Hydrocarbons

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I Alkanes

GMP

1. **Catalytic hydrogenation of unsaturated compounds.**
   - Alkene / Alkyne $\xrightarrow[Ni, Pd, Pt]{H_2}$ alkane
   - syn addition
   - Pd, Pt can react at room temp. But Ni requires high temp. 200 – 300°C ⇒ Sabatier Reaction. But by using (Ni – Al/NaOH) Raney Ni. reaction can be completed at room temp.
   - cis alkene + syn addition ⟶ meso compound
     trans alkene + syn addition ⟶ racemic mixture.
   - case of hydrogenation ∝ π e⁻ density ∝ $\frac{1}{\text{steric hindrance}}$
   - when there are 2 π bonds and H_2 (not in excess), then follow above rule to decide which bond gets reduced.

2. **Wurtz Reaction** – $R-X \xrightarrow[\text{dry ether}]{Na} R-R$ (doubling of C)
   - Ionic mechanism (S_N2) reactivity of substrate ∝ 1/steric hindrance
   - FR mechanism
   - methane cannot be prepared from Wurtz rx".
   - ether should be dry (free from moisture) or else the product formed will be an alcohol.
   - to get odd no. of C in product, mixture of alkyl halides must be used. But by using mixture of RX, even product is a mixture, ∴ yield ↓es.

3. **Frankland Reaction** – $RX \xrightarrow[\text{dry ether}]{Zn} R-R$ (doubling)
   - similar mechanism as Wurtz.

4. **Corey House Synthesis** –
   R_2CuLi = Li dialkyl cuprate (Gilman's reagent) (organo-metallic)
   R⁻

   ① $RX \xrightarrow{2Li} R-Li + LiX$

   ② $R-Li + CuX \longrightarrow R_2CuLi + LiX$

   ③ $R_2CuLi + R'X \longrightarrow RR' + RCu$
   $R^{\ominus}$ ↗ S_N2 + LiX

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5. Reduction of RX $RX \xrightarrow{Zn/HCl} R-H$.

mechanism - ① $Zn \rightarrow Zn^{+2} + 2e^-$ ② $R-X \rightarrow R^+ + X^-$

③ $R^+ + 2e^- \rightarrow R^-$ ④ $R^- + HCl \rightarrow RH + Cl^-$

very highly pure CH_4 can be prepared from -

$CH_3I \xrightarrow[\text{ethanol}]{Zn-Cu} CH_4$

H^+

6. Clemmenson Reduction (reactant = aldehyde/ketone)

$>C=O \xrightarrow[\text{Conc. HCl}]{Zn-Hg} >C<_H^H$

7. Wolff Kishner Reduction (reactant = ald./ketone)

$>C=O \xrightarrow[\text{(ii) alc. KOH, } \Delta]{\text{(i) } NH_2NH_2 \text{ - hydrazine}} >C<_H^H$

This is the more preferred method because there is formation of gaseous product (N_2) ∴ leads to more forward reaction.

8. Red P + HI/Δ $R-OH \rightarrow RH$

$R-CHO \rightarrow RCH_3$ $RCOR' \rightarrow RCH_2R'$

$RCOOH \rightarrow RCH_3$.

9. Soda-Lime Decarboxylation (Product has 1C less)

$R-CH_2-COOH \xrightarrow[3:1]{NaOH + CaO, \Delta} RCH_2OH + Na_2CO_3$

$(R-CH_2^{\ominus})$

- CaO absorbs CO_2 and thus facilitates the formation of carbanion.
- Reactivity of carboxylic acid ∝ stability of C^- intermediate.
- β-keto acids undergo decarboxylation only on mild heating.

10. Kolbe's Electrolysis $RCOO^-Na^+/K^+ \xrightarrow{\text{electrolysis}} R-R$ (doubling, even no. C)

At anode - $R-\overset{\overset{O}{\|}}{C}-O^{\ominus} \rightarrow R-\overset{\overset{O}{\|}}{C}-O^{\cdot} \rightarrow R^{\cdot} + CO_2$.

$R^{\cdot} + R^{\cdot} \rightarrow R-R$

At cathode $Na^+ + 1e^- \rightarrow Na$ $Na + H_2O \rightarrow NaOH + H_2\uparrow$

- with time, the soln. becomes alkaline due to by-product NaOH.
- for formation of alkane with odd C, use mixture of salts as reactants.

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* Wurtz Fittig Rx^n - $RX + ArX \xrightarrow[\text{dry ether}]{Na} Ar-R$

* Fittig Reaction - $ArX + ArX \xrightarrow[\text{dry ether.}]{Na} Ar-Ar$

11. Alkanes - $RCH_2X + LiAlH_4 \longrightarrow RCH_3$ (H^- ↙)

12. Ullaman/Coupling Rx^n - $ArX \xrightarrow{Cu/\Delta} Ar-Ar$.

13. $RMgX$ + active H compound $\longrightarrow RH$.

14. From metal carbide - $Al_4C_3 / Be_2C + H_2O \longrightarrow CH_4 + Al(OH)_3/Be(OH)_2$

II Physical Properties

- London forces exist
- as no. of C ↑ ⇒ MP, BP ↑
- BP = $CH_4 < C_2H_6 < C_3H_8 < C_4H_{10} < C_5H_{12}$ .....
- MP = also depends on efficiency of packing
  ∴ even C > odd C.
  ∴ $CH_4 < C_2H_6 > C_3H_7 < C_4H_{10} > C_5H_{12}$ .....
- all alkanes are lighter than H_2O.
- density keep increasing with mass until a certain no. of C.
- not soluble in water.

