ALKANES: (Paraffins)

Preparation:

→ 1) Hydrolysis of Carbides:

Eg:

$Be_2C \xrightarrow{H_2O} CH_4$ (Eg in J.D. LEE)

$Al_4C_3 \xrightarrow{D_2O} 3CD_4$

$Mg_2C_3 \xrightarrow{H_2O} C_3H_4$ [$CH_2=C=CH_2$ Allene ; $CH_3-C\equiv CH$ propyne (Major)]

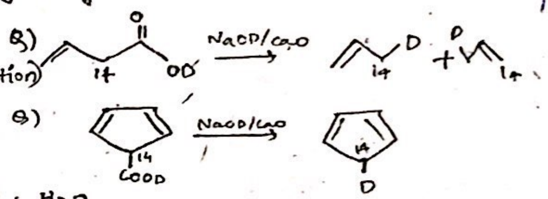
↓ C_3^{-4}

due to less π-$\bar{e}$ repulsion

$CaC_2 \xrightarrow{D_2O} D-C\equiv C-D + Ca(OD)_2$

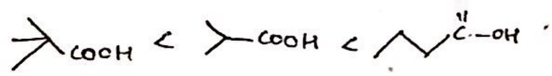
$SiC \xrightarrow{H_2O}$ Doesn't Undergo hydrolysis.
(Covalent structure)

→ 2) By Using Soda lime: (Decarboxylation)
(NaOH + CaO)
3 : 1



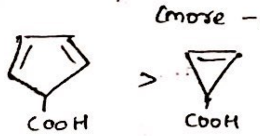
$R-\overset{O}{\overset{||}{C}}-OH$ (or) $R-\overset{O}{\overset{||}{C}}-O^{\ominus}Na^{\oplus}$ $\xrightarrow{CaO+NaOH} R^{\ominus} \xrightarrow{H_2O} R-H$ (alkane)
(carbanion)

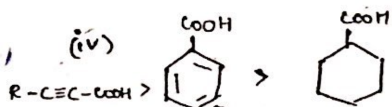
Reactivity:

(i) 

→ ease of decarboxylation depends on stability of carbanion.

(ii) $O \leftarrow \overset{O}{\overset{||}{N}}-CH_2-\overset{O}{\overset{||}{C}}-O-H > H-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-OH$
(more −R)

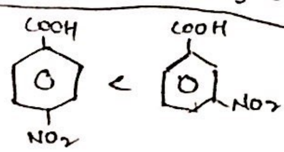
(iii) 

(iv) 

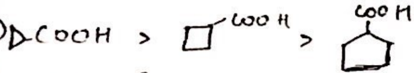
(less s-character)

(v) $CF_3-COOH < CCl_3-COOH$ (Back bonding)

(vi) $CF_3-CH_2-COOH > CCl_3-CH_2-COOH$ (−I)

* (vii) 

(more −I)
(not by −R since CH_2^- will be ⊥r)

* (viii) 

(more strain, more s-character)

→ 3) Kolbe's electrolysis:

→ aqeous Sodium (or) potassium salts of carboxylic acids upon electrolysis.

At anode:

$$R-\overset{O}{\overset{\|}{C}}-O^{\ominus} \xrightarrow{-e^-} R-\overset{O}{\overset{\|}{C}}-O^{\odot}$$

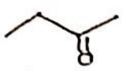
$$R-\overset{O}{\overset{\|}{C}}-O^{\odot} \longrightarrow R^{\odot} + O=C=O\uparrow \text{ (at anode)}$$

$$R^{\odot} \xrightarrow{\text{Fate}} \text{Products}$$

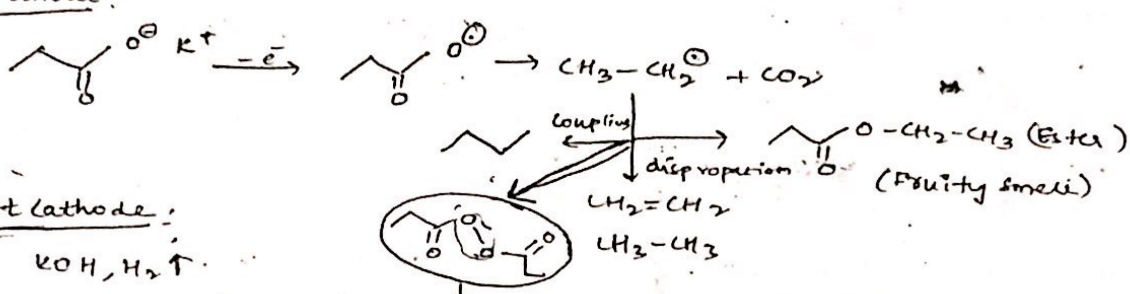
At cathode:

$$H_2O \xrightarrow{e^-} \tfrac{1}{2}H_2\uparrow + OH^-$$

$$Na^+ \xrightarrow{OH^-} NaOH$$

Eg:  $O^{\ominus}K^+ \xrightarrow[\text{Kolbe's electrolysis}]{K.E}$, Product (s)?

At anode:



At cathode:

KOH, $H_2\uparrow$

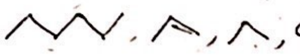
Never observed because of high unstability of peroxide bonds.

Other examples:

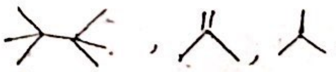
1) $CH_3-COOH \xrightarrow[NaOH]{K.E}$

at anode: C_2H_6, CO_2 at cathode: NaOH, H_2

2) $CH_3-CH_2-CH_2-COOH \xrightarrow{K.E}$

at anode: , CO_2 at cathode: NaOH, H_2

3) COOH $\xrightarrow{K.E}$

at anode: , CO_2

(zero%)

4) $H-COOH \xrightarrow{KE}$

at anodes H_2, CO_2 at cathode: H_2, NaOH

5) $D-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{KE}$

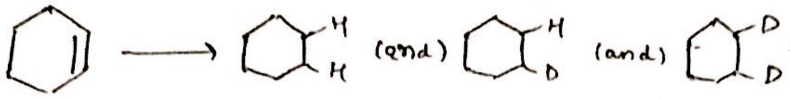
at anode: D_2, CO_2 at cathode: H_2, NaOH

6) $H-\overset{O}{\overset{\|}{C}}-OD \xrightarrow{KE}$

at anode: H_2 CO_2 at cathode: H_2, NaOH

Q) During catalytic hydrogenation, a little amount of D_2 is diffused. (4)
Product is/are ___?___ (on the given substrate).

Sol:

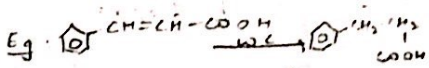


NOTE:
→ If we conduct specially the rxn under Nickel catalyst (Sabatier's-Senderen's rxn)

→ other reagents used for catalytic reduction are:

1) ~~H_2 Pd/C~~ $H_2/Pd-C$ → activates (increases activity of the catalyst)

2) $H_2/Pt-O_2$ (adam's catalyst)

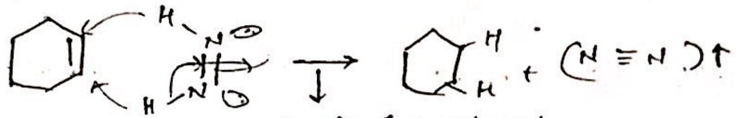


3) Wilkinson's catalyst $[Rh^{+1}(PPh_3)_3]Cl$ → (Syn phase addn) → ene becomes ane, yne becomes ene and becomes ane

(4) 4) Di-imide $[H_2N-NH_2 \xrightarrow{H_2O_2} H-N=N-H]$

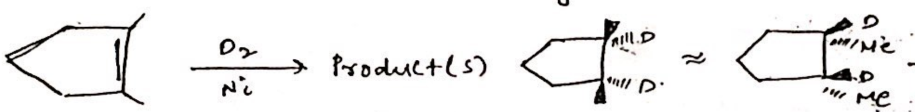
yne → ene → ane

Mech: Syn addn



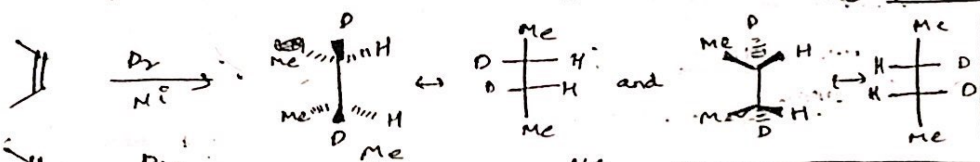
cyclic 6-membered ring transition state.

