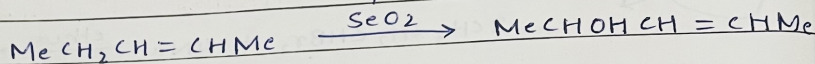


molecular mass ↑ b.p. ↑
 CIS TRANS
 b.p. >
 dipole >
 mp. <
 - strong intermolecular force
 - lattice fit symmetry

type of reaction depends upon the condns. given

reactivity of diff. types of H = allylic > 3° > 2° > 1°
 methyl > vinylic.

oxidation of alkenes, in case of ↑ affected in allylic pos



(I) Hydrogenation - wk it. Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$
 (syn-addn.) - $\text{CH}=\text{CH}_2 > \text{CH}=\text{CH}- > \text{ring double bond}$
 cis → meso trans → racemic

(II) Halogenation - (anti addition) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
 ordinary temp.
 $\text{Br}_2 \in \text{CCl}_4$ → when there is a choice of attack, then nu^\ominus will attack at the carbon \bar{c} more +ve
 gives reddish orange color when Br_2 is charge added to unsaturated comp. / more substituted alkene.

(III) Addition of Hydrogen Halide - Markownikoff pdts.
 [regioselective reaction] $\text{HI} > \text{HBr} > \text{HCl}$
 electrophilic addn. - more stable

conjugated systems - 1,4 addn. or 1,2 addn.
 \bar{c} peroxides - anti Markownikoff.

(IV) Hydroxylation (Glycol form) → simple dihydroxy groups when added to C=C bonds.

A) cold KMnO_4 - Bayer's reagent - syn addition (2OH)

B) $\text{KMnO}_4; \Delta$ - oxidative ozonolysis

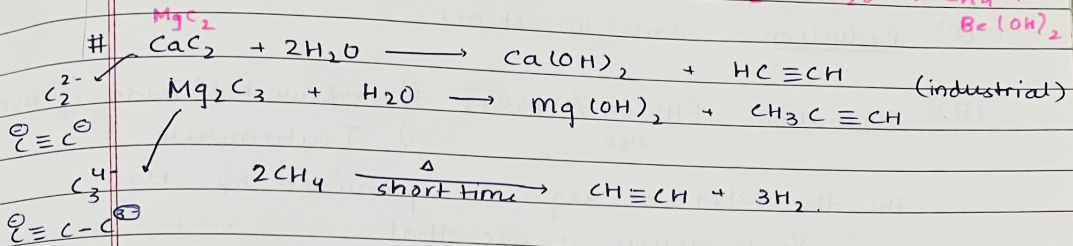
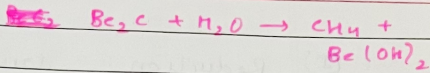
C) HCOOH (performic acid) or MCPBA - anti addn. (2OH)

D) per benzoic acid or per acetic acid - epoxides - Ag/O_2

strong enough to cleave the epoxide !! =

the more highly subs. = is more nucleophilic, ∴ reacts faster \bar{c} peroxide.

Alkynes Preparation

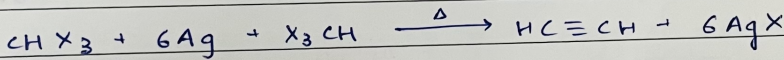
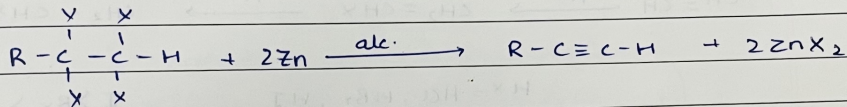


• Kolbe's method

[center bond]
 • dehydrohalogenation of 1,2-dihalides = alc. KOH E_2
 (vicinal)
 = sodamide (NaNH₂) in liq. NH₃ E_2 *fast*
 [side/end bond]

{such a strong base ; gives terminal alkyne when protonated $\bar{c} + H_2O$ }
 (geminal) of 1,1-dihalides = same reagent

interne diatom is vinyl halide



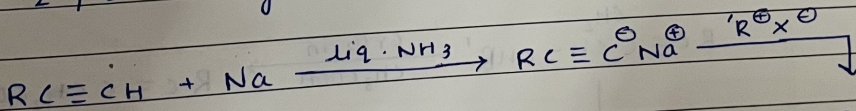
tetrahalides : Zn dust and methanol

dehalogenation

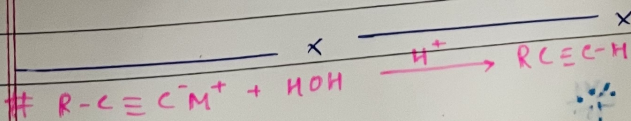
• alkylation : give higher alkynes ; acetylenic and terminal H are reactive, hence their salt formation is easy !!