III Chemical Properties

1. FR Halogenation $RH + X_2 \xrightarrow[\text{E- electricity}]{\text{H- heat/}\Delta} RX + HX$
   L- light, P- peroxide, R- radiation ($h\nu$)

- 3 steps = (i) chain initiation
  (ii) chain propagation
  (iii) chain termination.

(i) $X-X \rightarrow 2X^\circ$

(ii) $RH + X^\circ \rightarrow R^\circ + HX$ (RDS)

(iii) $R^\circ + X-X \rightarrow RX + X^\circ$

(iv) $R^\circ + R^\circ \longrightarrow RR$
$R^\circ + X^\circ \rightarrow RX$
$X^\circ + X^\circ \longrightarrow X_2$.

- reactivity of halogens -
  $F_2 > Cl_2 > Br_2 > I_2$.
- F_2 can react even in the dark.
- practically fluorination is done by halogen exchange reaction (Swart's Rx^n). $RCl/RBr \xrightarrow[HgF/CoF_3]{AgF/} RF$
- ∵ F_2 is highly reactive, generally multi fluorination takes place

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- if Cl_2 is excess ⇒ multichlorination
  if alkane is excess ⇒ monochlorination.
- Br_2 = less reactive ⇒ ∴ monobromination
- I_2 = least reactive $RH + I_2 \rightleftharpoons RI + HI$ (HI: less stable ∴ yield ↓)

To increase yield, OA like HNO_3 / HIO_3 / HIO_4 are used.

- Indirect iodination ⇒ Finkelstein's rxn.

$RCl/RBr \xrightarrow[\text{acetone}]{NaI} RI + NaCl/NaBr \downarrow$ (S_N2)

- calculation of no. of monohalogenated products.

2. **Sulphonation** $RH \xrightarrow[400^\circ C \text{ (prolonged heating)}]{H_2S_2O_7\ (H_2SO_4 + SO_3)} RSO_3H$

- FR mechanism
- reactivity ∝ stability of R·

3. **Chlorosulphonation (Reed Reaction)**

$RH \xrightarrow{(SO_2 + Cl_2)\ h\nu} R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl \xrightarrow[\text{hydrolysis}]{H_2O \text{ or aq. } NaOH} R-SO_3H$

- FR mechanism.

4. **Nitration** $RH \xrightarrow{\text{Conc. } HNO_3,\ 400^\circ C} RNO_2$ (mixture of diff. nitro alkanes formed due to thermal cracking).

- FR mechanism

Eg- $C_3H_8 \longrightarrow C_3H_7NO_2$ (2 isomers)
$C_2H_5NO_2$, CH_3NO_2.

5. **Isomerization** n butane $\xrightarrow[HCl/\Delta\ (200-250^\circ C)]{\text{anhy. } AlCl_3}$ iso-butane

6. **Aromatization / Reforming / Cyclization**

(i) $Cr_2O_3/MoO_3/V_2O_5$ (ii) Al_2O_3 (iii) 773K (iv) 10 - 20 atm.

7. **Pyrolysis / Thermal Cracking** C_4H_{10}

$\xrightarrow{\Delta} CH_3CH_2CH=CH_2 + H_2$
$\xrightarrow{\Delta} CH_3-CH=CH_2 + CH_4$
$\xrightarrow{\Delta} CH_2=CH_2 + C_2H_6$.

(Isooctane = 2,2,4-trimethyl pentane)

8. Combustion $C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$.

- Heat of Combustion (HOC)

HOC $\propto$ no. of C atoms $\propto$ $\frac{1}{\text{branching}}$ $\propto$ $\frac{1}{\text{stability}}$

9. Controlled Oxidation

$CH_4 + O_2 \xrightarrow[100\text{ atm}]{Cu,\ 523K} CH_3OH$

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

$C_2H_6 + O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mg} CH_3COOH$

Alkenes

I GMP

1. Controlled Hydrogenation of Alkynes

$R-C\equiv C-R' \xrightarrow[\text{Pd-BaSO}_4\text{ (quinoline)}]{H_2\ (1\ \text{mol. eq.})}$ (cis-alkene)

Lindlar's catalyst

100% cis alkene

2. Birch reduction

$R-C\equiv C-R' \xrightarrow[\text{in liq. } NH_3]{Li \text{ or } Na}$ (trans-alkene)

(internal alkyne) not terminal.

100% trans alkene

3. Dehydrohalogenation of Alkyl halides - E_1 / E_2.

4. Dehalogenation of vicinal dihalides

$Br-CH_2-CH_2-Br \xrightarrow{Zn/CH_3COOH} CH_2=CH_2$

$\xrightarrow{NaI/\text{acetone}} CH_2=CH_2$ } (E_2) anti

5. Dehalogenation of geminal dihalides

$CH_3-CH(Cl)(Cl) \xrightarrow[-2ZnCl_2]{Zn/300^\circ} CH_3-CH=CH-CH_3$

6. Pyrolysis of Ester (Hoffman rule) [less substituted alkene = major product.

7. Hoffman Elimination of Tetraalkyl ammonium salt

Remove βH, whereever $\oplus$ is more stable $\Rightarrow$ major product.

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8. Dehydration of Alcohols – conc. H_2SO_4 $C^{\oplus}$✓, E_1, say t_2 eff
Al_2O_3 $C^{\oplus}$X, E_2, say t_2 eff
ThO_2 $C^{\oplus}$X, E_2, hoffmann.

9. Kolbe's Electrolysis – (Reactant = Na/K salt of saturated dicarboxylic acid)
(Always 4C parent chain).

II Physical Properties

- MP, BP ↑ with mass
- MP, BP $\propto \frac{1}{\text{branching}}$ (for same no. of C)
- insoluble in water, soluble in non-polar solvents.

III Chemical Properties

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