1Q)



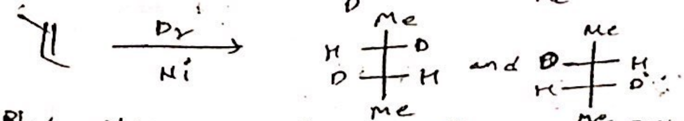
→ one prod (O.A) meso

2Q)



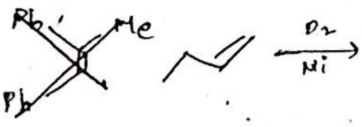
Erythro → One Prod. (O.I.A) Meso

3Q)



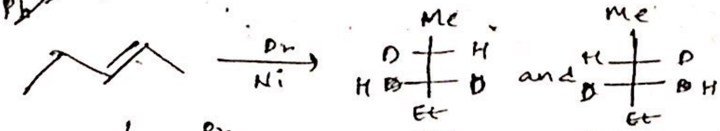
2 (threo) (enantiomers) Racemic mixture (±)

4Q)



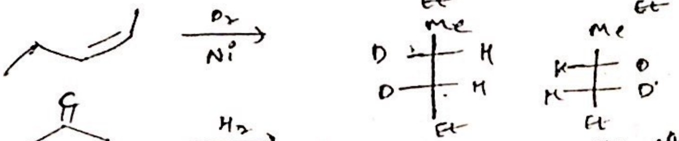
50% 50%
2 products.

5Q)



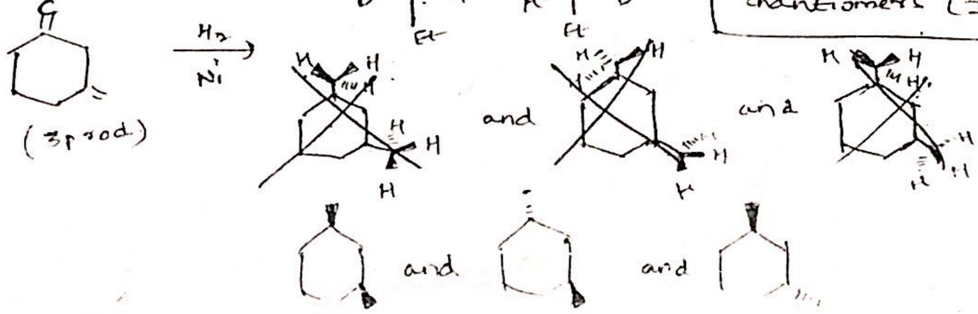
2 ~~(Erythro)~~ (threo) (Enantiomers) (±) → Rac. mix

6Q)

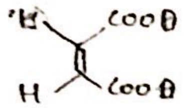


2 (erythro) Enantiomers (±)

7Q)



(3 prod)

7)  (Maleic acid) $\xrightarrow{KE}$

at anode: $H-C\equiv C-H$, CO_2 at cathode: H_2, NaOH

⑧ CH_2-COOH

$|$

CH_2-COOH (Succinic acid) $\xrightarrow{KE}$

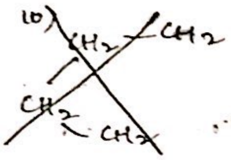
at anode: C_2H_4, CO_2 at cathode: H_2, NaOH

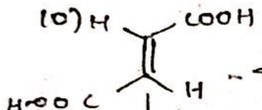
9) CH_2-COOH

CH_2

CH_2-COOH (glutaric acid) $\xrightarrow{KE}$

at anode: Δ, CO_2 at cathode: H_2; NaOH

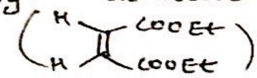
~~10)~~ 

10)  $\xrightarrow{KE}$

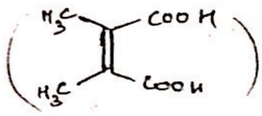
fumaric acid

at anode: $H-C\equiv C-H$, CO_2 at cathode: H_2, NaOH

11) Diethyl Malanoate (ester) $\xrightarrow{KE}$ No electrolysis

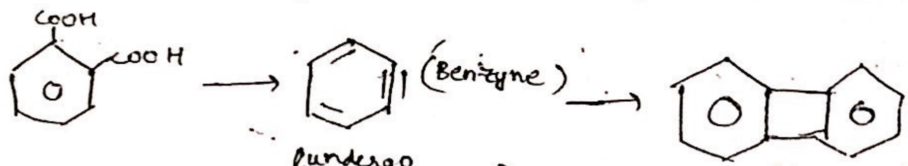


12) Dimethyl Maleic acid

 $\xrightarrow{KE}$

at anode: But-2-yne , CO_2

13) Pthalic acid



(Benzyne) (Biphenylene)

(undergo dimerisation) (Aromatic)

4) → Catalytic hydrogenation.

H_2 in Ni/Pt/Pd

Eg: $CH_2=CH_2 \longrightarrow CH_2-CH_2$ (with H on each carbon)

$R-C\equiv C-R \longrightarrow R-CH_2-CH_2-R$

Mechanism:- $CH_2=CH_2$

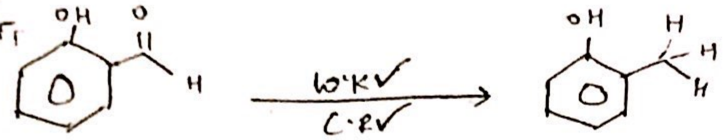
→ H-atoms due to high active metal surface

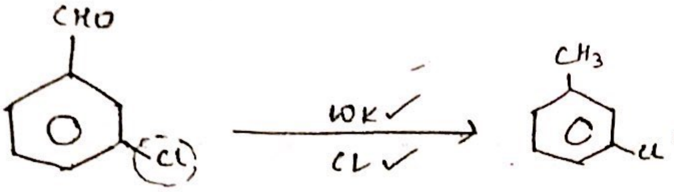
(Syn phase addition takes place) →

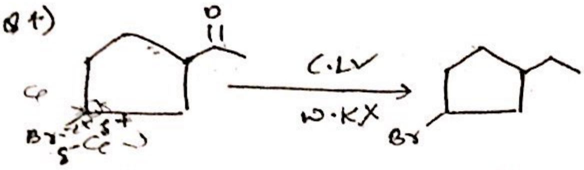
→ Metal Surface

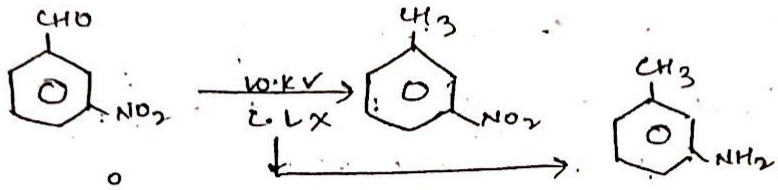
CH_2-CH_2 (with H on each carbon)

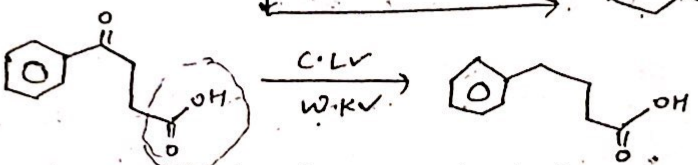
Vaibhav

Q2)


Q3)


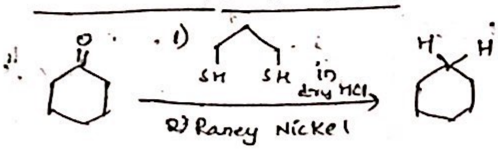
Q4)


Q5) *


Q6)


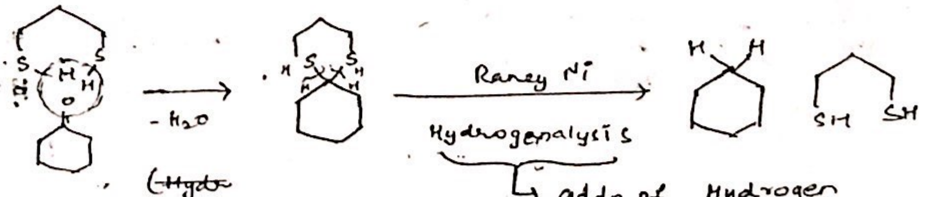
↳ doesn't get reduced by ~~and~~ metal acid.