S_N2
 # R or R' should be 1° alkyl halide coz with 2°/3° we get alkenes mainly. E_2

Kolbe's -sodium fumarate



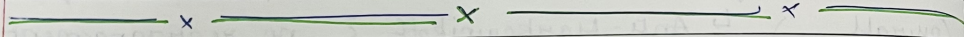
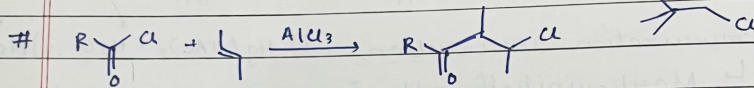
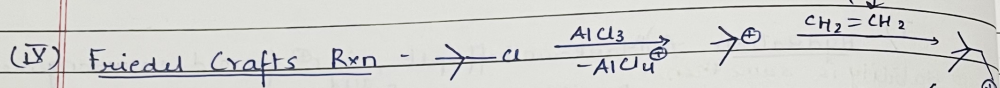
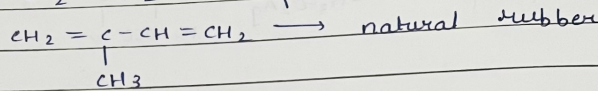
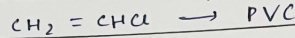
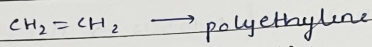
may also be done using Grignard reagent.



Alkenes + NBS \rightarrow addn. of Br at allylic position. #subs. at high temp.
 \downarrow free radical mech.
 \downarrow after rearrangement.
 #resonance stabilised...

$\text{SO}_2\text{Cl}_2 \rightarrow$ addn. of a sulphonyl chloride.

(VII) Polymerisation - free radical mechanism.



 C_2^-
 $\text{C} \equiv \text{C}^{\ominus}$
 C_3
 $\text{C} \equiv \text{C}-\text{C}$

intermediate is vinyl
 1/2
 5/10
 2/8
 2/10

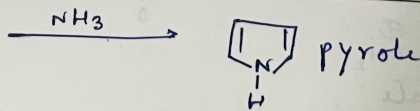
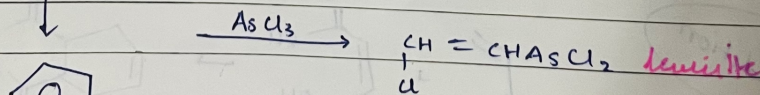
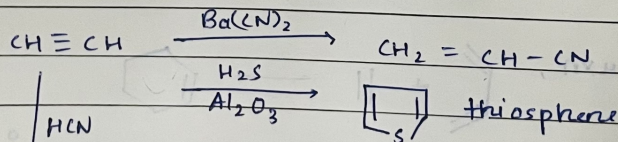
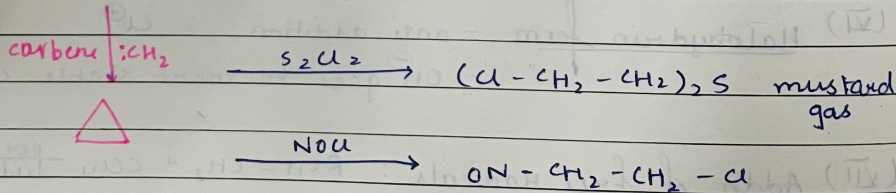
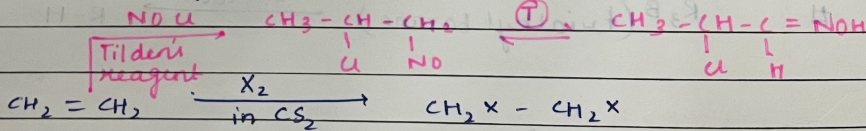
vinyl cyanide + 1,3-butadiene = Buna-N

poly neoprene \rightarrow chloroprene

dehale nati

alkynes generally show addition.

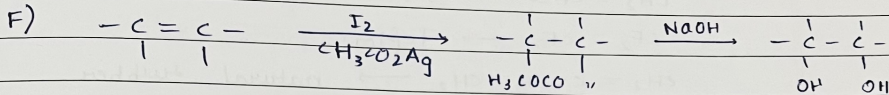
$\text{CH}_2 = \text{CH}_2 + \text{HOONO}_2$
 \downarrow
 $\text{CH}_2 - \text{CH}_2$
 | |
 $\text{NO}_2 \text{ NO}_2$
 M.P. \downarrow



Kalbe
 -sodi
 fu

Br₂ addn is anti... cyclic bromonium ion
 non-classical c⁺ → no rearrangeme.
 → resonance stabl.
 → all atoms octet.

