ALKANES

General Methods of Preparation:

1. Wurtz Reaction:

   * It is reaction of alkyl halides with sodium metal in anhydrous ether\((\text{Et}_2\text{O})\) solvent to form alkane with double the number of carbon atoms.
   * It is coupling between two \(R-(\text{alkyl groups})\) from two \(R-X\) molecules. Hence it is best suitable to prepare symmetrical alkanes with even number of carbon atoms \((R-R)\).
   * Unsymmetrical alkanes can be prepared by taking two different alkyl halides \(RX\) and \(R'X\) (Cross Wurtz Reaction), but there will be three products \(R-R'\) (cross product), \(R-R\) and \(R'-R'\) (self coupling products) in the ratio 2 : 1 : 1 and the separation of the components will be uneconomical. For unsymmetrical alkanes, the best method available now is Corey-House synthesis (to be discussed later).
   * Order of reactivity among alkyl halides: \(1^0 >> 2^0 >>>> 3^0\)
     Tert-halides are not used to prepare alkane by this method, as we shall see in sometime that the major product in that case will be alkene containing same number of carbon atoms, not alkane with double the number of carbon atoms.
   * Methane cannot be prepared by this method.

\[
\begin{align*}
R\text{--}X + 2\text{Na} + X\text{--}R & \xrightarrow{\text{ether(anhy.)}} R\text{--}R + 2\text{NaX} \\
\text{CH}_3\text{--}I + 2\text{Na} + I\text{--CH}_3 & \xrightarrow{\text{ether(anhy.)}} \text{CH}_3\text{--CH}_3 + 2\text{NaI} \\
\text{CH}_3\text{--CH--Br} + 2\text{Na} + \text{Br} & \xrightarrow{\text{Et}_2\text{O}} \text{CH}_3\text{--CH--CH--CH}_3 \\
\end{align*}
\]

Mechanism:

Wurtz coupling is \(S_n2\) reaction and as you know for \(3^0\) halide, E2 elimination completely takes over \(S_n2\). So \(3^0\) halides are not used for Wurtz reaction. In fact \(1^0\) halides are best candidates for Wurtz coupling, as \(2^0\) halides behave closer to \(3^0\) halides in reactions.

\[
\begin{align*}
\text{Step-I:} & \quad R\text{--}X + \text{Na} \rightarrow R + \text{Na}^+\text{Cl}^- \\
\text{Step-II:} & \quad R + \text{Na} \xrightarrow{\text{carbanion}} R + \text{Na} \\
\text{Step-III(S}_n2\text{):} & \quad R + R\text{--}X \rightarrow R\text{--}R + X
\end{align*}
\]
In the first step, alkyl free radical is formed, and in the second step alkyl carbanion is formed. That is why 2 moles of sodium are needed. In the final step, the carbanion acts as a nucleophile to bring about $S_N^2$ reaction with another alkyl halide molecule.

**Side Reaction (Elimination)**

You know that elimination and substitution go hand in hand. For $1^\text{st}$ halide, the elimination is the minor product. Hence some unwanted side products are always formed in Wurtz reaction along with alkane ($R-R$) in small quantities. For $3^\text{rd}$ halide, the elimination is the exclusive product, hence not used. For $2^\text{nd}$ halide, we get both $S_N^2$ and E2 products with appreciable quantities.

When ethyl bromide is subjected to Wurtz coupling, we get butane as the major product ($>90\%$), and also we get a mixture of ethane and ethene as byproducts. The latter mixture is due to the elimination reaction which always go together with substitution reaction.

For $2^\text{nd}$ halide, the elimination products will be quite appreciable and for $3^\text{rd}$ halide, there is only the elimination product. Moreover, the carbanion formation in a $3^\text{rd}$ halide is very less probable as it is the least stable carbanion.

**Precaution:** Why anydrous ether is used? If a trace of water would be there then all the carbanions will be destroyed by accepting protons from $H_2O$. The $S_N^2$ mechanism will not occur to give alkane.

**Wurtz reaction of dihalides:**

3,4,5,6-membered cycloalkanes can be prepared by the reaction of terminal dihalides with Na metal in ether. 1,3-dibromopropane reacts with Na metal in ether to form cyclopropane.

**Cross-Wurtz Reaction:**

If two different alkyl halides are used ($RX$ and $R'X$), then we can get cross-product of $R-R'$ along with homo coupling products $R-R$ and $R'-R'$ in the ration $50:25:25$. Hence it is not a convenient method to prepare $R-R'$.
So for getting propane, if we take mixture of methyl chloride and ethyl chloride, you will get the cross-product, propane(R-R') to the extent of 50% statistically and homo coupling products R-R and R'-R' i.e n-butane and ethane to the extents of 25% each. The separation of these alkanes from each other is really inconvenient and uneconomical. Hence cross Wurtz reaction is not popular to get an unsymmetrical alkane with odd number of carbon atoms.

**Frankland Reaction:**
If Zn metal is used in stead of Na metal, it is called Frankland reaction of preparing alkane. However the yield of alkane in this reaction is poor, though the bye products are minimum.

\[
\text{R-X} + \text{Zn} + \text{X-R} \rightarrow \text{R-R} + \text{ZnX}_2
\]

The preparation of R-R is similar to preparation of alkane from Grignard reagent(to be discussed later).

**2) Corey-House Synthesis:**
* This is the most convenient method of preparing an asymmetrical as well as unsymmetrical alkane in three steps.  
* Two different alkyl halides R–X and R’–X can be used in this method and the cross product R–R’ is obtained in pure condition unlike Wurtz Reaction.  
* It involves three steps.
  
  (a) **Formation of Alkyl Lithium from 1st Alkyl Halide:**
  
  The first alkyl halide reacts with Li metal in presence of ether solvent(anydrous) to form alkyl litium which is an organomatellac compound.

\[
\text{R-X} + 2\text{Li} \rightarrow \text{RLi} + \text{LiX}
\]

The first alkyl hilde(R–X) can be 1°, 2°, 3°.

(b) **Preparation of Gilman Regent (Lithium dilalkyl cuprate)**
Alkyl lithium formed in the first step reacts with cuprous halide to form Lithium dialkyl cuprate, called Gilman reagent.

\[
2\text{RLi} + \text{CuX} \rightarrow \text{R}_2\text{CuLi} \quad \text{lithium dialkyl cuprate(Gilman Reagent)}
\]

(c) Gilman reagent is then treated with the same(R-X) or different alkyl halide(R'-X) to form a pure homo coupling product or a cross-coupling product respectively.

\[
\text{R}_2\text{CuLi} + \text{R'-X} \rightarrow \text{R-R'} + \text{R'Cu} + \text{LiX}
\]

The alkane R–R’ is distilled out leaving behind the organo copper residue(RCu) along with LiX.
* The 2nd halide can be 1° and 2° alkyl, alkenyl(liky allyl, vinyl etc), alkynyl, benzyl, aryl(phenyl), cycloalkyl halides. Only 3° halides cannot be used as 2nd halide, although it can be used as the first halide.