(iii) MOZINGO REDUCTION:-



$Ni + Al \xrightarrow[\Delta]{NaOH}$ Raney Nickel

Mechanism:-

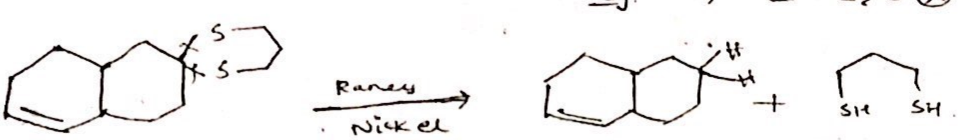


↳ addn of Hydrogen across unsymmetrical σ-bond

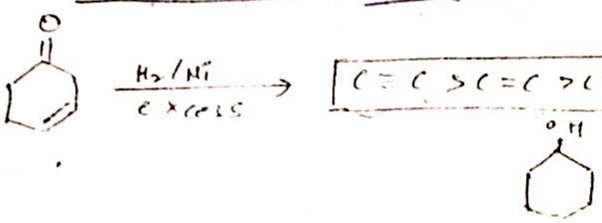
(takes place if bond is weak)

Eg. C–F ✗ C–O ✗ C–S ✓

Eg.

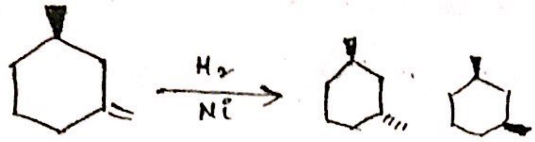
Q)


Note: Raney Nickel is more selective towards Hydrogenolysis

Q) *


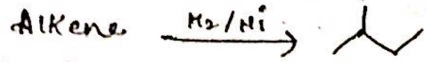
$\boxed{C\equiv C > C=C > C=O}$ (reactivity order)

8Q)



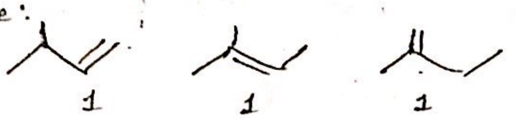
2 (pair of dia)

9Q)



(No-of alkenes)

Possible:



} 3

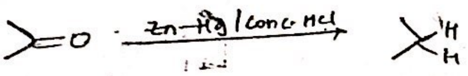
NOTE ·

→ Catalytic hydrogenation is classified into 2 types:

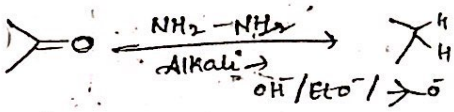
Homogeneous catalysis	Heterogeneous catalysis.
→ Reactant and Catalyst will maintain same phase.	→ Reactant and catalyst will maintain different phase.
Eg: Wintinson's catalyst	Eg: All metallic reductions (Ni, Pt, Pd)

5) PREPARATION OF ALKANES BY USING CARBONYL COMP:-

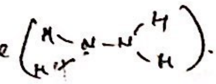
(i) Clemmensen reduction:-



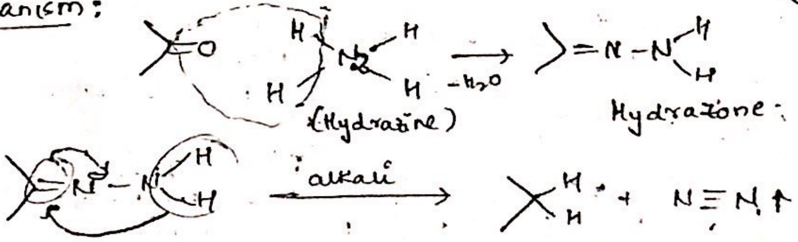
(ii) Wolf-Kishner reduction:



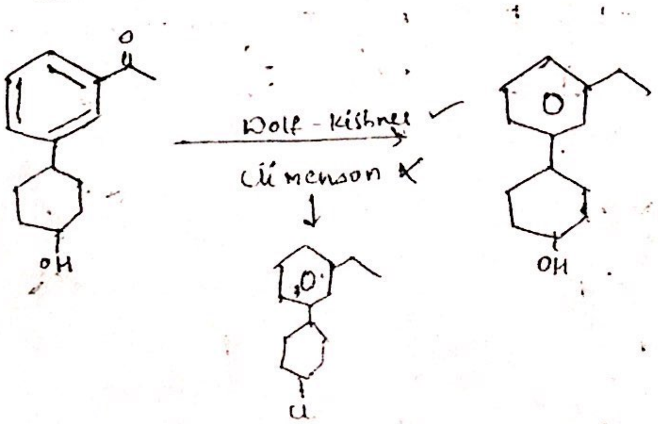
Hydrazine

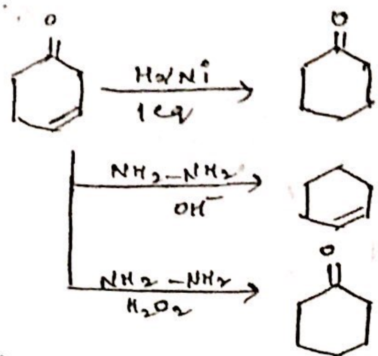


Mechanism:



Q1)





(Reduces only symmetrical π-bonds)

6) PREPARATION OF ALKANES BY USING ALKYL HALIDES:

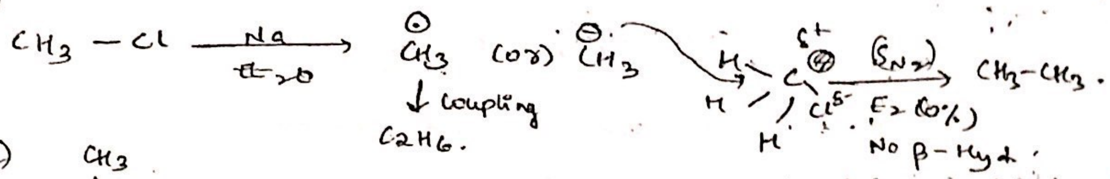
i) Wurtz reaction:

Reagent : ~~Used~~ Na in dry ether (Et_2O)

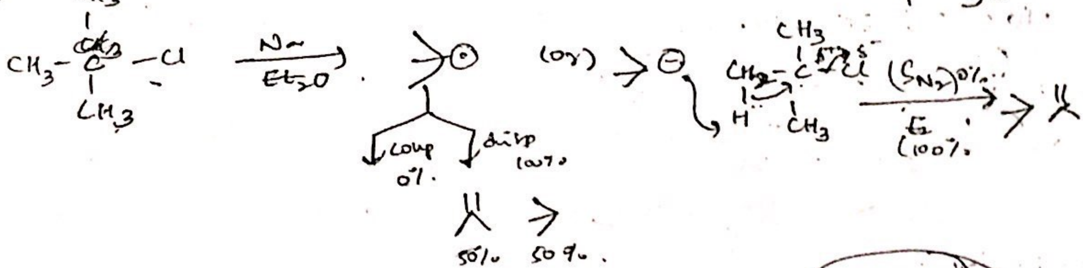
$$R \overset{\delta+}{-} \overset{\delta-}{Cl} \xrightarrow[Et_2O]{Na} \cancel{R^{\ominus} + Cl^{\ominus}} \quad Cl^{\ominus} + \dot{R} \text{ (or) } R^{\ominus} \checkmark \text{ (in ex. ans) for single}$$

(Mech. is uncertainity proposed by ~~wurtz~~ wurtz)