E) OsO₄ in ether at room temp - syn addition.
 [intermediate cyclic osmic ester which upon hydrolysis in the presence of Na₂SO₃ or H₂O₂ gives glycol]

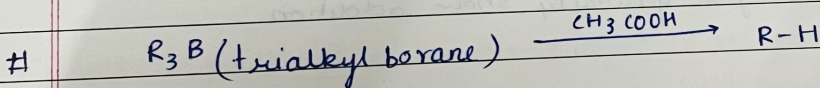
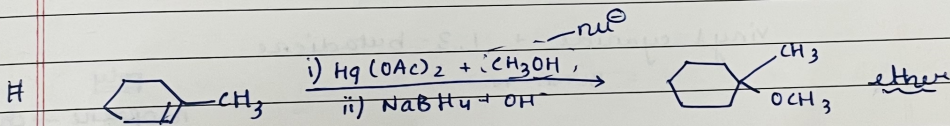


V) Hydration A) Markownikoff pdt, ∴ c⁺ formed rearrangement possible.
 (c⁺ stability is same then, less stable alkene gives faster rxn.)
 $\text{>C=C<} \xrightarrow[\text{H}_2\text{SO}_4/\text{H}_2\text{O}]{\text{acid}} \begin{array}{c} \text{H} & & \text{OH} & & \text{OH} & & \text{H} \\ & \swarrow & & \swarrow & & \swarrow & \\ & \text{C} & - & \text{C} & & \text{C} & - & \text{C} \\ & | & & | & & | & & | \\ & \text{H} & & \text{OH} & & \text{OH} & & \text{H} \end{array}$

B) Oxymmercuration-demercuration [i) Hg(OAc)₂ + H₂O ii) NaBH₄]
 ↳ Markownikoff pdt ∴ no rearrangement.

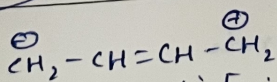
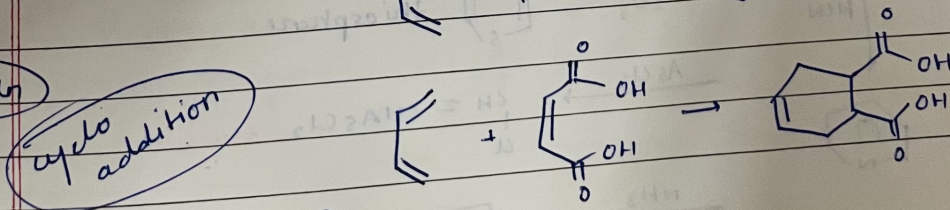
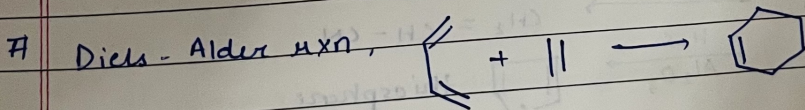
C) Hydroboration Oxidation [i) B₂H₆/THF ii) H₂O₂/NaOH]
 ↳ Anti-Markownikoff ∴ no rearrangement

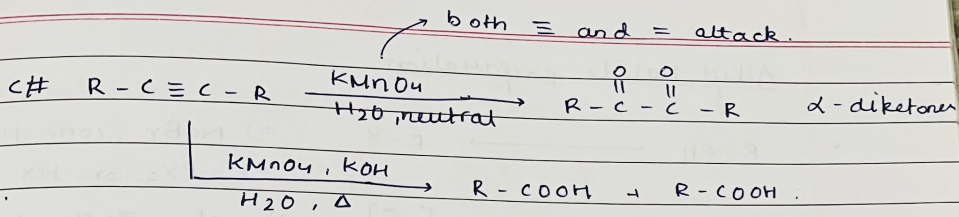
(overall syn addn)



(VI) Halohydrin form - anti addition ; Cl⁺ electrophile in cycloalkene, addn. is trans.
 (addn. of hypohalous acid) - OH⁻ goes to more stable c⁺.