**Example:**
Devise a Corey-House synthetic scheme for the prepaation of 2,2,3-trimethylbutane.

\[
\text{CH}_3\text{CH} = \text{CH} - \text{CH}_3 \quad \text{CH}_3\text{CH} = \text{CH}-\text{CH}_3 \quad \text{CH}_3\text{CH} = \text{CH}-\text{CH}_3
\]

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We have to take tert-butyl halide as first halide and isopropyl halide as second halide, as we cannot take the former as 2nd halide.

\[
\begin{align*}
2 \text{CH}_3\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} & \rightarrow (1) \text{Li/ether} & \rightarrow \text{CuLi} \\
& \rightarrow (2) \text{CuCl} & \rightarrow \text{CuLi} \\
& \text{lithium di-tert-butyl cuprate} & \\
\text{Cu} & + \text{LiCl} & \\
\end{align*}
\]

(We have not shown in three steps and also not balanced the equation)

(2)

In the 2nd example, you find that the stereochemistry of the 2nd halide is retained in the product. Note that although, we get an alkene here(not alkane), but Correy House synthesis is versatile to the extent of coupling an alkyl group with alkenyl group(or with alkynyl, benzyl, cycloalkyl group etc.)

Mechanism:

\[
\begin{align*}
\text{R} & \text{Cu} & + \text{R'} & \text{X} & \rightarrow \text{R}_2\text{CuR'} & \text{(trialky cupper)} \\
\text{Cu} & + \text{LiX} & \\
\end{align*}
\]

Dialkyl cuprate part is anionic(with R–Cu–R covalent bonds). $\text{S}_\text{N}$2 reaction takes place between $\text{R}_2\text{Cu}^-$ with $\text{R'}^-$X to form $\text{R}_2\text{CuR'}^-$ (trialky copper). This intermediate rearranges with a shift of $\text{R'}^-$ from Cu to R to form $\text{R-R'}$ and leaving behind the residue $\text{R-Cu}$. Some authors use fish hook arrow to show one-electron shift with radical transfer. Since there is no other intermediate formed in this reaction to corroborate the process, i chose a two-electron shift mechanism for the process.

(3) Hydrogenation of Alkenes and Alkynes:

* Alkenes react with one mole of $\text{H}_2$ in presence of catalyts like Ni(Raney Ni) at high temperature (200 - 300°C) to form alkanes. Pd (Pd-C), Pt (PtO$_2$) catalysts can be used at lower temperature and at lower pressure of $\text{H}_2$ gas and hence are more efficient. Similarly alkynes react with one mole of $\text{H}_2$ under similar catalytic conditions to give alkene and two moles of $\text{H}_2$ to form alkane.

* It is a case of heterogenous catalysis, in which both alkene/alkyne and $\text{H}_2$ get adsorbed on the surface of the catalyst to form the product.
* The mechanism of addition is SYN, i.e. both the H atoms join on the same side of the multiple bond. **Refer the detailed mechanism in GOC-part-III.**

* It is called Sabatier and Senderen’s reduction.

\[ R-CH=CH-R' + H_2 \xrightarrow{Ni/300^\circ C} R-CH_2-CH_2-R' \]

In the above example, where stereochemistry comes into picture, hydrogenation produces two chiral centres. The SYN addition produces meso-alkane from Z-alkene and rac. (d/l) product from E-alkene.

Alkyne, first gives alkene with SYN addition product and then gives alkane (which has no configurational aspect).

(In ‘alkene’ chapter we shall discuss more how an alkyne undergoes SYN addition to give Cis-alkene under heterogenous catalysis and trans-alkene under homogenous catalysis. This has also been discussed in GOC-III- mechanism).

### (4) Reduction of Alkyl Halides (Haloalkanes):

Alkyl halides (R–X) are reduced by suitable reducing agents (RAs) to form corresponding alkanes.

\[ R-\cdot-X \xrightarrow{RA} R-\cdot-H \]

**List of Reducing Agents:**

- There are many alternative RAs to carry out reduction of alkyl halides. These are
  1. Zn-Cu/Ethanol (Zin-Copper couple in presence of ethanol)
  2. LiAlH₄ (LAH) in ether (suitable for 1° and 2° halides)
  3. NaBH₄ in ether (suitable for 2° and 3° halides)
  4. Na/EtOH
  5. Zn/HCl
  6. Zn/CH₃COOH
7. Zn/NaOH
8. Bu₃SnH(tributyl stannane)/AIBN(benzene)
9. Pd/H₂ OR Pt/H₂ OR Ni/H₂
10. Red P/HI (high pressure/ temp) for RI only

\[ R-I + HI \xrightarrow{\text{red } P} R-H + I_2 \]

* **LiAlH₄ and NaBH₄**:
   LiAlH₄(LAH) produces H⁻ ion at a faster rate (as Al is a metal) and hence is hard nucleophile possessing high basicity. Hence it brings about easy elimination of 3° halides to alkenes. So only 1° and 2° halides can be used with LAH(S₄N₂ reaction: H⁻ substitutes X⁻) not 3° halide. In NaBH₄, the B–H bond is largely covalent (Boron is a metalloid having more nonmetallic character) and the H⁻ ions are generated at a slower rate. Hence it is a soft nucleophile and possesses low basicity and so will not carry out elimination reaction even in a 3° halide. Most importantly it cannot be used for 1° halide because, it cannot have a S₄N₂ attack as it is weak nucleophile in this condition. So only S₄N₁ could have been possible. Since 1° carboation is unstable, that pathway is also not favorable. 2° and 3° react by S₄N₁ pathway.

* Bu₃SnH reduces in presence of a free radical initiator like AIBN in free radical mechanism.

* In all other RAs using metal and acids like HCl, EtOH, CH₃COOH etc. carbanions are formed first via free radicals and then the carbanion abstracts a proton from the acid to form alkane. Similar is the case with Zn/NaOH in which Zn shows amphotericism to produce electrons. In case of P/HI, the mechanism could be similar. I₂ formed is eaten away by P to drive the equilibrium to the right. So small amount of red P is used in the reaction.

