is E_1.
$\rightarrow$ 1°, 2° R-X whose β-C is 1° & 2° is E_2.
$\rightarrow$ 1°, 2° R-X whose β-C is 4° in that case E_2 (Hoffmann product is major)

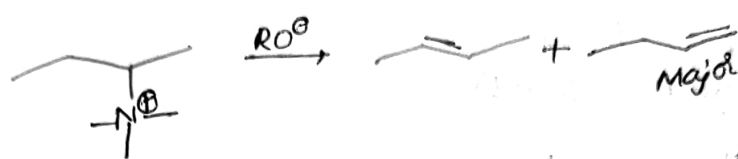$\rightarrow$ Hoffmann rule converse of Saytzeff's rule.

Exceptions in E_2

If fugacity (leaving group) is poor Hoffmann product is major
[E_1, E_2 follows same]

$$CH_3-CH_2-CH\overset{|}{\underset{F}{=}}CH_3 \xrightarrow[ROH]{RO^{\ominus}} CH_3-CH_2-CH=CH_2$$
Major
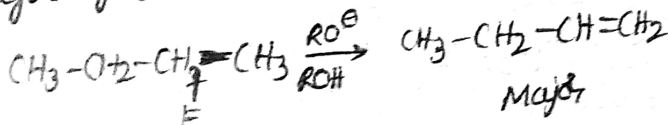
2. If the base is bulky like $(CH_3)_3CO^\ominus$ E_1 & E_2 molecules always gives Hoffmann product.

$$\xrightarrow{(CH_3)_3CO^\ominus \atop H-R}$$

mino + Majo

3. If leaving grp is +ve then also H·R product is major

$$\xrightarrow{RO^\ominus}$$

+ Major

→ If reactant is optically active then 2 asymmetric C thenEalkene is major.

$$\xrightarrow[\text{-}CH_3COOH]{\Delta}$$

HPG
$$Ph\!-\!C\!=\!C\!-\!H \atop Ph$$
HPG
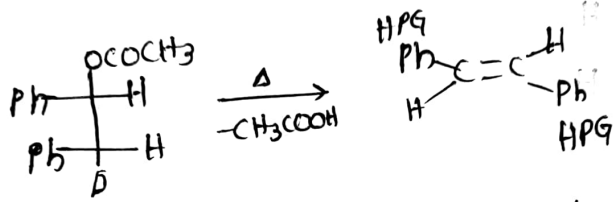
$\underline{E_1CB}$ — Compounds having poor fugacity & β-H should be highly acidic it is E_1CB rxn.

$$\xrightarrow[\Delta]{C_2H_5O^\ominus} F_2C=CCl_2$$
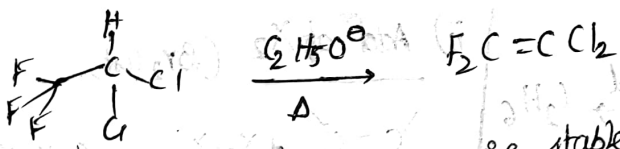
→ Conjugated alkenes are more stable.
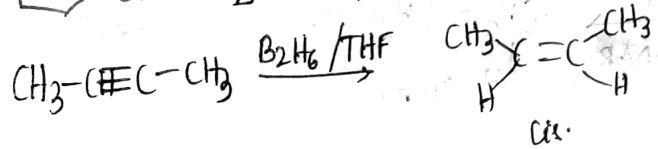
Ex: $CH=CH-CH_3$
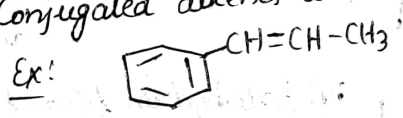
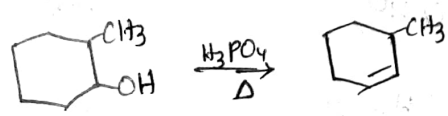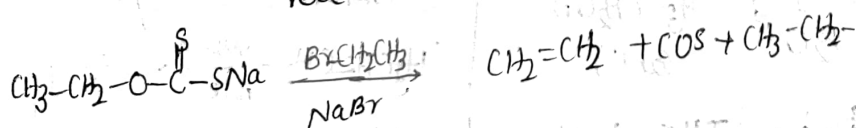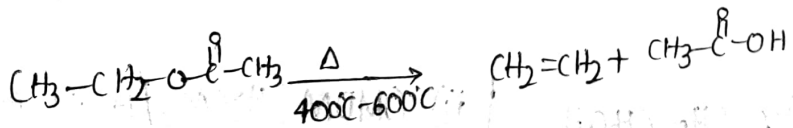Thermal elimination (&) pyrolytic :-

