Alkanes

Method of formation of alkanes

I Hydrogenation of Unsaturated hydrocarbons

Alkenes/alkynes react with hydrogen in the presence of nickel catalyst at 200°c to form alkanes. Hydrogenation under these conditions is called Sabatier Senderens Reaction

$$R-CH=CH_2 + H_2 \xrightarrow[200-300^\circ C]{Ni} R-CH_2-CH_3$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2 \xrightarrow[\Delta]{Ni} CH_3-CH_2-CH_3$$

$$\underset{\text{Acetylene}}{CH\equiv CH} + 2H_2 \xrightarrow[\Delta]{Ni} CH_3-CH_3$$

Other catalysts used for this hydrogenation are Platinum (Pt), Palladium (Pd). Platinum are Palladium are used in finely divided state adsorbed Over charcoal (Pt/C or Pd/C)

II from alkyl halides

a) Wurtz Reaction:-

In this reaction alkyl halide is treated with Sodium in the presence of dry ether to form alkanes

$$2RX + 2Na \xrightarrow{ether} R-R + 2NaX$$

$$2CH_3Br + 2Na \xrightarrow{ether} CH_3-CH_3 + 2NaBr$$

This method is useful only with One alkyl halide to give alkanes containing even number of Carbon atoms. If two diffrent alkyl halides are used, a mixture of three diffrent alkyl halides is obtained by:-

$$CH_3Br + C_2H_5Br + Na \longrightarrow \begin{cases} CH_3-CH_3 + NaBr \\ CH_3-C_2H_5 + NaBr \\ C_2H_5-C_2H_5 + NaBr \end{cases}$$

Mechanism of Wurtz rxn

1) Ionic mechanism

$$C_2H_5Br + 2Na \rightarrow C_2H_5\overset{-}{N}\overset{+}{a} + NaBr$$

$$C_2H_5Na^+ + C_2H_5-Br \longrightarrow C_2H_5-C_2H_5 + NaBr$$

2) Radical mechanism

$$C_2H_5-Br + Na \longrightarrow \dot{C}_2H_5 + NaBr$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_5-C_2H_5$$

Limitations

1) It is useful only for the preparation of alkanes with even number of carbon atom

2) Two diffrent alkyl halides in a wurtz reaction always leads to a mixture of alkanes & the separation of these alkanes is not easy because of little diffrence in their boiling point.

b) Corey-House reaction

Alkanes (containing odd or even number of Carbon atoms) can be prepared by the reaction of lithium dialkyl cuprate (Gilman reagent) with primary alkyl halides.

The lithium dialkyl cuprate can be prepared from 1°, 2° or 3° alkyl halides.

$$CH_3CH_2Br \xrightarrow[-LiBr]{2Li} CH_3CH_2Li \xrightarrow[-LiI]{CuI} (CH_3CH_2)_2CuLi$$

$$\downarrow CH_3CH_2CH_2Br$$

$$CH_3CH_2-CH_2-CH_2-CH_3$$

n-pentane

c) Using Grignard reagent

The grignard reagent prepared from alkyl halides react with compounds containing active hydrogen such as water, alcohol etc to give corresponding hydrocarbons.

$$R-X + Mg \xrightarrow{ether} RMgX$$

$$RMgX + H_2O \longrightarrow R-H + Mg(OH)Br$$

III from carbonylic acids

a) decarbonylation of carbonylic acids :-

When the sodium salt of carbonylic acid is heated with sodalime (NaOH + CaO), a molec of CO_2 is splitt off as carbonate and an alka

Is formed. Notice that the alkane so produced Contains One Carbon less than the Orignal acid.

$$R-COONa + NaOH \xrightarrow{\Delta} R-H + Na_2CO_3$$

b) Kolbe's electrolytic method

In this method a Concentrated Soln of pottasium/Na salt of Carbonylic acid is electrolyzed.