(VII) Addn of free radicals : $\text{RCH=CH}_2 + \text{CCl}_4 \xrightarrow[\text{oxide}]{\text{per}} \begin{array}{c} \text{RCHCH}_2\text{CCl}_3 \\ | \\ \text{Cl} \end{array}$

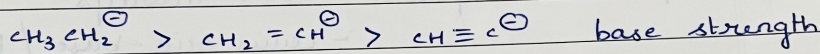
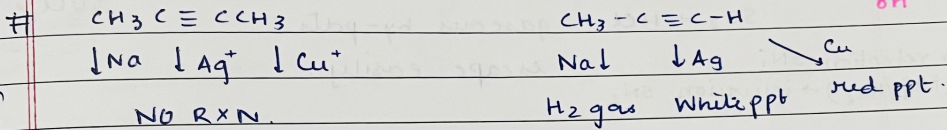
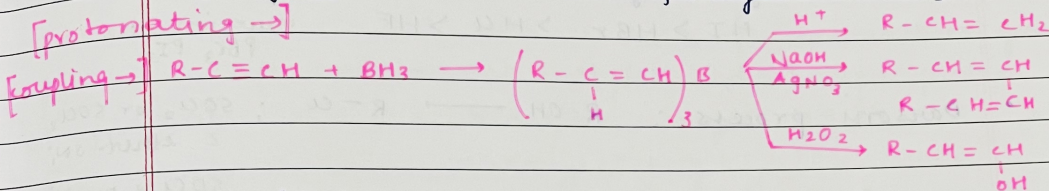




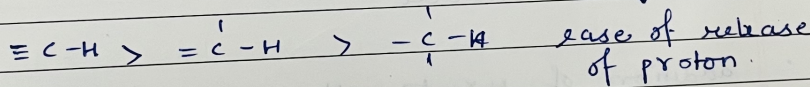
terminal
↓
CO₂

terminal - COOH # non-terminal - diketones

(V) Ethinylation = a methine hydrogen ($-\text{C}\equiv\text{CH}_2$)



↑ E_N carbon has ↑ s-character

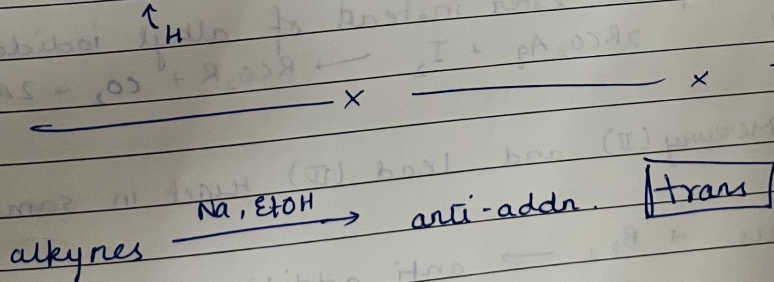


acidic
 $\text{CH}\equiv\text{CH} > \text{CH}_3-\text{C}\equiv\text{CH} > \text{CH}_3-\text{CH}_2-\text{CH}\equiv\text{CH}$
 $\text{CH}_2=\text{CH}_2 > \text{CH}_3-\text{CH}=\text{CH}_2$

(VI) HBO: anti-Markovnikov addn. of water, tautomeric
 [i) BH₃/THF ii) H₂O₂/OH⁻]

only way to make ald. from terminal alkyne
 which on hydration aint pass.

[i) BH₃/THF ii) CH₃COOH] pdt = cis isomer...

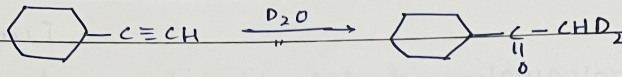


(I) Reduction: done in alkenes

(II) Hydration: $[H_2SO_4 / HgSO_4]$ H_2O i) Markownikoff addn. of H_2O
 ii) Tautomerise.

the the extra H req. are provided by H_2O ,
 \therefore if is given u use that

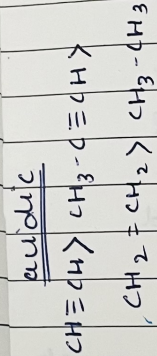
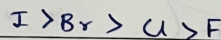
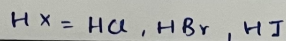
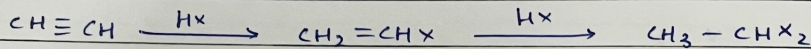
asymmet. alkynes
 give mixture of
 ketones, though
 Methyl ketone
 dominates



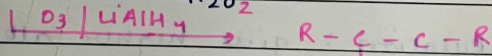
(III) Addn. of Halogens - 2 moles of halogen per mole of alkyne
 - trans isomer.