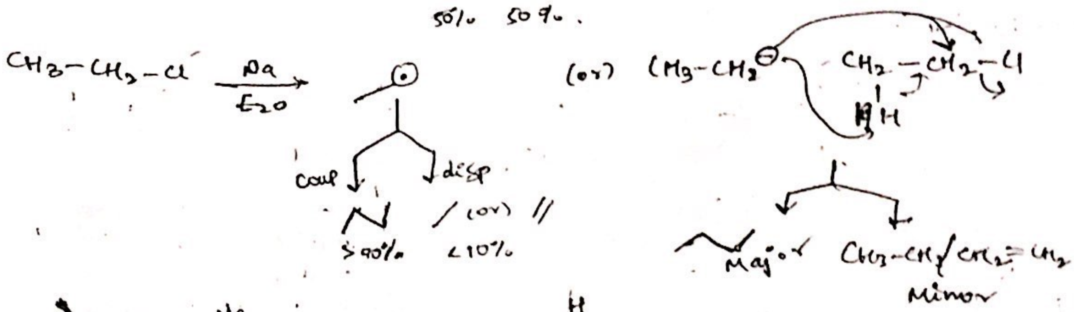
Q1)



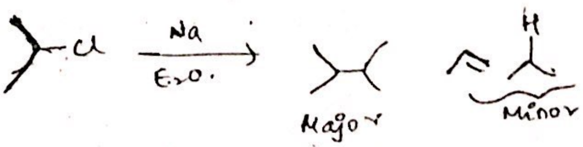
Q2)



Q3)



Q4)

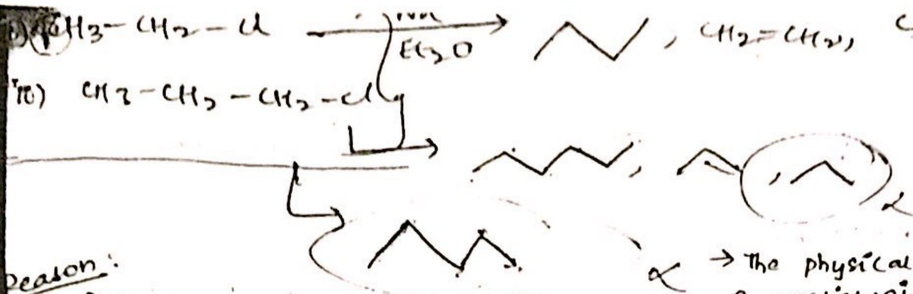


NOTE:

→ Methane doesnot get synthesized by ~~Ko~~ Kolb's electrolysis as well as wurtz's reaction.

→ wurtz's rxn is failed to synthesize alkanes which contains odd no-of carbons.

ii) No-of product(s):



any ~~sub~~ alkane which is obtained from mixed halides is minor

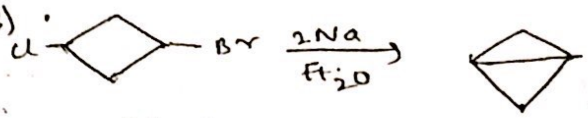
→ The physical properties will be very close and difficult to separate. (Not good yields)

Reason:

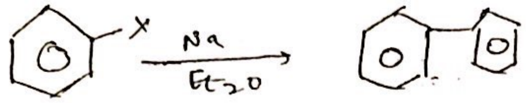
→ Mixture of alkanes are formed.

Therefore, odd no-of carbon compounds are not preffered by wurtz rxn.

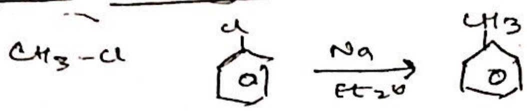
Q)



FITTING REACTION:

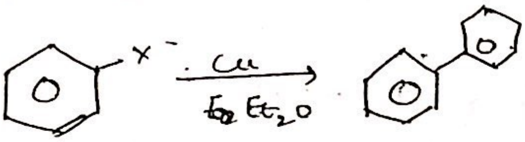


2) Wurtz Fitting:

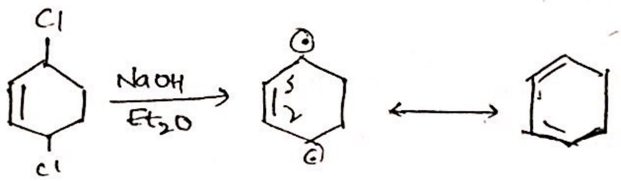


3) Ullmann reaction:

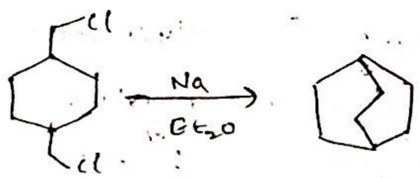
Fact: allyl halides are betterly coupled in presence of copper metal



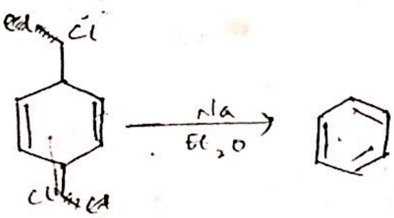
Q)



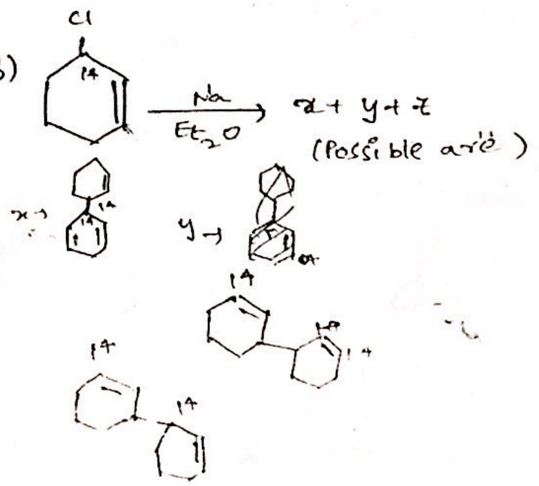
Q)



Q)



Q)



than 6-membered ring. but entropically 5-membered (10) ring is formed easily than 6-member formation. Finally, ease of formation : (5) > (6) > (3) > (4) (rings)

→ (vii) METAL + ACID: (NCERT)

Reagent: Zn + HCl [solvent is either a dil soln of acid (or) protic solvent]

→ Develops Nascent Hydrogens.

→ That is helpful to convert R–X → R–H except Flourine.

other reagents: Zn + CH_3COOH (or) Na + EtOH

E) $CH_3-CH_2-Cl \xrightarrow{Na/Et_2O} CH_3-CH_2-CH_2-CH_3$

$CH_3-CH_2-Cl \xrightarrow{Na/EtOH} CH_3-CH_3$

(viii) ACTIVE METALS:

Ni ✗, Pd ✗, Pt ✗, Raney Nickel ✓, $H_2/Pd-C$ ✓

→ used for Hydrogenalysis:

C–F, C–O } ✗ (Highly polar)

C–S, C–Cl, C–Br, C–I } → C–H

(ix) Metal + Base:-

Reagent. $\underbrace{Zn + NaOH \,/\, \{Zn + Al + Cu\} + NaOH}_{\text{Developes Nacent Hydrogen}}$ (Devarda's alloy)

$R-X \longrightarrow R-H.$

(x) HI & Red P_4:

→ Powerful reducing agent

→ Doesnot reduce C=C / C≡C / benzene etc.

① $R-X \longrightarrow R-H$

→ if –X is Iodide, red phosphorous is not needed

$R-I \xrightarrow{HI} R-H$

→ ② $R-OH \xrightarrow[\text{Red } P_4]{2HI} R-H + H_2O$

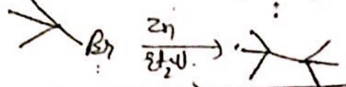
③ $R-\underset{H}{\underset{|}{C}}=O \xrightarrow[\text{Red } P_4]{4HI} R-CH_3.$

(v) Frankland's reaction:-

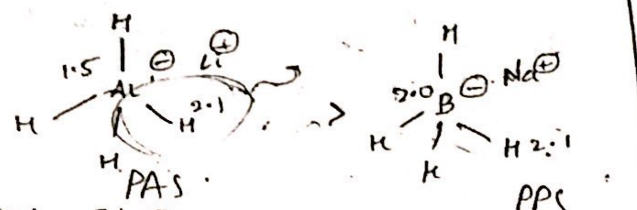
$R-X \xrightarrow[Et_2O]{Zn} R-R$

↓ all

Eg: $CH_3-Br + CH_3-Br \xrightarrow[Et_2O]{Zn} CH_3-CH_3 + ZnBr_2$



(vi) $LiAlH_4$ & $NaBH_4$:-



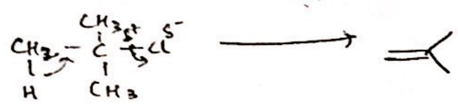
Solvent: Et_2O (Dry ether) CH_3OH (methanol)

→ $LiAlH_4$ with 3° R-X give elimination product as major product.