$$2RCOOK + 2H_2O \xrightarrow{electrolysis} R-R + 2CO_2 + H_2 + 2KOH$$

Mechanism

When pottasium salt of Carbonylic acid (eg:- pottasium acetate) is electrolyzed, acetate Ion migrates towards anode, gives up One electron to produce acetoxy radical ($CH_3CO\dot{O}$) which decompses to give a methyl free radical ($\dot{C}H_3$) & CO_2. Two such methyl radical Combine to form ethane

$$CH_3COOK \xrightarrow{electrolysis} CH_3COO^- + K^+$$

Anode:

$$CH_3COO^- \xrightarrow{-e^-} CH_3CO\dot{O} \longrightarrow \dot{C}H_3 + CO_2$$

Cathode:

$$2K^+ \xrightarrow{+2e^-} 2K \xrightarrow{2H_2O} 3KOH + H_2$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

If a mix. of pottassium salts of two diffrent carbonylic acids is electrolyzed, a mixture of alkanes is obtained.

c) Reduction of carbonylic acids

carbonylic acids on heating with hydroiodic acid & red phosphorous gives alkanes.

$$RCOOH + 6HI \xrightarrow[150^\circ C]{P} RH + 3I_2 + 2H_2O$$

IV from alcohols, aldehydes and ketones

Alkanes can be obtained by the reduction of alcohols, aldehydes and ketones with hot concentrated HI in combination with red phosphorous.

$$ROH + 2HI \xrightarrow[150^\circ C]{P} R-H + I_2 + H_2O$$

$$RCHO + 4HI \xrightarrow[150^\circ C]{P} R-CH_3 + 2I_2 + H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-R' + 4HI \xrightarrow[150^\circ C]{P} R-CH_2-R' + 2I_2 + H_2O$$

In above reductions, HI is effective reducing agent. Red phosphorous (P) reacts with HI to form Iodine in the rxn to regenerate HI

$$2P + 3I_2 + 6H_2O \xrightarrow[\Delta]{} 6HI + 2H_3PO_3$$

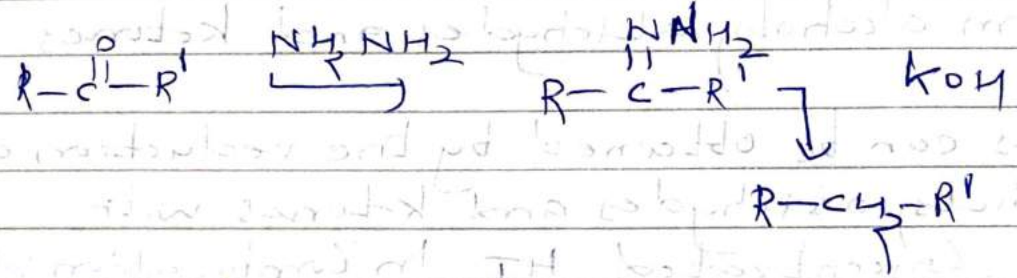
Aldehydes & Ketones can also be ~~used~~ reduced to alkanes by clemmenson reduction or Wolf-kishner reduction.

clemmenson rxn

carbonyl Compounds are treated with Zn amalgam & conc. HCl acid.

$$RCOR' \xrightarrow[\text{conc. HCl}]{\text{Zn amalgam}} RCH_2R'$$

Wolf-kishner reduction



$$R-\overset{O}{\overset{||}{C}}-R' \xrightarrow{NH_2NH_2} R-\overset{NNH_2}{\overset{||}{C}}-R' \xrightarrow{KOH} R-CH_2-R'$$

Physical properties

$C_1-C_4 \rightarrow$ colourless gases (methane to butane)

$C_5-C_{17} \rightarrow$ colourless liquids

$C_{18} \rightarrow$ Waxy solids

→ Being non polar, alkanes are insoluble in water & soluble in non polar solvents like CCl_4.

← [illegible]

→ The b.p of n-alkanes, Increases with molecular Wt. & decreases with branching.

chemical Properties

I Substitution Reactions

a) Halogenation – Alkanes react with halogens In the presence of light or high temperature to form alkyl halides. This reaction is of lower Synthetic Value since a mixture of products are obtained.

$$\underbrace{CH_4}_{\text{Methane}} + Cl_2 \longrightarrow CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \Big\downarrow Cl_2,$$

$$CH_1Cl_3 \Big\downarrow Cl_2$$

$$CCl_4$$

If excess of methane is used, then the formation of di, -tri, tetra chloro products can be avoided.