1. Only F. Grp like esters, amines, oxides, xanthates are involved.
→ No catalyst, only trans state, syn add".
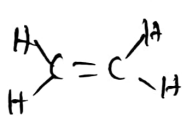→ above 130°C temp, Hoffmann product is major.

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[400°C-600°C]{\Delta} CH_2=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3-CH_2-O-\overset{S}{\overset{\|}{C}}-SNa \xrightarrow[NaBr]{BrCH_2CH_3} CH_2=CH_2 + COS + CH_3-CH_2-$$

$$\xrightarrow[\Delta]{H_3PO_4}$$

$$CH_3-C\!\equiv\!C-CH_3 \xrightarrow{B_2H_6 /THF} \overset{CH_3}{\underset{H}{C}}=C\overset{CH_3}{\underset{H}{}}$$

cis.

⇒ **Physical properties**

→ C_2, C_3 fv (g), $C_5 - C_{17}$ (L), $>C_{17}$ (S), colourless, no smell but ethene having oder

→ Soluble in non polar solvents; m.p & b.p's ↑ w.r.t mol.wt.

→ Exhibit geometrical isomerism.

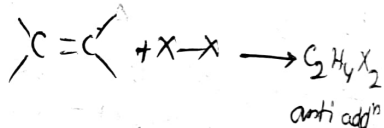|		Cis	trans
B	B·P	High (H)	Low (L)
D	dipole	H	L
S	Solubility	H	L
M	M·P	L	H
S	Stability	L	H

⇒ **Chemical properties**

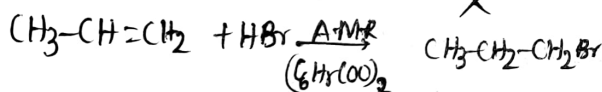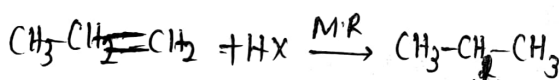→ undergo e⊕ addn rxns, special conditions . free radical subn.

① i) Addn of H_2

$$\underset{H}{\overset{H}{\diagdown}}C=C\underset{H}{\overset{H}{\diagup}} \xrightarrow{H_2/Ni/Pt/Pd} C_2H_6$$

ii) Add^n of X_2 (Br$_2$ test)

$$\diagup C=C\diagdown + X-X \longrightarrow C_2H_4X_2$$
anti add^n

iii)· Add^n of HX

$$CH_3-CH=CH_2 + HX \xrightarrow{M.R} CH_3-\underset{X}{CH}-CH_3$$

$$CH_3-CH=CH_2 + HBr \xrightarrow[(C_6H_5COO)_2]{AMR} CH_3-CH_2-CH_2Br$$

iv) Halohydrin formation

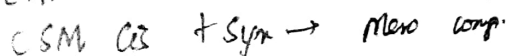$$CH_2=CH_2 + Cl_2 \xrightarrow{H_2O} \underset{OH}{\overset{Cl}{CH_2-CH_2}}$$

(anti add^n)

② Hydration

i) $CH_2=CH_2 \xrightarrow[H_2O]{dil. H_2SO_4} CH_3-CH_2OH$
(anti)

ii) OMDM ($Hg OAc)_2/H_2O + NaBH_4/OH^-$)

$$CH_3CH=CH_2 \xrightarrow[MR]{OMDM} \underset{OH}{CH_3-CH-CH_3}$$
(anti)

iii) HBO (B_2H_6 / THF + H_2O_2/O·H⊖)

$$CH_2=CH-CH_3 \xrightarrow[AMR]{HBO} \underset{OH}{CH_2-CH_2-CH_3}$$
(syn)

Trick

(TSR) Tr + Syn → Racemic Mix

(TAM) Tr + Anti → Meso comp.