→ $NaBH_4$ only reduces 3°, 2° R-X

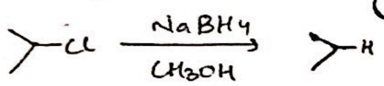
Eg i) $CH_3-CH_2-Cl \xrightarrow[S_N2]{LiAlH_4} CH_3-CH_3$.

2) $CH_3-CH(CH_3)-Cl \xrightarrow{S_N2}$ isobutane-type product (Major)

3) 

4) ✱ $CH_3-C(CH_3)_2-Cl \xrightarrow[CH_3-OH]{NaBH_4}$ carbocation $\xrightarrow{BH_4^{\ominus}}$ product–H

S_N1 $R \propto [R-X]^1$

5) 

6) $CH_3-CH_2-Cl \xrightarrow{NaBH_4}$ ~~CH_3-CH_3~~ No reaction.

(carbocation is unstable)

7) $(R_3)SnH$ (or) $(\phi_3)SnH$ Trialkyl tin hydride

$C-X \longrightarrow C-H$..

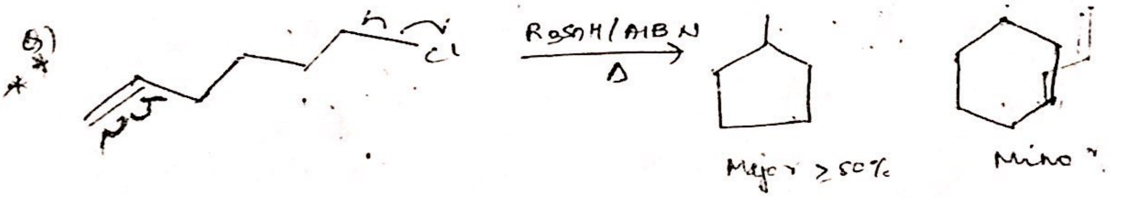
for all

→ Industry will use this reagent in AIBN catalyst at high temparature.

AIBN: Azo iso butyro Nitrile.

$Me-C(Me)(Me)-N=N-C(Me)(Me)-Me$ ↓ N_2

→ Net reaction is free radical substitution.

8) ✱ 

Reason: Thermodynamically 6-membered ring more stable

(4) $R-\overset{\|}{C}-R \xrightarrow[\text{Red } PR_4]{4HI} R-CH_2-R$

(3) $R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\text{Red } PR_4]{6HI} R-CH_3 + 2H_2O$

(XI) GRIGNARD'S REAGENT: (RMgX)

1) $\overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow[\text{Dry Ether}]{Mg} \overset{\delta-}{R}-\overset{\delta+}{Mg}X$

Precautions:

→ In absence of air, reagent should be prepared.

$\overset{\delta-}{R}-\overset{\delta+}{Mg}X \xrightarrow{O=O} R-O-O-MgX$ (In air)

↓ Hydrolysis

$R-OH$

→ **Hint:** like $NaOH$, $NaNH_2$, $NaHCO_3$ etc-- these reagents

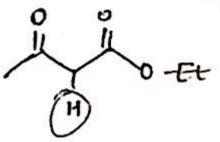
RMgX does not follow acid-base rule.

It takes only ~~like~~ acidic Hydrogen.

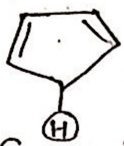
(It acts as a base)

→ Any sp C-H ($C\equiv C-H$ or $H-C\equiv N$ (Active sites (like))

N-H, O-H,



,

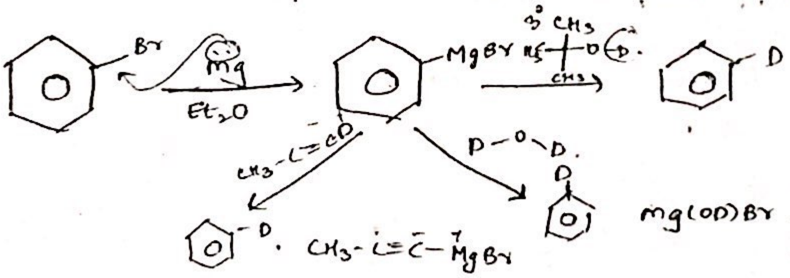


(aromatic)

, S-H,

H-X

→ In the above cases only, it acts as a base



→ Which substances does not yield grignard reagent.

Doubt

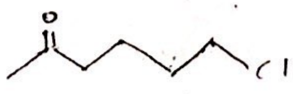
A) 

E) 

B) $H-C\equiv C-CH_2-Cl$

F) 

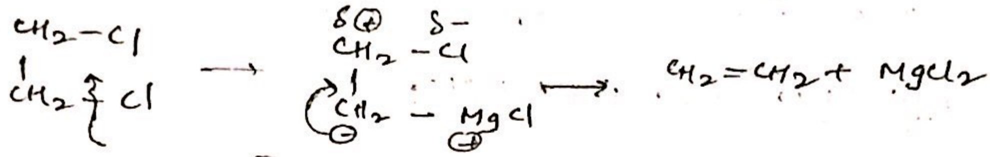
C) CH_2-Cl, CH_2-Cl

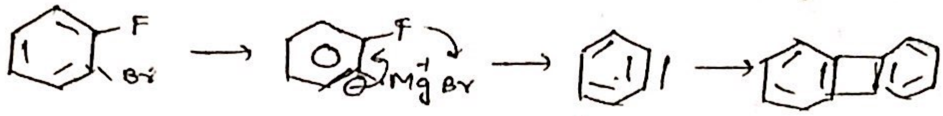
G) 

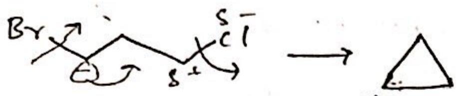
D) 

A)

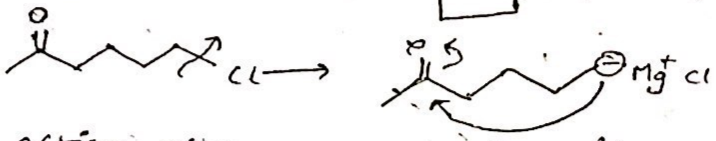

B) $H-C\equiv C-CH_2-MgCl \Rightarrow Cl\,\overset{+}{Mg}-\overset{-}{C}\equiv C-CH_3$

C)


D)


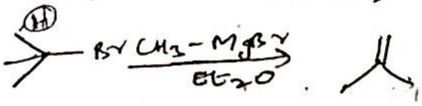
E)


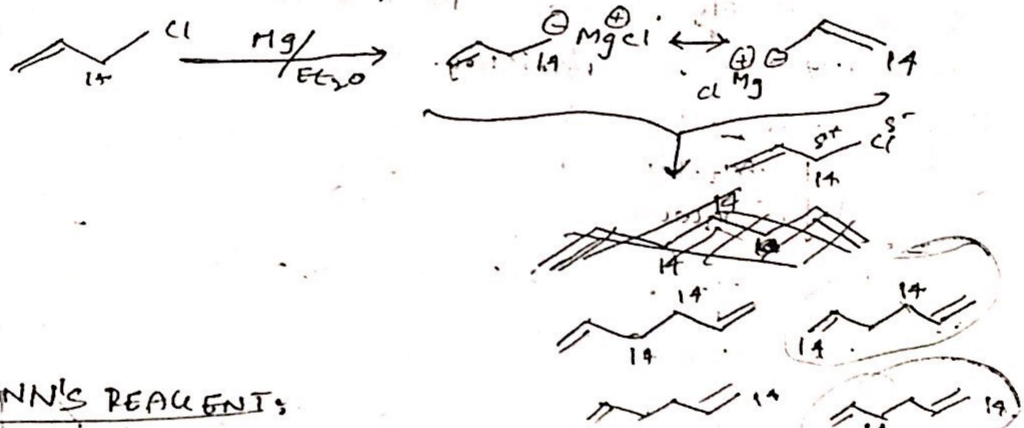
F)


(G)


→ If active sites are not there, it acts as nucleophile.