[anti addn]

- less reactive than alkene towards
 this rxn



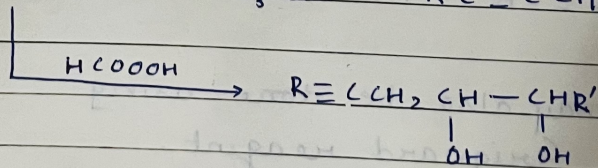
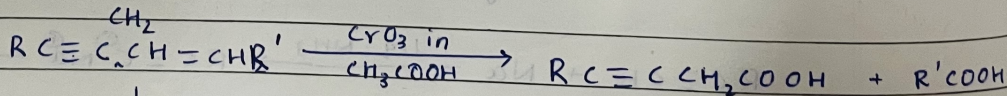
(IV) Ozonolysis $R-C\equiv C-R' \xrightarrow[H_2O_2]{O_3} R-COOH + R'-COOH$



A# if \equiv and $=$ is +nt, then only \equiv is affected
 coz \equiv it is very slow reaction. $[CrO_3 \text{ in } CH_3COOH]$

Oxidation

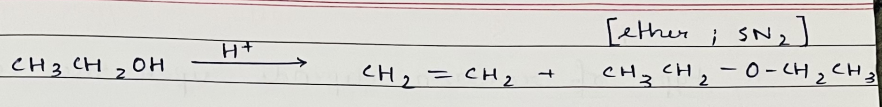
B# HCO_3H hydroxylates $C=C$ bond \neq affecting $C\equiv C$.



170-alkene
140-ether
110-~~as~~-O-SO₃H-

⊙ greater stability of vinyl radical in trans, where alkyl groups are farther.

ROH or
>T
s > 1

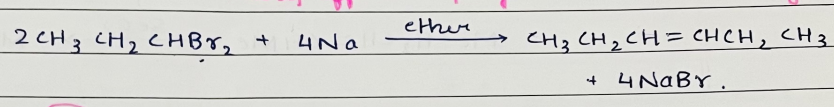


easily
mann

dihalogenation

dihalogenes (geminal/vicinal) $\xrightarrow{\text{free radical}}$ alkenes

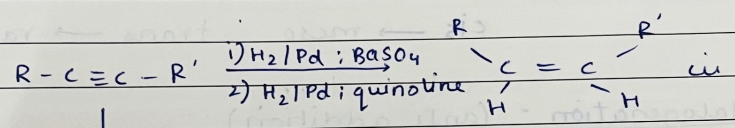
if Na is used instead of zinc then u get pdts like Wurtz rxn. \hookrightarrow very effective for gem
or Zn dust in methanol
NaI in acetone
* ϵ_2 anti-elimina. it gives alkyne



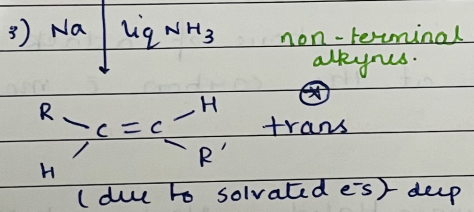
ly it

meso $\xrightarrow{\text{TRANS}}$ trans d/d mixture $\xrightarrow{\text{CIS}}$ cis
just like u add to alkene !! u get mixture
anti addition;

somer...

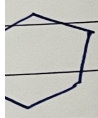


reduction of alkyne



- 1) Rosenmund's catalyst
- 2) Lindlar's reagent
- 3) Birch "

clusively



hydroboration of alkynes \bar{c} B₂H₆ then protolysis \bar{c} H⁺ will give pure cis alkene.

Kolbe's of dibasic salt. potassium succinate $\left[\begin{matrix} \text{COOK} \\ \text{COOK} \end{matrix} \right]$

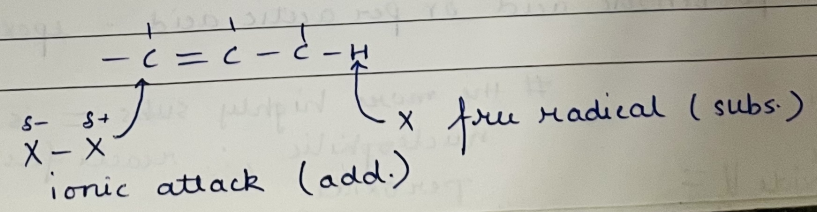
ing

Assignard = higher alkenes ... vinyl halide doesn't go
Mg in ether/A coz of \uparrow stability \rightarrow \bar{X} bond and l.p. in resonance.