CAR Cis + Anti → Racemic Mix

CSM Cis + Syn → Meso comp.

(II) Oxidation

i) Combustion: $C_nH_{2n} + 3\frac{n}{2}O_2 \longrightarrow nCO_2 + nH_2O$
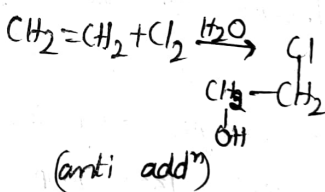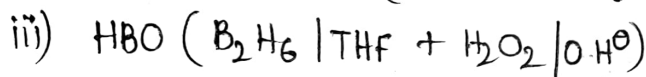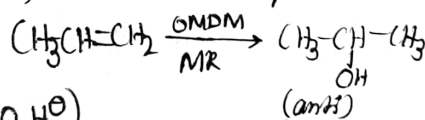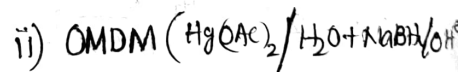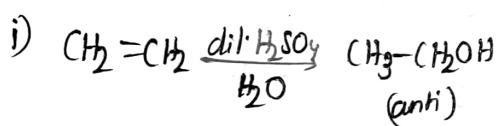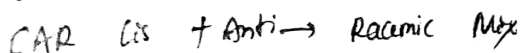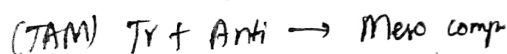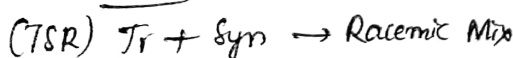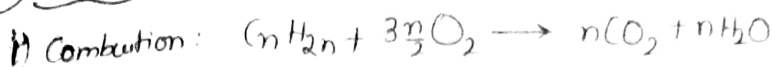
ii) Oxidation without cleavage of C-C bond.

A	B (add^n of 2 OH gp)
a) cold/dil. KMnO₄ (Bayer's reagent)	**a) peracids (peroxy acids)** $R-\overset{O}{\overset{\|}{C}}-OOH$ ($R CO_3H$)
b) OsO₄ /pyridine	**b) Ph-$\overset{O}{\overset{\|}{C}}$-O-OH** ⎫ Anti hydroxy
c) Na₂SO₃ /H₂O₂	**c) H₂O₂ /Ag** ⎬ anh-diol
d) Na₂SO₄ /H₂O	**d) CH₃COO Ag (dry)/I₂** ⎭
e) NaHSO₄ /H₂O	
f) CH₃COO Ag (wet)/I₂	

For column A → syn add^n, cis diol (4), syn diol

for A

Ex. $\overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} + [O] + H_2O \xrightarrow[\text{pink colour}]{KMnO_4/OH^\ominus}$ (H₂O₂) $\overset{}{\underset{HO\ \ OH}{C-C}} + MnO_2\downarrow$ (brown ppt)