Eg: 1) $\overset{\ominus}{CH_3}-MgBr \xrightarrow{\overset{\delta+}{CH_3}-Br} CH_3-CH_3$; S_N2

2)


3)


(XII) GILMANN'S REAGENT:

$R-X \xrightarrow{Li} R-Li$ (Organo Lithium reagent)

Me/⌐/etc --

$\xrightarrow{CuI}$ R_2CuLi

Power: $R-Li >> R-MgX >> R_2CuLi$

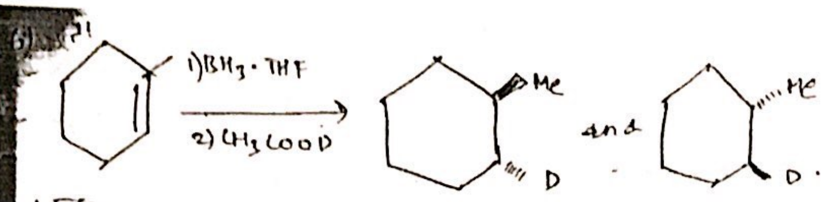
R_2CuLi Function:

→ It gives S_N2 reaction with alkyl halide

$\rightarrow 3°X$ (i..)

$R_2CuLi \xrightarrow[S_N2]{R'X} R\,R'$ Corey House synthesis.

6)



NOTE:

$CH_3-CH=CH_2 \xrightarrow{BH_3\cdot THF} CH_3-\underset{H}{CH}-\underset{BH_2}{CH_2} \longrightarrow (CH_3-CH_2-CH_2)_3B$

$\downarrow AgNO_3$ (Dimerisation)

$\boxed{\text{Left over preparations, read from NCERT}}$

PROPERTIES OF ALKANES:

PHYSICAL PROPERTIES:

1) Non-polar

possess weak vanderwaal force of attraction [compared to dipole & H-bonding]

→ Thus C_1 to C_4 are gases

C_5 to C_{17} are liquids and rest are solids at room tempature.

→ colourless and odourless

→ less denser than water (0.7 gm/cc)

→ ∴ Alkanes float on water.

2) Boiling point:

→ Increases with molecular weight

$C_1 \to -162°C$ $\quad$ $C_5 \to 36°C$

$C_2 \to -88°C$ $\quad$ $C_6 \to 69°C$

$C_3 \to -42°C$ $\quad$ $C_7 \to 98°C$

$C_4 \to 0°C$

→ If Branching ↑, B.P decreases [S.A ↓, vand. ↓]

Surface area

3) Melting point:

→ Smooth increasing trend is not observed with increase in no. of carbons

4. SOLUBILITY:

→ Insoluble in water but soluble in non-polar solvents [C_6H_6, CCl_4, ether]

→ decreases with increase in molecular weight

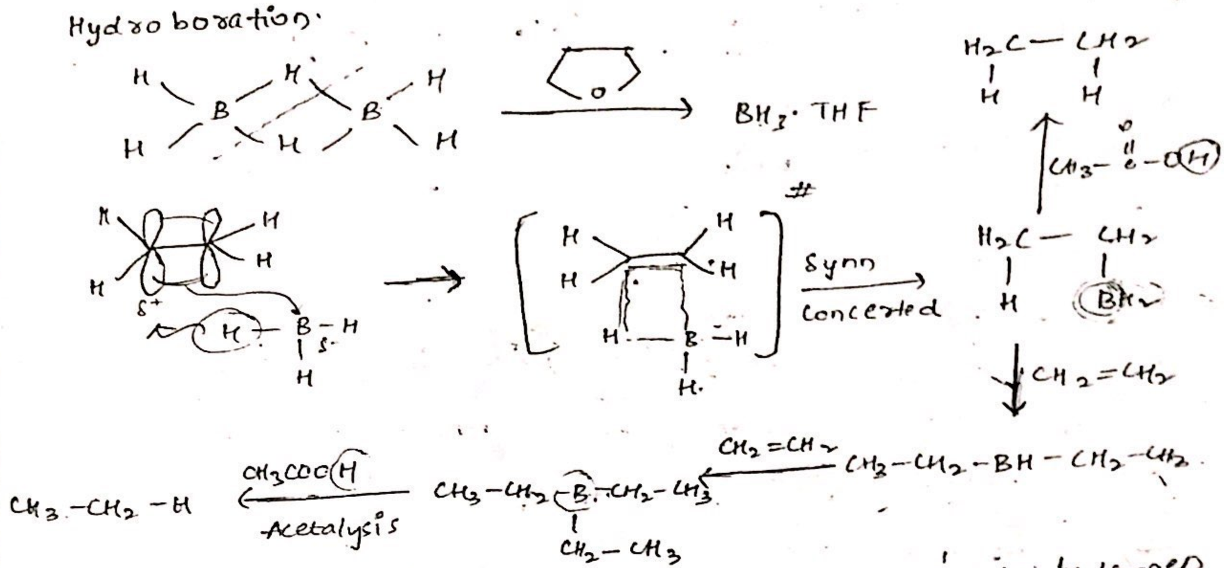
$CH_2=CH-Cl \xrightarrow{R_2CuLi} CH_2=CH-R$

Vinyl halide

→ By using this method, we can prepare all types of alkanes and alkenes except methane.

7) HYDRO BORATION - ACETALYSIS:-

→ addition of B-H across C=C (or) C≡C is known as Hydroboration.

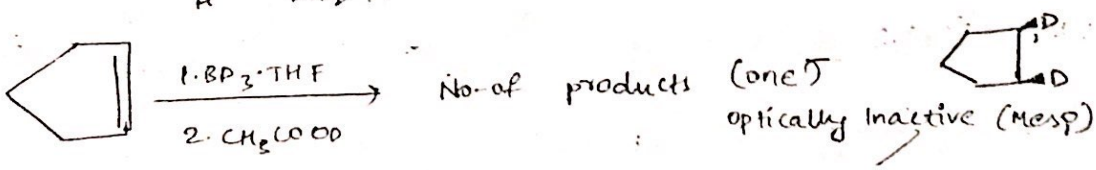


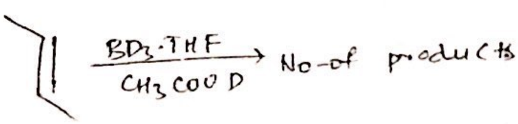
→ During Acetalysis, boron position is replaced by hydrogen including stereo chemistry.