Similar rxn with bromine gives alkyl bromides

$$CH_4(g) + Br_2(g) \xrightarrow[127°C]{light} CH_3Br + HBr$$

Flourine is very reactive & rxn is Violent.

$$F_2 + CH_4 \longrightarrow CH_3F + HF$$

Order of reactivity

$F_2 > Cl_2 > Br_2 > I_2$

Note:- chlorination is brought about at room temperature but bromination needs higher temperature (127°C). Iodination is not energetically favourable & doesnot occur. However, Iodination can be brought about in presence of Oxidizing agent

Eg. $CH_3-CH_3 + I_2 \xrightarrow{HNO_3} CH_3CH_2I + HI$

($CH_3-CH_3 + I_2 \rightleftharpoons CH_3CH_2I + HI$

$5HI + HNO_3 \rightarrow 3I_2 + 3H_2O$)

Mechanism:-

Halogenation occurs by free radical mechanism.

step1:-

Initiation $Cl-Cl \xrightarrow[h\nu]{light\ uv} :\dot{Cl}: + :\dot{Cl}:$

step2 $\Delta H = +244\ kJ/mol$

Propagation $\dot{Cl} + H-CH_3 \xrightarrow{h\nu}$

$H-Cl + \dot{C}H_3$

$\Delta H = 418\ kJ/m$

[illegible]

$$CH_3^{\bullet} + Cl-Cl \longrightarrow CH_3Cl + Cl^{\bullet}$$

$\Delta H = -108\ kJ/mol$

The methyl free radical combines with active chlorine molecule to form methyl chloride & generates fresh chlorine radical.

Step 3

chain termination

$$2CH_3^{\bullet} \longrightarrow CH_3-CH_3$$

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$$

Orientation In halogenation of alkanes.

eg Propane

$$\overset{1^\circ}{CH_3}-\overset{2^\circ}{CH_2}-\overset{1^\circ}{CH_3}$$

Abstraction of 1° hydrogen $\quad CH_3CH_2\dot{C}H_2 \xrightarrow{Cl_2} CH_3CH_2CH_2Cl$

Abstraction of 2° hydrogen $\quad CH_3-\dot{C}H-CH_3 \xrightarrow{Cl_2} CH_3-\underset{Cl}{CH}-CH_3$

Abstraction of 2° hydrogen is faster as it leads to the formation of more stable 2° radical & hence formation of iso propyl chloride is favourable.

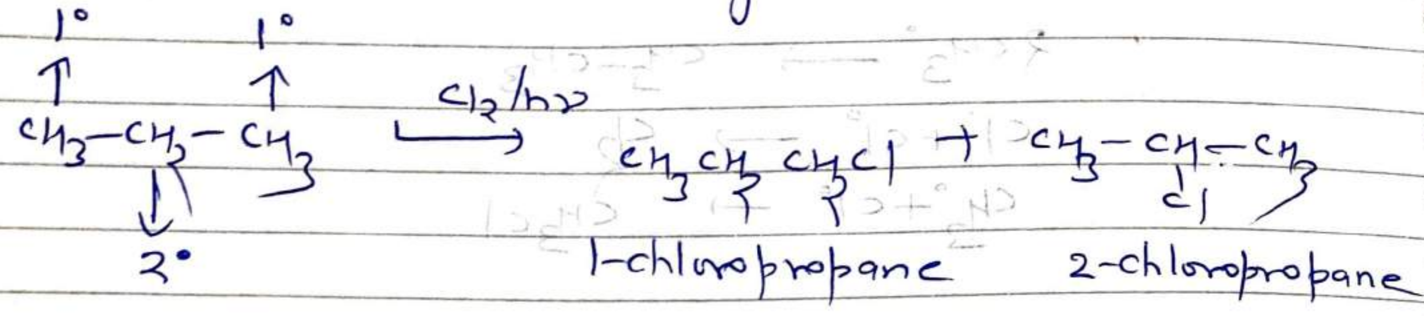
Thus three kinds of hydrogens in alkanes are abstracted in order at room temp.

$$3^\circ > 2^\circ > 1^\circ$$

It is also found that the relative rates of abstraction of 3°, 2° & 1° hydrogen are in ratio of

$5 : 3.9 : 1$

→ Relative amounts of Various Isomeric chlorination can be calculated by these Values.