syn -diol
colourless

for B

$\overset{}{\underset{}{C}}=\overset{}{\underset{}{C}} + RCO_3H \longrightarrow -\overset{OH}{\underset{OH}{\overset{\|}{C}-\overset{\|}{C}}-}$ · interm- $\overset{}{\underset{}{\triangle O}} + R-COOH$
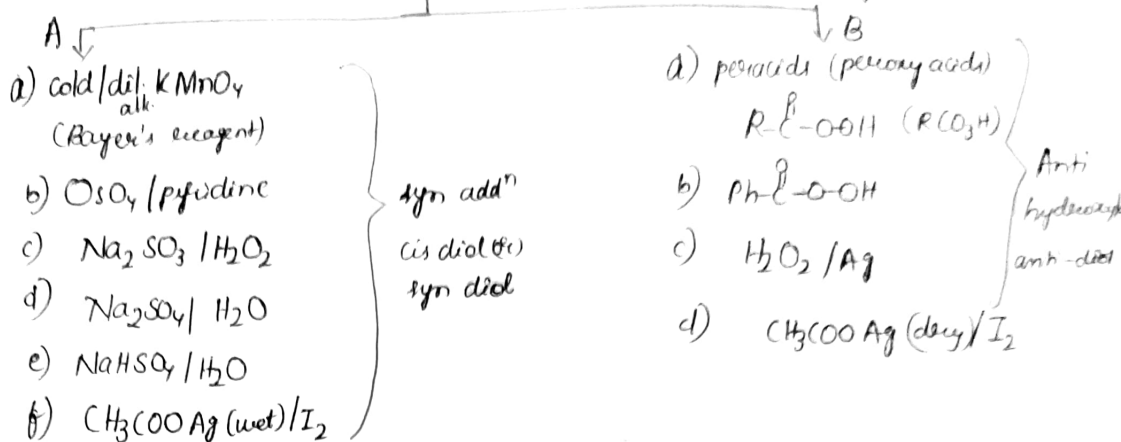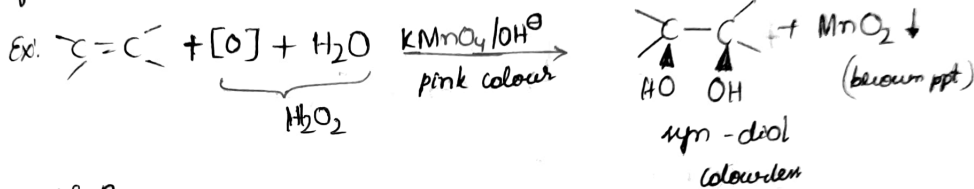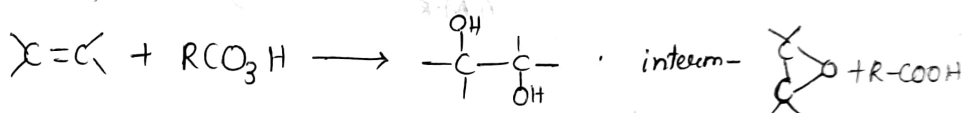
iii) Oxidation with cleavage of C-C

O·A
a) Δ, alk. KMnO₄
b) Δ, H⊕, KMnO₄
c) Δ, H⊕, K₂Cr₂O₇
*d) OsO₄ /NaIO₄
e) Pb (OAc)₄
f) leimeux reagent (KMnO₄ +NaIO₄)
g) HIO₄ → $\neq$ → $\overset{C-C}{\underset{OH\ OH}{}}$
h) SeO₂ → allylic carbon
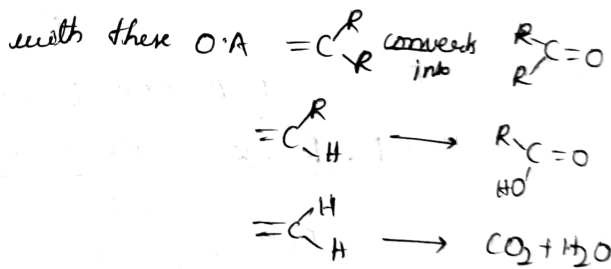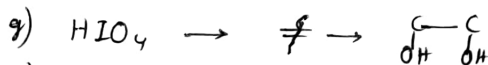
with these O·A $=C\overset{R}{\underset{R}{}}$ converts into $\overset{R}{\underset{R}{}}C=O$

$=C\overset{R}{\underset{H}{}} \longrightarrow \overset{R}{\underset{HO}{}}C=O$

$=C\overset{H}{\underset{H}{}} \longrightarrow CO_2+H_2O$

Ozonolysis

→ Reductive
ⓐ Zn+acid
ⓑ H₂ +(Pt /Pd/ Ni)
ⓒ Me₂S (dimethyl sulphide)
ⓓ Ph₃P (Triphenyl phosphine/Wikinson's catalyst)
} Ozonide to aldehydes & ketones