the electron density of sp²-C lies more closer to the nucleus than sp³-C, \therefore kinda is more EN. thus a dipole is created $\text{sp}^3\text{-C} \xrightarrow{(+ve)}$ $\text{sp}^2\text{-C} \xrightarrow{(-ve)}$

comps.

rms on i'

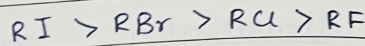


Alkene Preparation [conc. KOH in ethanol, RO⁻ in ROH or DBN (diazobicyclononane)]

170 - alkene
140 - ether
110 - 55-0-3

- alkyl halide → alkene isotropic effect H > D > T
- ease of this process of alkyl halide: 3° > 2° > 1°

E₂ ↳ the more stable the alkene, the more easily it is formed



dehalogenation

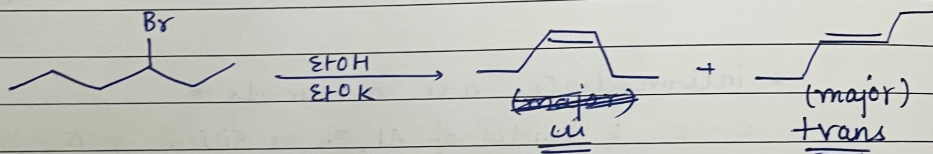
(Et₃N can also be used) + -butoxide; bulky - Hoffmann

E₂ elimination

greater the conjugation ↑ stability more easily it is dehydrohalogenated. anti (ANTI)

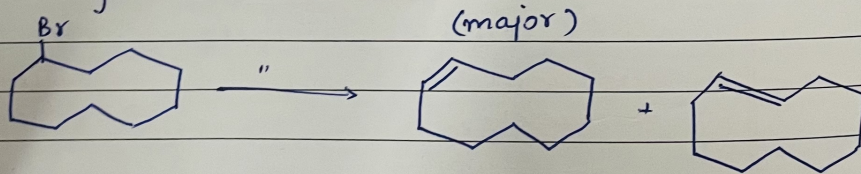
in addition to being regioselective, it is also stereoselective i.e. favors more stable stereoisomer...

hindered base'll give Hoffmann prod.



product of alk

Elimination rxns. of cycloalkyl halides lead exclusively to cis-cycloalkenes.



not a bulky group

heating of alc. Σ H₂SO₄ / H₃PO₄ acid or passing the vapours through Al₂O₃

no isotropic effect.

E₂ 1° < 2° < 3° (becoz of difficulty in form of 1° c⁺) E₁

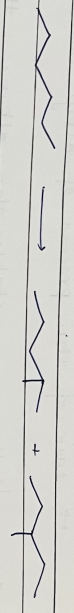
dehyd of alcohols

↳ there's 1,2-shift of -H < -CH₃ < -Ph

(retro-pinacol rearrangement) (=) Wagner rearr. in open-chain comp.

direct method is alc. Σ POCl₃ (phosphoryl chloride) good leaving grp forms fast elimination

(V) Isomerization - involves 1,2 shift of -H or -CH₃.
 radical: $\text{AlCl}_3 \cdot \text{HCl}$ - rearrangement occurs via e^- .



(VI) Aromatization - isomerized then dehydrogenated.
 $[\text{Cr}, \text{O}_3, \text{Al}_2\text{O}_3]$

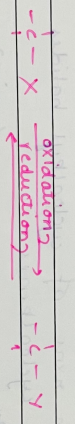


aliphatic alkanes
 benzene (aromatic)

(VII) Pyrolysis / Cracking - less volatile \bar{c} high molecular wt
 \uparrow temp, alkane higher breaks to more volatile \bar{c} less wt.
 lower alkane / alkanes in +ve of catalyst.
 $2 \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 + \text{CH}_4$

* intermediates are radicals *

C-C : oxides of Al, Zn or silica + Δ
 C-H : " " Cr, Mo, Vn + Δ



X is less
 EN than C

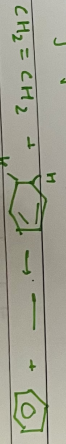
Y is more EN
 than C.

chain initiation - always ends.

propagation - exo \rightarrow F₂ / Cl₂ / Br₂, \bar{c} free radical
 endo \rightarrow I₂

termination

transfer hydrogenation : driving force - aromatics !!



selective " form more stable alkyl. \rightarrow K-H

Unsymmetrical Alkanes = hydrogenation = always racemic !!