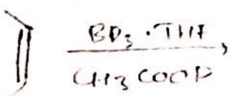
Eg: 1) $CH_3-CH=CH_2$ better nucleophile

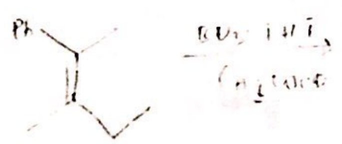
① $BH_3\cdot THF$
② CH_3COOD

$CH_3-CH(H)-CH_2(BH_2) \longrightarrow CH_3-CH_2-CH_2D$

2) 

3) 

4) 

5) 

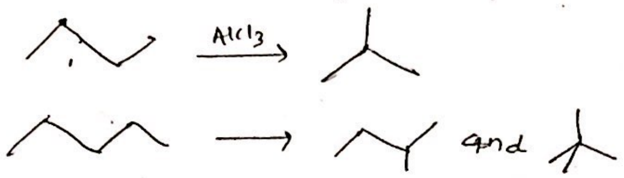
Industrial preparation of H_2:-

→ Methane react with steam in presence of 'Ni' catalyst Produce water gas. (Industrial method)

$$CH_4 + H_2O \xrightarrow[\Delta]{Ni} \underbrace{CO + 3H_2}_{\text{water gas}}$$

3) Isomerisation:-

→ Reagents: Anhyd. ~~AlCl3~~ $AlCl_3$ + HCl → Reactant should have four (or) more no. of carbons.
→ B.pt of prod. < B.pt of reactant

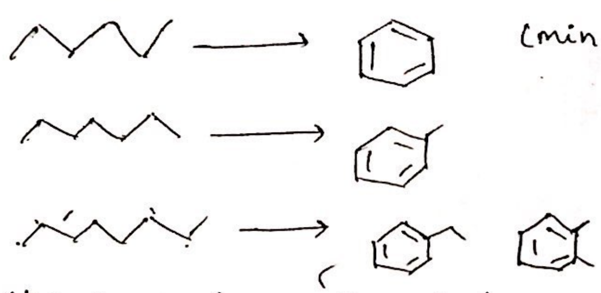


4) AROMATISATION:-

Reagents: Oxides of ~~p~~ Vanadium, molybdenum, chromium (V, Mo, Cr)

$[V_2O_5, Mo_2O_3, Cr_2O_3, Cr_2O_3 \cdot Al_2O_3]$ alone / along with Al_2O_3

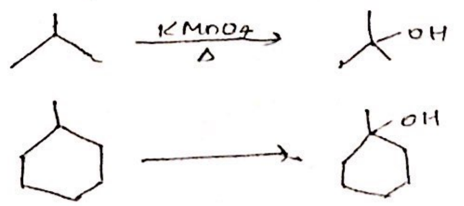
Eg: (min. 6)



Fact: Cyclisation followed by dehydrogenation.
(through radical)

5) OXIDATION:

→ only teritiary hydrogen oxidised to alcohol by means of $KMnO_4$.



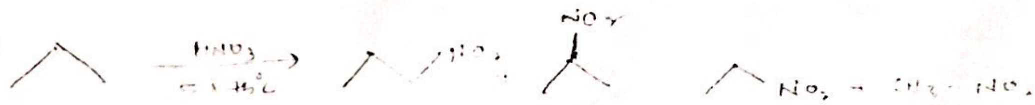
→ $2CH_4 + O_2 \xrightarrow{Cu/523K} 2CH_3OH$.

→ $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

→ $2CH_3-CH_3 + 3O_2 \xrightarrow[\Delta]{Mn(CH_3COO)_2} 2CH_3COOH + 2H_2O$.

6) NITRATION:

→ Alkanes undergo Nitration in vapour phase medium around ~475°C.



(all C-C & C-H bonds breaks)

$C_1 \rightarrow -183\,C$
$C_2 \rightarrow -172^{\circ}C$
$C_3 \rightarrow -187^{\circ}C$
$C_4 \rightarrow -138^{\circ}C$
$C_5 \rightarrow -130^{\circ}C$
$C_6 \rightarrow -95^{\circ}C$
$C_7 \rightarrow -90^{\circ}C$
$C_8 \rightarrow -57^{\circ}C$
$C_9 \rightarrow -54^{\circ}C$
$C_{10} \rightarrow -30^{\circ}C$

→ Even no-of carbons will be more packed than odd no-of carbons.

$\therefore$ $C_2 < C_4 < C_6 < C_8 < C_{10}$
$C_3 < C_1 < C_5 < C_7 < C_9$

$\therefore \boxed{C_3 < C_1 < C_2} < C_4 < C_5 < C_6 < C_7 < C_8 < C_9 < C_{10}$

→ Branching of an alkane gives it a more a ~~compared~~ compact 3-dimensional structure which packs more easily.

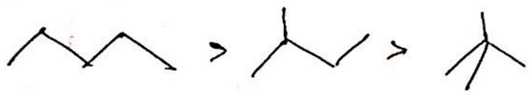
$\therefore$ Branching ↑, MP ↑.

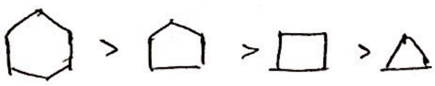
(M.P & also stability order)

3) Heat of Combustion:

→ Heat of Combustion $\propto$ No-of carbon atoms.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_{2(g)} + (n+1)H_2O_{(l)} + \text{Heat}$$

orders:
1) 

2) 

3) 

[Stability of cyclo alkanes: 6>5>3]

4)

CHEMICAL PROPERTIES:

→ Alkanes are chemically inert towards most of the labalatory reagents under normal conditions.

→ Therfore, alkanes are called as paraffins. (Latin)

1) PYPROLYSIS / CRACKING:

→ Heating of alkane in absence of air.

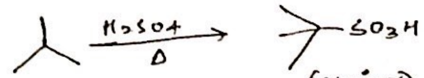
lower alkane(s) + alkene(s) + H_2 ↑

7) SULPHONATION :-

→ Linear alkanes undergo sulphonation if possess 6 (or) more carbons.

Reactivity: $3° > 2° > 1°$

Eg:

i) 

(Major)

→ other chemical properties read from NCERT.

*) PHOTO CHEMICAL HALOGENATION:

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3-Cl \text{ and } CH_2-Cl_2 \text{ and } CHCl_3 \text{ and } CCl_4$$

→ To get mono halogenated product predominately, take excess of alkane.

Mechanism:

→ initiation:

$$Cl-Cl \xrightarrow{h\nu} 2\dot{Cl}$$

→ Propagation

$$CH_4 + \dot{Cl} \xrightarrow{RDS} \dot{C}H_3 + HCl$$

$$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3Cl + \dot{Cl}$$

→ Termination:

$$\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$$

$$\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$$

→ More yield of halo-alkane is obtained in propagation

thermodynamic data:-

1) $CH_4 + \dot{X} \longrightarrow \dot{C}H_3 + HX$ → 1) $\Delta H_F = -31$ kcal/mole

2) $\dot{C}H_3 + X-X \longrightarrow CH_3-X + \dot{X}$ → 2) $\Delta H_F = -70$ kcal/mole

-101 kcal/mol (Exo)

1) $\Delta H_{Cl} = +2$ | 1) $\Delta H_{Br} = +18$ | 1) $\Delta H_I = +34$ kcal

2) $\Delta H_{Cl} = -26$ | 2) $\Delta H_{Br} = -24$ | $\Delta H_I = -21$ kcal

-24 (Exo) | -6 (Exo) | 13 (Endo)

→ Flourination is highly exothermic. Therefore, not possible to conduct experiment, not possible to get flouro alkanes.

→ Chlorination is more reactive than bromination, therefore bromination is highly selective

Iodination is endothermic and reaction is reversible.

Since HI is reducing agent, reduces alkyl ~~halide~~ Iodide to alkane.

∴ To get better yield of Iodo alkane, this reaction is carried out in presence of oxidising agents.

Eg: HNO_3, HIO_3, HgO etc --

(or)

→ carried out the rxn in presence of base.

Eg: NaOH, KOH etc-

Rate of halogenation: $F_2 > Cl_2 > Br_2 > I_2$

∴ overall reactivity: $F_2 >> Cl_2 > Br_2 > I_2$

∴ selectivity: $Br_2 > I_2 > Cl_2 > F_2$ (Doubt).

Reactivity w.r.t carbon:

→ overall reaction is Free radical substitution. Thus,

Benzylic and allylic better than $3^\circ > 2^\circ > 1^\circ$

→ sp^2 C–H & sp C–H will not effect in the reaction

For ~~Fer~~ Cl_2: 1 : 3.8 : 5 ($1^\circ : 2^\circ : 3^\circ$ reactivity)

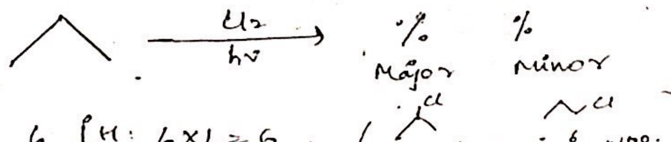
For Br_2: 1 : 82 : 1600

8) How many products are obtained if ethane undergo Photochemical Chlorination? Ans: 9

Sol: C_2H_5Cl – 1 $C_2H_3Cl_3$ – 2 C_2HCl_5 – 1

$C_2H_4Cl_2$ – 2 $C_2H_2Cl_4$ – 2 C_2Cl_6 – 1

9) Photochemical mono chlorination of propane: major, minor

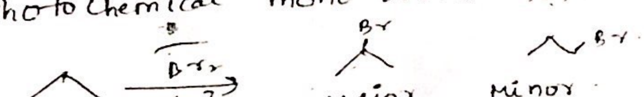


6 1°H: 6×1 = 6 . ($\frac{7.6}{13.6}\times 100$ $\frac{6}{13.6}\times 100$.)