**Mechanism for metal/acid reduction:** (eg Zn/Cu - EtOH)

\[
\begin{align*}
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2e^- \\
R-X + e^- & \rightarrow \text{R}^- + X \\
\text{EtOH}^- & \rightarrow \text{EtO}^- + e^-
\end{align*}
\]

**Examples:**

\[
\begin{align*}
\text{CH}_3\text{C}-\text{Cl} + \text{NaBH}_4 & \rightarrow \text{CH}_3\text{C}-\text{H} + \text{BH}_3 + \text{NaCl} \\
\text{CH}_3\text{CCH}_2\text{Br} + \text{LiAlH}_4 & \rightarrow \text{CH}_3\text{CCH}_3 + \text{AlH}_3 + \text{LiBr} \\
\text{CH}_3\text{CCH}_2\text{I} + \text{Zn-Cu/EtOH} & \rightarrow 2\text{[H]} + \text{CH}_3\text{CCH}_2\text{CH}_3 + \text{HI}
\end{align*}
\]
(5) Kolbe’s Electrolytic Method:
* Na'/K' salts of carboxylic acids(RCOOK/RCOONa) on electrolysis produces a mixture of higher alkane(R–R) and CO₂ at anode. Alkane is easily separated from CO₂ by passing the mixture through an alkaline solution in which CO₂ is absorbed.
* It is best suitable for the preparation of ethane by the electrolysis of sodium/potassium acetate(ethanoate).
* Salts of higher carboxylic acids give a mixture of higher alkane alongwith lower alkane and alkene as bye products. A small quantity of ester is formed also as bye product.
* Salts of straight chain c.acids give better yield of alkanes than branched acids.
* The reaction occurs via free radical mechanism.
* DMF solvent favours the reaction.

\[
\begin{align*}
\text{At anode:} \\
2 R\text{C}O_k^+ \rightarrow R-R + 2\text{CO}_2 + 2\text{e} \\
\end{align*}
\]

At anode two moles of alkanoate ion participats such that two R groups join to form one mole of higher alkane R–R and 2 moles of CO₂ at anode alongwith 2 moles of electrons which the anode captures.

At cathode:

\[
2\text{H}_2\text{O} + 2\text{e} \rightarrow \text{H}_2 + 2\text{OH}^\ominus \\
\begin{align*}
2\text{H}^\ominus + 2\text{e} \rightarrow \text{H}_2 
\end{align*}
\]

Hydrogen is evolved at cathode.

Example: (1) Electrolysis of potassium acetate(ethanote) produces ethane at anode.

\[
2\text{CH}_3\text{C}O_k^+ \rightarrow \text{CH}_3\text{CH}_3 + 2\text{CO}_2 + 2\text{e} \\
\text{ethane}
\]

We get almost pure ethane in this as other contaminating hydrocarbos are absent. However a small quantity of methyl acetate(ester) is formed as byeproduct.

(2)

\[
\text{CH}_3\text{C}O_k^+ \xrightarrow{\text{electrolysis}} \text{butane} + (\text{ethane} + \text{ethene} + \text{ethyl propanoate})
\]
**Mechanism:**
To explain the mechanism, we have chosen potassium propanoate.

**Step-I:** Formation of acyloxy free radical at anode:

\[
\text{CH}_3\text{CH}_2\text{C} = \text{O} \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{O}^* + \text{e}^-
\]

(acyloxy free radical) (propanoyloxy)

**Step-II:** Formation of alkyl free radical: (loss of CO₂)

\[
\text{CH}_3\text{CH}_2\text{C} = \text{O} \rightarrow \text{CH}_3\text{CH}_2^* + \text{CO}_2
\]

(ethyl radical)

**Step-III:** Termination of Radicals:
(a) **Mutual combination** of alkyl free radicals to form alkane(R–R)

\[
\text{CH}_3^* + \text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

(butane)

(b) **Disproportionation:**

\[
\text{CH}_3^* + \text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_3 + \text{CH}_2=\text{CH}_2
\]

(etane ethene)

(c) **Combination of alkyl radical with acyloxy radical:**

\[
\text{CH}_3\text{CH}_2\text{C} = \text{O}^* + \text{CH}_3\text{CH}_2^* \rightarrow \text{CH}_3\text{CH}_2\text{C} = \text{O} = \text{CH}_2\text{CH}_3
\]

(ethyl propanoate)

The combination of two bulky acyloxy radicals is highly improbable and hence does not occur.

N.B: Ethanoate(acetate) salts will not involve the disproportionation reaction of methyl radicals. But the first and the third combination steps will produce ethane and methyl acetate respectively.

**SAQ:** What products and bye-products will be obtained by electrolysing potassium butanoate at anode?

Ans: Hexane, propane, propene, propyl butanoate (of course CO₂)

**6) From Grignard Reagents:**

* Alkyl Magnesium Halides(RMgX) are commonly called Grignard regents(GR). These are a special class of organometallic compounds which are used for the synthesis of wide varieties of organic compounds. Organometallics are compounds in which there a C–Metal bond. Alkyl lithium(RLi), Gilman Reagent(R₂CuLi) and Grignard reagents(RMgX) are examples of organometallics.

* GR is prepared easily by refluxing(heating with condenser) a suspension of magnesium in ether with alkyl halide(RX) or aryl chloride(ArCl).
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Interestingly, $R-X$ carries the electrophilic $R-$ part, but when it is converted to GR, $R-$ part becomes nucleophilic. $R-Mg$ bond though covalent is strongly polar and $R$ carries appreciable $\delta-$ charge. Hence the $R-$ end can make a nucleophilic attack onto an electrophile or electrophilic centre. Note that the bond between Mg and halogen(X) ionic.

**Mechanism of formation of GR:**

\[
\begin{align*}
R-X & \quad + \quad \cdot \quad Mg \\
\cdot & \quad + \quad \cdot \quad Mg \quad X \\
R & \quad + \quad Mg \quad X & \quad \rightarrow \quad R-Mg \quad X
\end{align*}
\]

GR is formed by a non-chain radical mechanism. First alkyl free radical is formed along with magnesium radical cation along with halide ion. These combine in the 2nd step to form the $R-Mg$ covalent bond and thus $R-Mg^+X^-$ is formed. The solvent ether effectively solvates the cation part of GR and stabilises it. Note that trace of water or any acidic solvent like alcohol etc. will kill the GR, as we shall discuss below.

* GR reacts with any compound having acidic hydrogen (more acidic than $R-H$) like $H_2O$, ROH, RCOOH, $NH_2$, RNH$_2$, acetylene etc. form alkane($R-H$).

\[
\begin{align*}
R-Mg \quad X & \quad + \quad + \delta \quad - \delta \\
H & \quad + \quad A \\
R & \quad + \quad Mg(A) \quad X
\end{align*}
\]

A stronger acid $HA$ displaces a weaker acid alkane($R-H$) in this case.

**Examples:**

Isopropyl magnesium bromide reacts with water to form propane and basic magnesium bromide.

\[
\begin{align*}
CH_3 & \quad \quad CH_3 \quad Mg(Br) \\
CH & \quad \quad CH_3 \quad OH \\
CH_3 & \quad \quad CH_3 \quad H_2O
\end{align*}
\]

Sec-butyl magnesium chloride reacts with ethyl alcohol to form butane and ethoxymagnesium chloride.

\[
\begin{align*}
CH_3 & \quad \quad CH_3 \quad Mg(Cl) \\
CH_3 & \quad \quad CH_3 \quad OEt \\
CH_3 & \quad \quad CH_3 \quad HOC(CH_3)_2
\end{align*}
\]

Ethyl magnesium bromide reacts with acetylene to form ethane. Here acetylene is more acidic than ethane, hence the above displacement reaction is possible.

\[
\begin{align*}
CH_3 & \quad \quad CH_3 \quad Mg(Cl) \\
CH_3 & \quad \quad CH_3 \quad NH(CH_3)_2
\end{align*}
\]

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Even ethyl amine can give its acidic H atom to make alkane from a GR. Isobutyl magnesium chloride reacts with ethyl amine to form isobutane. NH$_3$ and aliphatic amines are more acidic than R–H.