(I) Halogenation of Alkanes !! (free radicals)

-F₂ ksh. p. ksh. attack
-Br₂ gen. at replacement of 1°, 2°, 3° H of alkanes by more stable free radicals
→ 1°, 3°: 5/3 → 3.8/1 → 1
ratio → for a given type of abs. (say 1° H) : F₂ > Cl₂ > Br₂ > I₂
for " " halogen ease of abs = 1° < 2° < 3°

bromine in general is less reactive towards alkanes but when it does react, it's v. selective

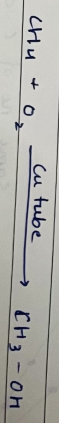
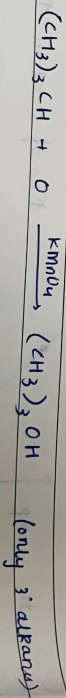
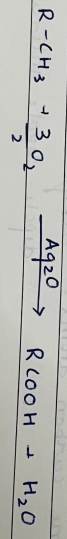
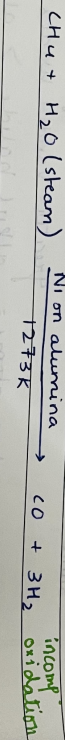
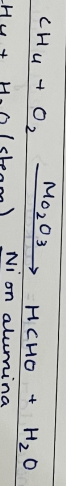
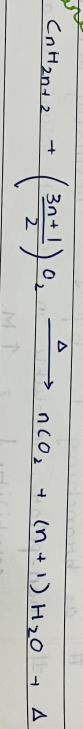
iodination takes place; reversible
SOA → HNO₃, HIO₃, HI
↳ [HI → I₂]

(II) Nitration - replacement of H by NO₂; small grp, faster
[free radical]
↳ leads to chain fission of alkanes (imp)

(III) Sulphonation - replacement of H by SO₃H
source - oleum (H₂S₂O₇) [free radical]

no C-C bond break
[only n-hexane and forwards can be sulphonated]

(IV) Oxidation - excess of air → CO₂ + H₂O



(V) Isonitroalkanes

Aryl
[C₆H₅]

aliphatic alkyl
benzene

(VI) Py

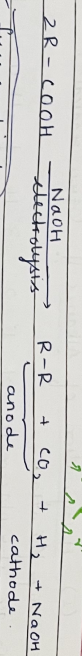
↑ temp, alkyl
lower alkane

transfeer

selective form
Mayman

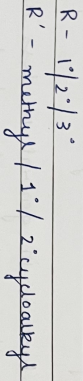
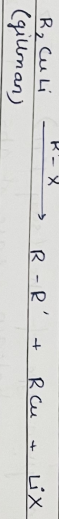
Synthetic

Valley
Alkyne

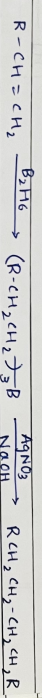
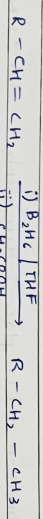


*reducing soln.
basic
pH 7
no. protons*

free radical

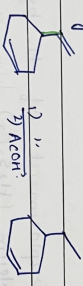


2-CH₃
 beta (NS)
 pentane
 SN₂



M. deborat.

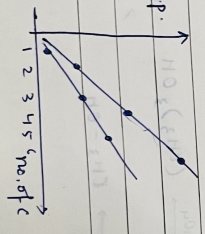
in case diene selectively the less substituted alkene by using a hindered borane, diazomay borane (s₁s₂BH)



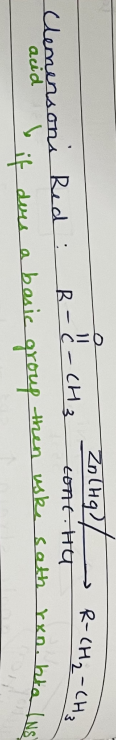
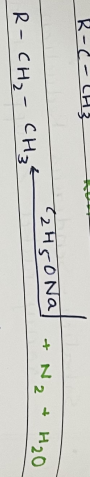
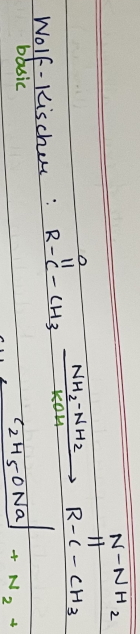
as branching ↑ b.p. ↓ ; normally M ↑ b.p. ↑
 # non-polar; insoluble in H₂O but soluble in alc. & ethers;
 solubility ↓ ↑ M.

same molecular wt = alkane > alkyl halide
 = greater Van der Waals contact.
 same carbon atoms = alkyl halide > alkane
 = dipole-dipole interaction + VWF.