ⓔ LiAlH₄
ⓕ NaBH₄
} aldehydes /ketones → alcohols

→ Oxidative

Reagents

@ H_2O_2

ⓑ Ag_2O

ⓒ H_2O_2

ⓓ $KMnO_4/NaIO_4$

ⓔ peracids ($RCO_3H, PhCO_3H$)

} aldehydes ⟶ carboxylic acids
ketones ⟶ xx (ketones)

→ addⁿ of NOCl (Tildon's reagent) (M·R)

$$CH_3-CH=CH_2 \xrightarrow{NOCl \overset{\oplus}{}\ominus} CH_3-\underset{Cl}{CH}-\underset{}{CH_2}\overset{NO}{}$$

→ $CH_2=CH_2 + CO + H_2$
- $\xrightarrow[75-150°C]{CO_2 (CO)_8}$ $CH_3-CH_2-\overset{O}{\underset{}{C}}-H$
- $\xrightarrow[200°-300°C]{CO_2(CO)_8}$ $CH_3-CH_2-\overset{O}{\underset{}{C}}-OH$

$$CH_3-CH=CH_2 + CO + H_2O \xrightarrow[A·M·R]{H^\oplus} CH_3-CH_2-CH_2-COOH$$

→ with S_2Cl_2

$$2CH_2=CH_2 + S_2Cl_2 \xrightarrow{\Delta} Cl-CH_2^\beta-CH_2^\alpha-S + S$$
$$Cl-CH_2-CH_2$$
Mustard gas
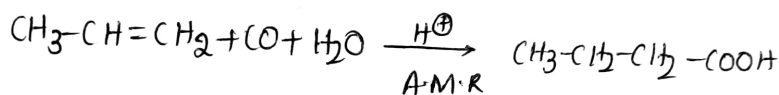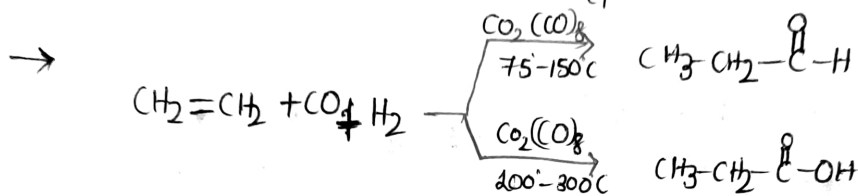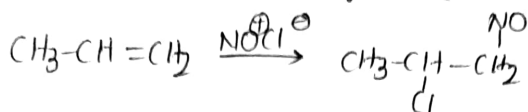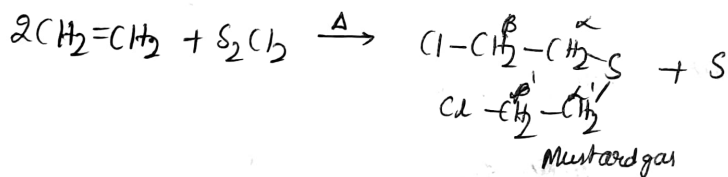
→ Wacker's process — preparation of carbonyl compounds

$$CH_2=CH_2 + PdCl_2 + H_2O \xrightarrow[O_2 (8t) air]{CuCl_2, 323K} CH_3-\overset{O}{\underset{}{C}}-H + Pd + 2HCl$$

$$CH_3-CH=CH_2 \xrightarrow[H_2O]{Pd/CuCl_2} CH_3-\overset{O}{\underset{}{C}}-CH_3$$
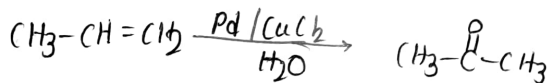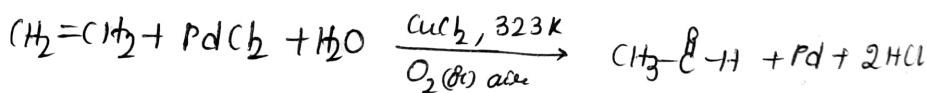
→ Halogenation :