SAQ: Write the products:
(a) Phenyl magnesium chloride + acetic acid
(b) tert-butyl magnesium bromide + ammonia

(7) Reduction of Carbonyl Compounds:
(a) Clemmensen Reduction:

* Aldehydes and ketones are reduced by Zinc-amalgam(Zn-Hg) and conc. HCl to form their respective alkanes.
* It is suitable for those compounds which are stable under acidic conditions, but unstable in basic conditions. Aryl alkyl ketones, aldehydes/ketones not containing C-C multiple bonds are most suitable substrates for this reactions. A C-C multiple bond is always attacked by acids and hence should not be a part of the structure. The complimentary reaction which reduce a carbonyl compound to alkane in basic medium is “Wolff Kishner Reduction” to be discussed a bit later.

$$
\text{RC} = \text{C} = \text{R'}(\text{H}/\text{Ar}) + 2\text{[H]} \xrightarrow{\text{Zn(Hg)}} \text{HCl} \quad \xrightarrow{\text{alkane}} \text{RC} \text{H}_2 \text{R'}(\text{H}/\text{Ar})
$$

In fact water and zinc chloride are formed are the co-products. Amalgamation of zinc is done to increases its reactivity towards the substrate.

Mechanism:
The mechanism of this reduction is not clearly understood. The most widely acceptable mechanism is ‘Carbenoid Mechanism’. You remember that carbenoids are organometallics which produce carbenes during the course of reaction. Iornically, carbene is not formed in the proposed mechanism. Just see to it casually.

Two Zn atoms react with the carbonyl group so as to fix the compound on the surface of the zinc metal. Then the unpaired electrons take part in the rearrangment involving breaking of C–O and formation of ZnO and carbenoid [Zn=C(R)(R’)]. Then the carbenoid undergoes the following changes.
I think, you understand what happened with carbenoid to produce alkane and ZnCl₂. Interestingly, carbene is not produced in the mechanism, although a carbenoid has been proposed to have been formed.

ZnO reacts with 2HCl to form ZnCl₂ and H₂O.

Examples:

![Reaction diagram for producing ethylbenzene](attachment:reaction_diagram.png)

(b) Wolff Kishner Reduction:

* Carbonyl compound (Aldehyde and ketones) which are not otherwise affected by base are reduced to alkanes by heating (180 - 200°C) the compound in a mixture of hydrazine (H₂N-NH₂) in alkali (NaOH). Simple aldehydes and ketones also are reduced to alkanes by this method like Clemmensen’s method.

![Reaction diagram for Wolff Kishner reduction](attachment:wolff_kishner_diagram.png)

Mechanism:

The carbonyl compound first forms hydrazone by reacting with hydrazine. This is a case of Ad₅ followed by dehydration. The hydrazone is then transferred to a carbanion by losing a molecule of N₂ in multip-step mechanisms. See below.
N.B: The mechanism is self-explanatory.
(Like hydrzones, semicarbazones of aldehydes and ketones also on heating give alkanes).
* In case of $\alpha,\beta$-unsaturated carbonyl compounds, this reduction may lead to migration of C=C.

(8) Decarboxylation of Salt of Carboxylic acids:
* A mixture of Na salt of carboxylic acid (RCOONa) and sodalime [NaOH(CaO)] on heating gives alkane (RH) with Na$_2$CO$_3$ as residue. The alkane contains one carbon atom less than the c.acid salt due to decarboxylation.
* Removal of CO$_2$ from c. acids is called decarboxylation.
* Sodium acetate(ethanolate) on heating with sodalime gives only one hydrocarbon CH$_4$.
However, salts of higher carboxylic acids on decarboxylation gives a mixture of hydrocarbons(alkane alongwith H$_2$ whose separation would be difficult. Hence, this method is best suitable for the preparation of CH$_4$, not for higher alkanes.
* In fact, NaOH does the job. But sodalime is used for the process. Sadalime contains a mixture of NaOH, CaO and Ca(OH)$_2$. It is much less deliquescent that NaOH alone. It means, NaOH would absorb mositure from air and will be soluble in it, however sodalime has much less tendency for it. Thus the solid mixture of the two remains stable and is taken in a hard glass fitted with a delivery tube. On heating alkane(other gaseous products, if any) escape out and residue contains Na$_2$CO$_3$(CaO).

\[
\begin{align*}
R-C-O\text{Na} + NaOH(CaO) \xrightarrow{\text{heat}} & \quad R-H + Na_2CO_3(CaO) \\
CH_3-C-O\text{Na} + NaOH(CaO) \xrightarrow{\text{heat}} & \quad CH_4 + Na_2CO_3(CaO) \\
\text{methyl acetate} & \\
CH_3-CH_2-C-O\text{Na} + NaOH(CaO) \xrightarrow{\text{heat}} & \quad CH_4 + \text{CH}_2=\text{CH}_2 + \text{CH}_4 + H_2 \\
methyl propanoate & \quad \text{(44\%)} \quad \text{(3\%)} \quad \text{(20\%)} \quad \text{(33\%)}
\end{align*}
\]

Sodium propanoate on decarboxylation gives a mixture of ethane, methane, H$_2$ and ethene.

Mechanism:

Decarboxylation occurs via the carbanion intermediate as shown above. The mechnasim for the formation of other hydrocarbon products and H$_2$ from higher acid salts are not shown here.
A good natural source of alkanes is the petroleum oil also called Crude oil, which has the following compositions.

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Average %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>30%</td>
</tr>
<tr>
<td>Naphthenics</td>
<td>49%</td>
</tr>
<tr>
<td>Aromatics</td>
<td>15%</td>
</tr>
<tr>
<td>Asphalatics</td>
<td>6%</td>
</tr>
</tbody>
</table>

(Naphthene is the other name of cycloalkane. Don’t confuse it with naphthalene. Asphalt or Bitumen(two alternative names) is the viscous black coloured semisolid which is the fraction of petroleum obtained at the highest temperature. This is used as PITCH for road construction).

The crude petroleum oil is vapoured and is allowed to travel vertically through a long fractionating column. As the vapour ascends upwards, gets cooled and liquefied (distilled out). The bottom of the column is at highest temperature and temperature gradually decreases upwards and ends at room temperature. The fractions distilled out at different temperature zones are separately collected. Each fraction is a mixture of several hydrocarbons.

Below we present a table to show the different fractions from TOP to BOTTOM.