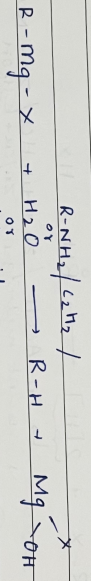
m.p. ↑ no. of C-atom ↑ b.p. ↑ branching in isomeric alkanes



same no. of C-atoms, ↑ branches more compact molecule, forces are strong. m.p. ↑

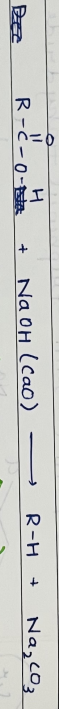


no alkene can be hydrogenated to form neopentane for isopentane



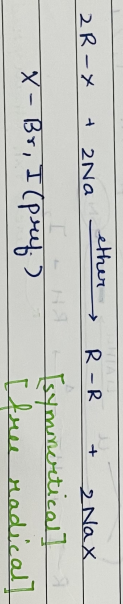
R-alkyl/aryl
X-Cl, Br, I

if D_2O is used, $R-D + Mg-OH-X$ form the alkane only.

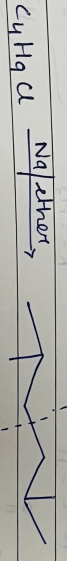


Y.d.s. \rightarrow carbocation (\uparrow stable \uparrow reactivity)

$R \rightarrow CH_3$ yield is good of CH_3 , but if it is C_2H_5 various prod. are obtained.

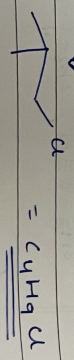


if the prod. has symmetry, it helps to decide to original struc. of alkyl halide.



free radicals undergo reduction, disproportionation

FRANKLAND (Zn + dry ether)



Symmetrical

SN

Free radicals

disorder of chain

Multiz Rm.

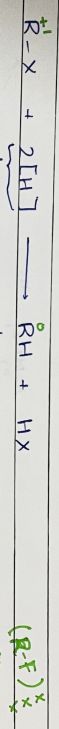
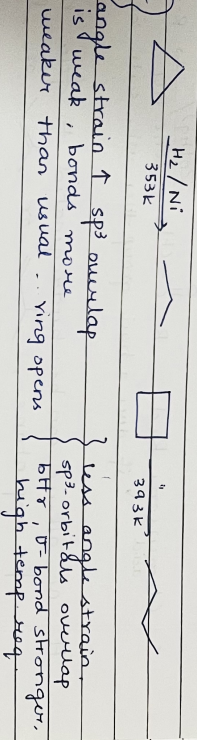
Alkene Preparation:

rate of rxn: alkyne > alkene.
(linear) (trigonal p)

5th ADD.

Sabotier - Sandmeyer Reduction; $CH_2=CH_2 \xrightarrow[Ni/Pt]{+H_2} CH_3-CH_3$
 rarely nickel > supported nickel
 Pd

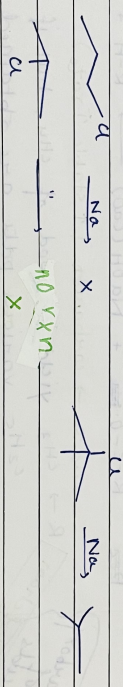
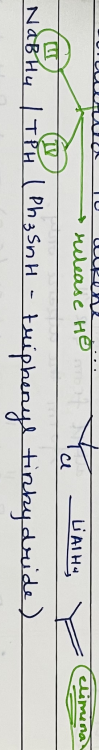
Multiple C-C
addition



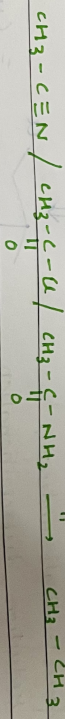
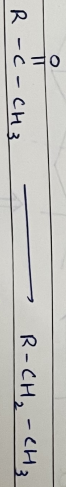
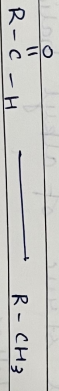
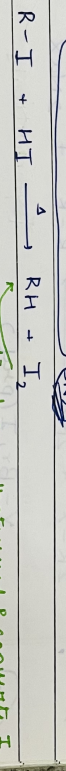
sources: Zn/AcOH / Zn/dil. HCl / Zn + NaOH
 Zn/ox + EtOH

reduction
alkene

LiAlH₄ is not useful for 3° alkyl halide, coz it's
 connected to alkene
 release H⁺



Transfer
from
major
Ithor
position
addition



red P
 + HI
 reduction

(ketones \rightarrow Alkane) \rightarrow 3 reagents !!