allylic subⁿ
i) NBS

[structure: N-Br succinimide ring with two C=O]
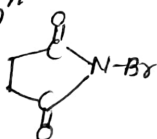
Removal of H — allylic > 3 > 2 > i > CH_2 > Vinyl

ii) SO_2Cl_2

if conc. of halogen ↓ free radical subⁿ

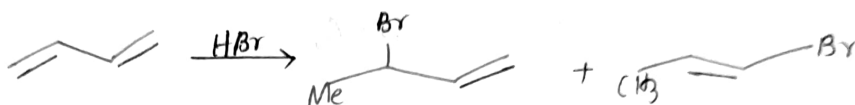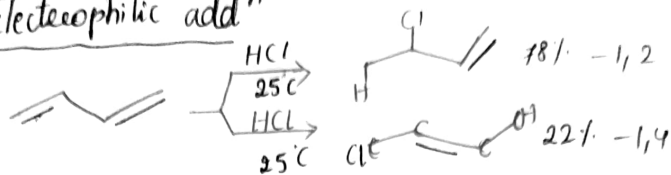if conc. of halogen ↑ free radical addⁿ.

Alkadienes:

→ ┌ Cumulated — 2 double bonds on same C atom
  ├ Conjugated — alternative double bonds
  └ isolated — at least 1 sp^3 C b/w 2 C=C

alkynes and alkadienes are functional isomers

stability — conjugated > isolated > cumulated

Electrophilic add^n

$$\xrightarrow[25°C]{HCl}$$
$$\xrightarrow[25°C]{HCl}$$

18% — 1,2
22% — 1,4

$$\xrightarrow{HBr}$$

1,2 – Major
1,2 – Minor

+

1,4 – minor
1,4 – major

at low temp
(kinetically controlled)

at high temp.
(thermodynamically controlled)

Djel's Alder exn:

Diene + Dienophile → min. 6 membered ring
  ↓   ↓
(e rich)   (e poor)

* to ↑ reactivity +I grps on dienes, −I grps on dienophiles

+I / diene   dienophile

COOMe →
COOMe COOMe →

+ COOMe, COOMe
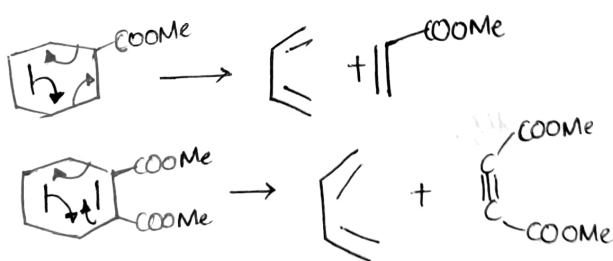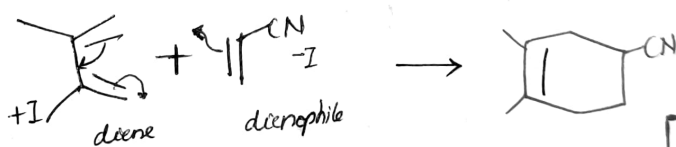
Heat of combustion

$$T↑ > TC > CC$$

Stereochemical requirement:

+ CHO → No rxn
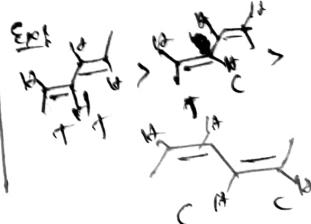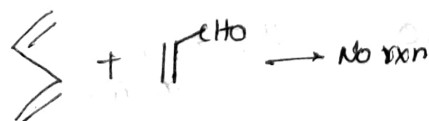
S-trans

S-trans of diene don't give djel's aldere exn.
S-cis of diene gives djel's aldere exn.