<table>
<thead>
<tr>
<th>Temperature Range(°C)</th>
<th>Fraction</th>
<th>No. of carbon atoms in hydrocarbon mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 30°</td>
<td>Petroleum Gas</td>
<td>2– 4 (LPG)</td>
</tr>
<tr>
<td>70 – 100</td>
<td>Petrol(Gasoline)</td>
<td>4 – 9</td>
</tr>
<tr>
<td>120 – 160</td>
<td>Naphtha</td>
<td>8 – 12</td>
</tr>
<tr>
<td>170 – 230</td>
<td>Kerosine (paraffin oil)</td>
<td>10 – 14</td>
</tr>
<tr>
<td>260 – 320</td>
<td>Diesel Oil(gas oil)</td>
<td>14 – 25</td>
</tr>
<tr>
<td>&gt;300</td>
<td>Lubricating Oil</td>
<td>20 – 24</td>
</tr>
<tr>
<td></td>
<td>(mineral oil)1</td>
<td></td>
</tr>
<tr>
<td>&gt; 300(vacuum)</td>
<td>Paraffin Wax</td>
<td>21 – 30</td>
</tr>
<tr>
<td>Residue</td>
<td>Bitumen/asphalt(Pitch)</td>
<td>&gt; 35</td>
</tr>
</tbody>
</table>
Organic Chemistry : Alkanes

(N.B: All the fractions possess some common hydrocarbons in the border regions. Note that the temperature ranges and the no. of carbon atoms of different fractions often do not match with each other in many literature, mostly due to quality of crude oil varying from place to place. The picture borrowed from Wikipedia does not completely match with the above table, for the reason already spelt out)

**PHYSICAL PROPERTIES**

1. \( \text{C}_n \text{–C}_4 \) are colourless gases, \( \text{C}_5 \text{–C}_{17} \) are colourless liquids and \( \text{C}_{18} \) onwards waxy solids.
2. Soluble in ethanol and ether but sparingly soluble in water. The solubility decreases with increase in molecular mass. This is because, the solvents cited above, are weakly polar, while the alkanes are non-polar. So increase in size increases the London Dispersion type of forces against dipole-dipole attraction type of forces present in solvent. This mismatch between the types of intermolecular forces reduces the solubility.
3. They are non-polar (whether branched or unbranched). The resultant dipole moment theoretically is zero.
4. **Boiling Points (BP):**
   - Boiling points of alkanes increases with increase in molecular mass among straight chain homologous series almost on a regular basis due to increase in Van der Waals forces.

<table>
<thead>
<tr>
<th>Carbons (Name)</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (methane)</td>
<td>-182.5</td>
<td>-161.6</td>
</tr>
<tr>
<td>2 (ethane)</td>
<td>-181.76</td>
<td>-89</td>
</tr>
<tr>
<td>3 (propane)</td>
<td>-187.7</td>
<td>-42.1</td>
</tr>
<tr>
<td>4 (butane)</td>
<td>-138.4</td>
<td>-0.5</td>
</tr>
<tr>
<td>5 (pentane)</td>
<td>-129.8</td>
<td>36.1</td>
</tr>
<tr>
<td>6 (hexane)</td>
<td>-95</td>
<td>69</td>
</tr>
<tr>
<td>7 (heptane)</td>
<td>-90.61</td>
<td>98.42</td>
</tr>
<tr>
<td>8 (octane)</td>
<td>-57</td>
<td>125.52</td>
</tr>
<tr>
<td>9 (nonane)</td>
<td>-53</td>
<td>151</td>
</tr>
<tr>
<td>10 (decane)</td>
<td>-27.9</td>
<td>174.1</td>
</tr>
<tr>
<td>11 (undecane)</td>
<td>-26</td>
<td>196</td>
</tr>
<tr>
<td>12 (dodecane)</td>
<td>-9.6</td>
<td>216.2</td>
</tr>
<tr>
<td>13 (tridecane)</td>
<td>-5</td>
<td>234</td>
</tr>
<tr>
<td>14 (tetradecane)</td>
<td>5.5</td>
<td>253</td>
</tr>
<tr>
<td>15 (pentadecane)</td>
<td>9.9</td>
<td>269</td>
</tr>
<tr>
<td>16 (hexadecane)</td>
<td>18</td>
<td>287</td>
</tr>
<tr>
<td>17 (heptadecane)</td>
<td>21</td>
<td>302</td>
</tr>
<tr>
<td>18 (octadecane)</td>
<td>29</td>
<td>317</td>
</tr>
<tr>
<td>19 (nonadecane)</td>
<td>33</td>
<td>330</td>
</tr>
<tr>
<td>20 (icosane)</td>
<td>36.7</td>
<td>342.7</td>
</tr>
<tr>
<td>21 (henticosane)</td>
<td>40.5</td>
<td>356.5</td>
</tr>
<tr>
<td>22 (dicosane)</td>
<td>42</td>
<td>369</td>
</tr>
<tr>
<td>23 (tricosane)</td>
<td>49</td>
<td>380</td>
</tr>
<tr>
<td>24 (tetracosane)</td>
<td>52</td>
<td>391.3</td>
</tr>
<tr>
<td>25 (pentacosane)</td>
<td>54</td>
<td>401.9</td>
</tr>
<tr>
<td>26 (hexacosane)</td>
<td>56.4</td>
<td>412.2</td>
</tr>
<tr>
<td>27 (heptacosane)</td>
<td>59.5</td>
<td>422</td>
</tr>
<tr>
<td>28 (octacosane)</td>
<td>64.5</td>
<td>431.6</td>
</tr>
<tr>
<td>29 (nonacosane)</td>
<td>63.7</td>
<td>440.8</td>
</tr>
<tr>
<td>30 (triacontane)</td>
<td>65.8</td>
<td>449.7</td>
</tr>
<tr>
<td>31 (hentriacontane)</td>
<td>67.9</td>
<td>458</td>
</tr>
<tr>
<td>32 (dotriacontane)</td>
<td>69</td>
<td>467</td>
</tr>
</tbody>
</table>
In the graph of bp vs. number of carbon atoms of st. chain alkanes (upper graph), we find a smooth curve.

(b) Among isomeric alkanes, BP decreases with increase in degree of branching due to decrease in V.W forces.

\[
\begin{align*}
& \text{C}_4\text{H}_{10}: \quad \text{n-butane: } \text{bp}= 0^\circ \text{C} \quad \text{isobutane : bp= } -12^\circ \text{C}. \\
& \text{C}_5\text{H}_{12}: \\
& \text{n-pentane: } \text{bp} = 36^\circ \text{C} \quad \text{isopentane: } \text{bp} = 28^\circ \text{C} \quad \text{neopentane: } \text{bp} = 9.5^\circ \text{C}.
\end{align*}
\]

5. Melting Points (MP):

Melting points of straight chain alkanes increase also with increase in number of carbon atoms. However, the increase is very much typical upto 16 carbon atoms. While moving from an even carbon alkane to the next odd carbon alkane, the increase in MP is small while moving from an odd carbon alkane to the next even carbon alkane, the increase in MP is drastic.

Example: butane: mp = \(-138.4^\circ \text{C}\) pentane: mp = \(-129.8^\circ \text{C}\); hexane: mp = \(-95^\circ \text{C}\)

From butane to pentane the increase is about 9\(^\circ\)C, but from pentane to hexane, the increase is more than 30\(^\circ\)C.