2 2°H – 2×3.8 = 7.6

13.6

5) Photochemical mono bromination

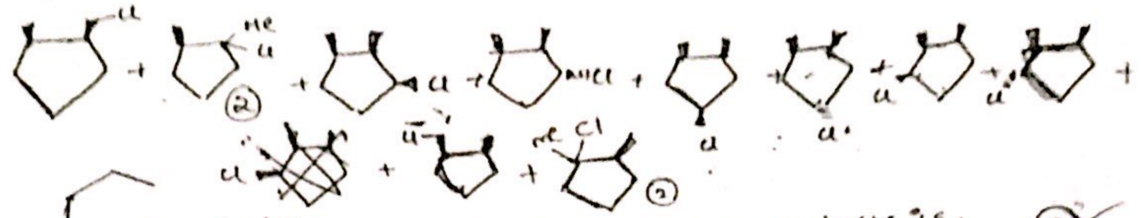


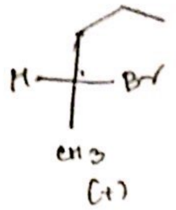
6 1°H : 6×1 = 6 $\frac{164}{170}\times 100$ % $\frac{6}{170}\times 100$%

2 2°H 2×82 = 164

170

Q)  $\xrightarrow[\text{mono}]{Cl_2/h\nu}$ no of products ?

Sol: 

Q)  $\xrightarrow[\text{mono}]{Br_2/h\nu}$ No of chiral dibromo products is. (5)

Q) $CH_4 + Cl_2^{35} \xrightarrow[r_1]{h\nu}$

$CH_4 + Cl_2^{37} \xrightarrow[r_2]{h\nu}$

$\boxed{r_1 \approx r_2}$

Q) ~~CH_4Cl_2~~ $CH_4 + Cl_2 \xrightarrow[r_1]{h\nu}$

$CD_4 + Cl_2 \xrightarrow[r_2]{h\nu}$

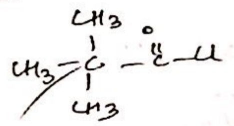
$\boxed{\frac{r_H}{r_D} \simeq 7.2}$

$\boxed{r_1 >> r_2}$ is known as

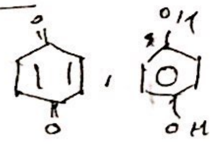
Kinetic isotopic effect.
kinetics are affected by changing isotope in crucial step.

NOTE: Not only Cl_2 sunlight, other reagents are also used for photochemical halogenation.

Eg. SO_2Cl_2, $[Cl-\overset{O}{\underset{O}{S}}-Cl]$ ✓, $SOCl_2$ $[Cl-\overset{O}{S}-Cl]$ ✗, HCl ✗, Cl_2/H_2O ✗



Inhibiters

Eg: O_2, , NO etc.

→ Initially minimise the formation of product.

Eg: $Cl_2 \longrightarrow 2\dot{Cl}$

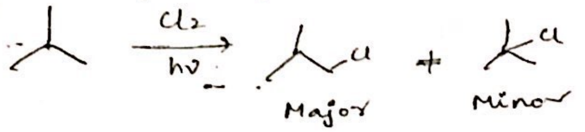
$CH_4 + \dot{Cl} \longrightarrow \dot{C}H_3 + HCl$

$\dot{C}H_3 + O=O \longrightarrow CH_3-O-O^{\cdot}$ (or) $CH_3-O-O-CH_3$

$CH_3-O-O-CH_3 \xrightarrow{h\nu} CH_3O^{\cdot}$

$CH_3O^{\cdot} + CH_4 \longrightarrow \dot{C}H_3$

8)



~~9×1~~ 9 $1 \times 9(1^\circ) = 9$ $\frac{9}{14} \times 100$ $\frac{5}{14} \times 100$

~~5×1~~ $5 \times 1(3^\circ) = \frac{5}{14}$

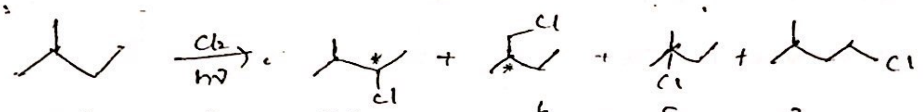
2)

$9 \times 1 = 9$ $\frac{1600}{1609} \times 100\%$ $\frac{9}{1609} \times 100\%$

$1 \times 1600 = 1600$

<u>NOTE</u>. For all alkanes, major product is common either in Photochemical Chlorination / Bromination. (False)

Eg:



$9 \times 1H \rightarrow 9$ $\frac{7.6}{21.6} \times 100$ $\frac{6}{21.6} \times 100$ $\frac{5}{21.6} \times 100$ $\frac{3}{21.6} \times 100$

$2 \times 3.8H \rightarrow 7.6$ $1^\circ > 2^\circ > 3^\circ$.

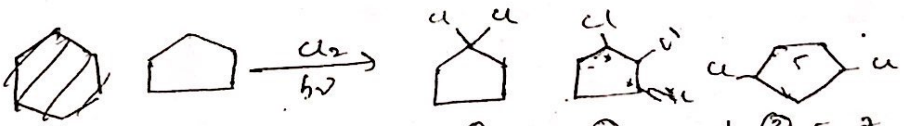
$1 \times 5H \rightarrow 5$ No. of pair of enantiomers: 2

Tot: 21.6. No. of O.A. compounds: 4

Tot. no. of products: 6

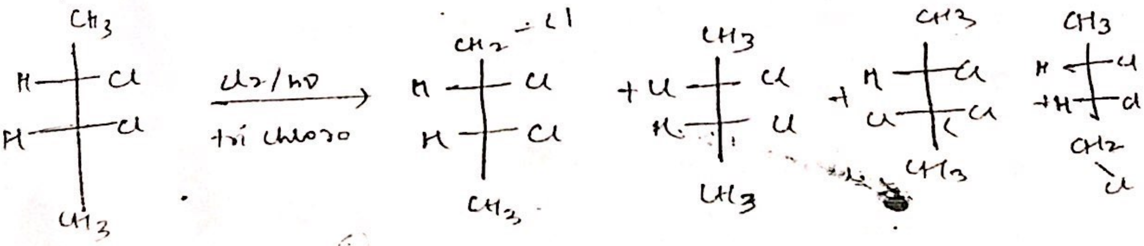
Tot. no. of fractions: 4

Q) How many di chlorinated products are possible



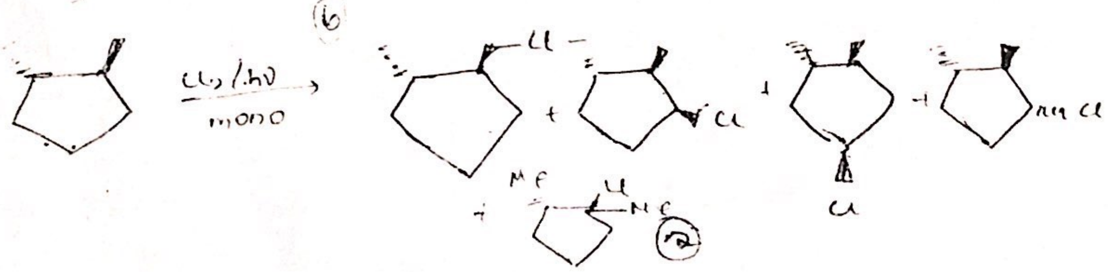
1 + 3 + 3 = 7

8)



(6)

S)



(12)