% of 1-chloropropane

$$= \frac{100\left(\text{no. of } 1^\circ \text{ hydrogen}\right) \times \text{reactivity of } 1^\circ \text{ hydrogen}}{\text{No. of } 1^\circ \text{ hydrogen} \times \text{reactivity of } 1^\circ \text{ hydrogen} + \text{No. of } 2^\circ \text{ hydrogen} \times \text{reactivity of } 2^\circ \text{ hydrogen}}$$

$$= \frac{100(6\times1)}{6\times1+2\times3.9} = 43.5$$

(Experimental 44%)

% of 2-chloropropane

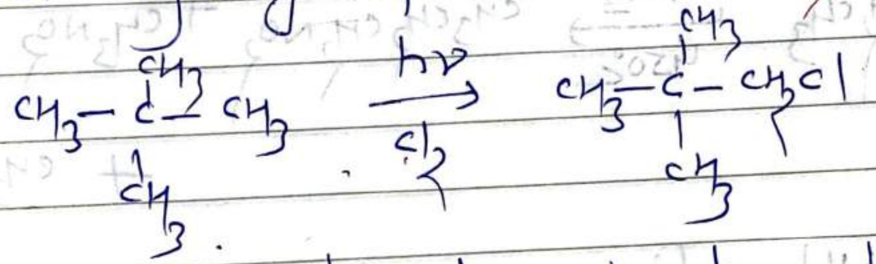
$= 56.5$ (Experimental 56%)

Note:-

Relative rates of abstraction of 3°, 2° and 1° hydrogens (In case of bromination) is
1640 : 82 : 1

Selectivity In halogenation

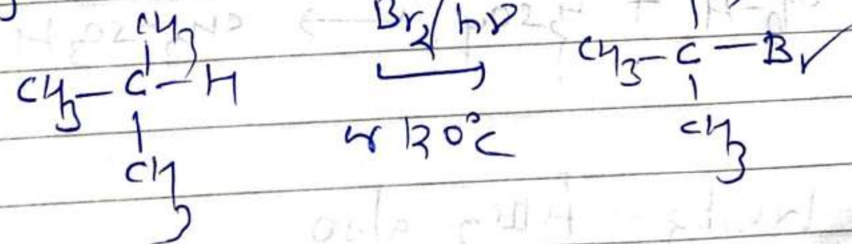
According to reactivity and selectivity principle, the greater is the reactivity of a species, less will be selectivity.
Thus chlorination rxn is not a selective reaction: it is useful only when there is one kind of hydrogen present in the molecule.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \xrightarrow[Cl_2]{h\nu} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Cl$$

As Br_2 is less reactive than Cl_2, thus bromination is more selective.

Eg:- Isobutane on rxn with Br_2 gives tertiary butyl bromide



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H \xrightarrow[\text{or } 130°C]{Br_2/h\nu} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$$

b) Nitration

At ordinary temperature, alkanes donot react with conc. HNO_3. However, nitration is possible at higher temperature.

$$CH_3{-}H + HO{-}NO_2 \xrightarrow{450^\circ C} CH_3NO_2 + H_2O$$

(Vapour phase nitration)

In higher alkanes, nitration is complicated as cracking of alkanes also occurs

$$CH_3CH_2CH_3 \xrightarrow[450^\circ C]{HNO_3} CH_3CH_2CH_2NO_2 + CH_3NO_2 + CH_3CH_2NO_2 + CH_3{-}\overset{NO_2}{\overset{|}{CH}}{-}CH_3$$

c) Sulphonation

Alkanes on heating with fuming H_2SO_4 (oleum) gives alkyl sulphonic acids.

$$CH_3{-}H + H_2SO_4 \longrightarrow CH_3{-}SO_3H$$

Read Wurtz- Fittig also