This typical variation of MP is also shown in the graph above (burrowed from Wikipedia. Thanks to Wikipedia. Thanks Wikipedia)

Explantion:

In any odd carbon alkane (say propane), the two terminal methyl groups lie on the same side in the most stable zig-zag conformation and hence the close packing is not much favoured in the solid state, for which increase in V.W forces and hence MP is small. But in any even carbon alkane (say butane), the two terminal Me groups lie on the opposite sides which do not pose steric hindrance for close packing of molecules. Since close packing is favoured, the increase in V.W forces and hence MP is large. Note that while the carbon number increases, the V.W forces is bound to increase due increase in mass(size), but whether to a smaller extent or drastically, that is a matter of discussion here.

Exception: Propane has the lowest MP among alkanes (less than methane). This may be due to the very high steric hindrance for close packing as the Me groups are very near to each other on the same side.
CHEMICAL:

1. Substitution Reactions:

(A) HALOGENATION:

* Alkanes can be halogenated (chlorinated and brominated) in presence of light and heat with free radical mechanism, shortly called $S_f$ mechanism. This has been already discussed in the GOC-III (mechanism), involving three steps namely initiation, propagationa and termination. Have a look to that, if not studied before.

\[
R-H + X_2 \xrightarrow{h\nu \text{ or heat}} R-X + HX
\]

Chlorination is faster, hence should be done under diffused sunlight.

\[
R-H + Cl_2 \xrightarrow{h\nu \text{ or heat}} R-Cl + HCl
\]

Bromination is slower, hence both light and heat are required.

\[
R-H + Br_2 \xrightarrow{127^0C} R-Br + HBr
\]

* Fluoration is explosive even under dark. Hence direct fluorination is not done.

* Iodination is extremely slow and reversible, occurring in presence of HIO$_3$, which eats away the product HI formed and drives the equilibrium to right. The mechanism of this reaction is not $S_f$. This reaction is therefore not favourable for preparing alkyl iodides.

\[
R-H + I_2 \xrightarrow{\text{HIO}_3} R-I + HI
\]

HI + HIO$_3$ \xrightarrow{} I$_2$ + H$_2$O

R–I is best prepared from R–Cl or R–Br by reaction with KI, by $S_N^2$ reaction, which we shall discuss later.

* Controlled fluorination can be done by using a mixture of F$_2$ with large excess of inert gas like N$_2$ at a higher temperature of 150 – 350$^\circ$C in presence of CuF$_2$ catalyst. Even then, a mixture of mono, di, tri and polyfluoroalkanes are produced. R–F are best prepared by Swarts reaction (to be discussed in the chapter alkyl halides)

\[
R-Cl + AgF \rightarrow R-F + AgCl
\]

* Reactivity order: F$_2$ >>>> Cl$_2$ >> Br$_2$ >> I$_2$.

* The H atoms can be successively replaced by using larger excess of halogen (particularly Cl$_2$).

\[
\text{CH}_4 \xrightarrow{Cl_2 \text{ h\nu}} \text{CH}_3Cl \xrightarrow{Cl_2 \text{ h\nu}} \text{CH}_2Cl_2 \xrightarrow{Cl_2 \text{ h\nu}} \text{CHCl}_3 \xrightarrow{Cl_2 \text{ h\nu}} \text{CCl}_4
\]

Monochloro, dichloro, trichloro and tetrachloro methanes can be prepared as major products by taking 1, 2, 3 and 4 moles of Cl$_2$ for each mole of methane. Each product will always be associated with three other products in small amounts, as the reactions occur very fast.

(N.B: SO$_2$Cl$_2$ i.e sulfuryl chloride can be used in stead of Cl$_2$ for chlorination of alkanes)
**Monohaloalkanes:**

Methane and ethane give only one monohalo products. Isomeric monohalo alkanes can be prepared from propane onwards.

SAQ: How many isomeric monochloroalkanes the following alkanes give?

(a) propane  (b) butane  (c) isobutane  (d) pentane  (e) neopentane  
(f) isopentane

Answer: 
(a) 2 i.e 1-chloropropane and 2-chloropropane  
(b) 2 i.e 1-chlorobutane and 2-chlorobutane  
(c) 2 i.e isobutyl chloride and tert-butyl chloride  
(d) 3 i.e 1-chloro, 2-chloro and 3-chloropentanes.  
(e) 1 i.e neopentyl chloride  
(f) 4 (shown in the diagram below)

In isopentane(2-methylbutane) there are four non-equivalent H atoms, shown by marks. So there will be four different isomeric monochlorocompounds that will be formed from isopentane. But what will be their relative amounts, which one is major product, all these, we shall know when the following two things are discussed i.e

(i) relative reactivity among various carbon atoms  
(ii) selectivity of halogenation

(A) Reactivity Among Various Carbon Atoms:

$$3^\circ \text{C} > 2^\circ \text{C} > 1^\circ \text{C}$$

Since the mechanism is free radical based, and stability of alkyl free radical follows the above order, hence the reactivity follows the above order. A $3^\circ$ carbon atom is most reactive for halogenation, followed by $2^\circ$ carbon atom and the least reactive is $1^\circ$ carbon atom.
SELECTIVITY IN HALOGENATION(\(\text{Cl}_2/\text{Br}_2\)):

More is the reactivity, less is the selectivity. Chlorination is fast, hence it distinguishes between 3\(^{\circ}\), 2\(^{\circ}\) and 1\(^{\circ}\) carbon atom less efficiently than bromination which is slow. Look to the ratio of reactivity.

**Chlorination**: (reactivity ratio at room temperature)

\[
3^{\circ} : 2^{\circ} : 1^{\circ} = 5.0 : 3.8 : 1.0
\]

(per H atom)

**Bromination**: (reactivity ratio at 127\(^\circ\)C)

\[
3^{\circ} : 2^{\circ} : 1^{\circ} = 1600 : 82 : 1
\]

(per H atom)

N.B: The ratio has been determined from the actual yields of the isomeric halides and the probability factor(number of equivalent H atoms), these two taken together. This is explained by the relative differences between activation energy\((E_A)\) of alkyl radical formation for 3\(^{\circ}\), 2\(^{\circ}\) 1\(^{\circ}\) carbona toms for chlorination and bromination separately in the first propagation step(graph shown GOC-III –mechanism). For chlorination, the differences are small and hence the figures are small(5:3.8:1). In bromination, the differences are largers and hence the figures are larger(1600:82:1)

You saw, that selectivity of chlorination is poor as the difference between the three types of carbon atoms is small(5 : 3.8 : 1). You imagine, if you meet three of your friends successivley at a faster speed, you spend less time with each of them, to see a big difference between them. Bromination is higly selective (1600 : 82 : 1), as it takes place slowly. If you walk down slowly to three of your friends, you get enough time to interact with each of them, hence can distinguish more efficiently. Hence a big difference between their reactivities. To put it in a lighter note: if you do any work very fast, then your efficiency is less and vice versa.

* Since chlorination is less selective, it gives all monochloro products from a given alkane with appreciable amounts, with none having an absolute preponderance.
* Since bromination is highly selective, the major product obtained by the substitution at the most reactive carbon atoms with exclusive abundance. The minor product is present in negligible proportions.
* Free radical inhibitors like phenol, quiniol, \(\text{O}_2\) etc. scavange(eat away) the alkyl radicals by combining with them and slow down the reaction and in large doses, completely stops the reaction.

Calculation of Relative Abundance of Monochloro and monobromo alkanes:

1. **Chlorination of Propane**:

   ![Diagram of Chlorination of Propane]

   \[
   \begin{align*}
   \text{H}_3\text{C} & \text{C} \text{CH}_2\text{Cl} & \text{H}_2 & \text{H}_3\text{C} \text{C} \text{CH}_3 \\
   \text{n-propyl chloride} & \text{major product} & \text{(45\%)} & \text{(55\%)}
   \end{align*}
   \]

   \[
   \begin{align*}
   \text{H}_3\text{C} & \text{C} \text{CH}_3 \\
   \text{isoproyl chloride} & \text{minor product}
   \end{align*}
   \]
In propane, there 6 primary($1^0$) equivalent H atoms and 2 secondary($2^0$) equivalent H atoms. So these statistical factors have been multiplied with the respective figures per H atom basis given before. We reiterate here that the ratio, given before are on the basis of one H atom. If there are ‘n’ number of H atoms of a particular type, the probability of its substitution by a halogen atom will be ‘n’ times greater. So we found that although 2-chloropropane(isopropyl chloride) is the major product, the % is only 55.88%, while the minor product 1-chloropropane(n-propyl chloride) is quite appreciable(44.12%).

2. Bromination of Propane

\[ \frac{2^0 \text{ bromide}}{1^0 \text{ bromide}} = \frac{2 \times 82}{6 \times 1} = \frac{164}{6} = 27.33\% \]

For monobromo products, the calculation on the respective reactive ratio, yields $2^0$-product i.e isopropyl bromide with 96.5% and n-propyl bromide only 3.5%. All these calculations closely match with the experimental results. Hence you found that bromination is much more selective than chlorination.

(3) Monochlorination of isobutane(2-methylpropane):

\[ \frac{3^0 \text{ chloride}}{1^0 \text{ chloride}} = \frac{1 \times 5}{9 \times 1} = \frac{5}{9} = 35.7\% \]

Dr. S. S. Tripathy
Surprising results you find here because of the probability factor. There are 9 equivalent primary H atoms as against only one tertiary H atom. Hence the winner is primary carbon atom. Isobutyl chloride is the major product(64.3%) and tert-butyl chloride is the minor product(35.7%). This seems to contradict the reactivity order: $3^0 > 2^0 > 1^0$ carbon atoms, but in reality it is not. The reactivity ratio given was on the basis of one H atom. When the probaility factors are included in the calculation, the lead was for $1^0$ product.

N.B: You are to remember that, this is the only example where a $1^0$ product is the major, pushing the $3^0$-product behind it. Also note that there is no free radical rearrangement like carbocations, which is evidenced from the above results that isobutyl chloride from a $1^0$ radical becomes the major product.

(4) Monobromination of isobutane(2-methylpropane):

\[
\begin{align*}
\text{H}_3\text{C} - \text{CH} - \text{CH}_2\text{Br} & \quad \text{isobutyl bromide} \\
\text{H}_3\text{C} - \text{CH} - \text{CH}_3 & \quad \text{(trace)} \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 & \quad \text{tert-butyl bromide} \\
\text{H}_3\text{C} - \text{C} - \text{CH}_3 & \quad (>99\%) \\
\end{align*}
\]

\[
\begin{align*}
\frac{3^0 \text{ bromide}}{1^0 \text{ bromide}} &= \frac{1 \times 1600}{9 \times 1} = \frac{1600}{9} = 99.5\% \\
&= 0.5\%
\end{align*}
\]

Here, the 1600 factor makes one tert- H atom the hero, as against 9 primary H atoms with total of 9 factor. Hence, bromination, tert-butyl bromide($3^0$ product) is formed in exclusive abundance. The $1^0$-product(isobutyl bromide) is almost absent.

**Effect of temperature on Selectivity:**

Since chlorination is fast, it is done at room temperature conditions(subjected to diffused sunlight). The ratio per H atom that we had used before( 5 : 3.8 : 1) has been obtained at 25°C. As the temperature increases, the ratio levels up i.e the reagent becomes less selective. This is because, you shall learn from the chapter ‘chemical kinetics’ that greater the activation energy($E_a$) of a reaction, greater is the increase in rate for a given rise in temperature. Hence at very high temeprature, the ratio 5: 3.8 : 1 will become 1 : 1 : 1. However, chlorination occurs at room temeperature with farely fast rate.

Bromination is slow at room temperature even in presence of light, the reaction does not take place at room temperature. Appreciable rate with high selectivity has been found at an optimum temperature of 127°C at which the reactivity ratio is 1600 : 82 : 1. If temperature increases, the rate, no doubt will rise, but the selectivity will decrease due to the same reason explained before for chlorination.

SAQ: (1) Write expected % of all isomeric monochloro and monobromo substitution products from (a) pentane (b) 2-methylbutane
Solution:
(a) Monochloroproducts:
1-chloropentane : 2-chloropentane : 3-chloropentane = 6 × 1 : 4 × 3.8 : 2 × 3.8
= 20.8% : 52.7% : 26.5%

Monobromoproducts:
1-bromopentane : 2-bromopentane : 3-bromopentane = 6 × 1 : 4 × 82 : 2 × 82
= 1.3% : 65.8% : 32.9%

So in bromination, you find that the 1\textsuperscript{st} product is negligible. Since there are two non-equivalent 2\textsuperscript{nd} bromides, hence a distribution between them. Together the 2\textsuperscript{nd} bromides constitute 98.7%.
(b) Try yourself.

(B) NITRATION:
* Alkanes are mononitrated by heating alkane and vapours of HNO\textsubscript{3} in vapour phase between 150 - 475°C to form nitroalkanes. Lower alkanes upto pentane are nitrated at higher temperature(350 - 400°C), while higher alkanes at lower temperature of 160 - 180°C. Substitution of –H atom by –NO\textsubscript{2}(nitro) group is called nitration.

\[ R\text{-}H + \text{HNO}_3 \xrightarrow{400°C} R\text{-}NO_2 + \text{H}_2\text{O} \]

(nitroalkane)

* All isomeric products are formed including chain scission products(lower nitroalkanes). Hence the nitration reaction lacks the integrity of halogenatio reactions..
* Reactivity order: 3\textsuperscript{rd} > 2\textsuperscript{nd} > 1\textsuperscript{st}

\[ \text{CH}_3\text{-CH}_2\text{-CH}_3 \xrightarrow{400°C} \text{CH}_3\text{-CH}_2\text{-CH}_2 + \text{CH}_3\text{-CH}_3 + \text{CH}_3\text{-CH}_2\text{-CH}_3 + \text{CH}_2\text{-CH}_2\text{-CH}_3 \]

(25%) (40%) (10%) (25%)

Methane gives only one product i.e nitromethane. However higher alkane gives a mixture of products. Propane on nitration gives a mixture of 1-nitropropane and 2-nitropropanes(major product), nitroethane and nitromethane.
* Mechanism is believed to be Free Radical substitution similar to halogenation, though it is not fully understood. HNO\textsubscript{3} on thermal decomposition produces nitronium free radicals. It is a non-chain reaction(unlike halogenation) and can be like the following.

\[ \text{HNO}_3 \xrightarrow{400°C} \text{NO}_2 + \text{OH} \]

\[ \text{R}\text{-}H + \text{OH} \xrightarrow{} \text{R} + \text{H}_2\text{O} \]

\[ \text{R} + \text{NO}_2 \xrightarrow{} \text{R}\text{-}NO_2 \]

* NO\textsubscript{2} - N\textsubscript{2}O\textsubscript{4} mixture can be used to nitrate lower alkanes like propane with Cl\textsubscript{2} as catalyst at relatively lower temperature(180 - 320°C). Presence of Cl\textsubscript{2} facilitates the formation of alkyl radicals.
Nitration of propane, butane, isobutane, pentane, isopentane and cyclohexane can be done easily by this method.

(C) SULFONATION:
* Substitution of –H of alkane by –SO$_3$H group is called sulfonation.
* Alkanes from hexane onwards react with fuming sulfuric acid(oleum) to form alkane sulfonic acid (R–SO$_3$H). No C–C scission products are formed in this case like nitration. Lower members do not undergo sulfonation easily.
* Reactivity order : $3^0 >> 2^0 > 1^0$

The mechanism suggested also is $S_f$ similar to nitration.

2. OXIDATION:
* (1) Alkanes containing $3^0$ H atom are oxidised to $3^0$-alcohols by KMnO$_4$/OH$^-$. 

<table>
<thead>
<tr>
<th>Isobutane</th>
<th>tert-butyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$C–CH–CH$_3$</td>
<td>H$_3$C–C–CH$_3$</td>
</tr>
</tbody>
</table>

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<tbody>
<tr>
<td>H$_3$C–CH–CH$_3$</td>
<td>H$_3$C–C–CH$_3$</td>
</tr>
</tbody>
</table>

2-methylpropane-2-sulfonic acid

2-methylpropane-2-sulfonic acid
Since 3° C–H bond is weak (homolytic BDE is minimum), this oxidation is possible only with alkanes containing such H atoms. Oxidation does not occur at 1° and 2° C–H positions.

(2) Alkanes are oxidised to carboxylic acids by heating with oxygen in presence of Mn(OAc)₂.

\[
R-\text{CH}_3 \xrightarrow{\Delta \text{Mn(OAc)}_2} R-\text{COOH}
\]

\[
2\text{CH}_3\text{CH}_3 + 3\text{O}_2 \xrightarrow{\text{heat} \text{Mn(OAc)}_2} 2\text{CH}_3\text{COOH} + 2\text{H}_2\text{O}
\]

Alkanes can also be converted to carbonyl compounds by specific catalysts. Methane is oxidised to methanal by air in presence of molybdenum(III) oxide catalyst.

\[
\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Mo}_2\text{O}_3} \text{HCHO} + \text{H}_2\text{O}
\]

(3) Methane is converted to methanol by catalytic oxidation process.

\[
2\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Cu} \ 200^\circ\text{C} / 100\text{atm}} 2\ \text{CH}_3\text{OH}
\]

3. Combustion:

Alkanes (in fact all hydrocarbons or organic compounds) burn in presence of air/ \text{O}_2 to produce a lot of heat energy along with combustion products depending on conditions.

(a) Complete Combustion: With sufficient air or oxygen, \text{CO}_2 and \text{H}_2\text{O} are formed. Fuels like LPG, CNG etc contain alkanes, the former contain mostly liquified butane along with propane, ethane and methane while the latter contain predominantly methane. Petrol(Gasoline) primarily is a mixture of alkanes in the range C_4 – C_9. Similarly diesel, kerosine also contain different alkanes and other hydrocarbons. We shall learn more about this in “Petroleum Refining” and “Cracking of hydrocarbons”

(b) Incomplete Combustion: With limited supply of air/oxygen, \text{CO}, aldehydes like HCHO, alcohols like \text{CH}_3\text{OH} etc are obtained. With very less amount of air/\text{O}_2, carbon black(lamp black/soot) is formed.

4. CRACKING:

* Thermal decomposition of an organic compound by the action of heat in the absence of air/\text{O}_2 is generally called PYROLYSIS. Destructive distillation of any carbonaceous matter is also a pyrolytic process.

* Pyrolysis of alkanes is called CRACKING. Cracking brings about the conversion of a higher(long chain) alkane to mixture of lower alkanes, alkenes and hydrogen gas. A higher fraction of crude oil, which is less valuable(useful) on cracking is converted to more useful and valuable product containing shorter chains and branched chain alkanes and alkenes.

Example: (1) Fraction naphtha or kerosine is being cracked to more useful petrol

(2) Cracking produces more alkene product from saturated alkanes and these alkenes(ethene, propene etc.) are useful as important monomers to form plastics(polyethene, polypropylene etc.)

(3) Cracking is also a source of \text{H}_2.

Types of Cracking:

(a) Thermal Cracking
(b) Catalytic Cracking
(c) Steam Cracking
(d) Hydro Cracking
Thermal Cracking: Heating the alkane or fraction of crude oil at a high temperature of 500 – 600°C at high pressure of the vapour (70 atm.) is called Thermal cracking. C–C and C–H bond scission (cleavage) occurs at all possible positions to give a mixture of simpler (lighter) alkanes, alkenes and H₂.

Cracking of butane: Butane on cracking gives a mixture of methane, propene, ethane, ethene, but-1-ene (also but-2-ene) and H₂.

\[
\begin{align*}
\text{H}_3\text{C} & \rightleftharpoons \text{CH}_2 \rightleftharpoons \text{CH}_3 \\
& \xrightarrow{500-600^\circ\text{C}} \text{CH}_4 & + \text{H}_2 \text{C} \rightleftharpoons \text{CH} \rightleftharpoons \text{CH}_3 \\
\text{butane} & & \text{methane} & \text{propene} \\
\end{align*}
\]

Cracking of pentane: Similar to butane, pentane on cracking will give the following mixture: (methane + but-1-ene), (ethane + propene), (propane + ethene) and (pentenes + H₂).

Mechanism of Cracking:

Mechanism of thermal cracking is free radical. Let me show the simplest case of cracking of ethane.

Initiation: Homolytic cleavage of C–C bond takes place first to form two methyl free radicals.

\[
\begin{align*}
\text{CH}_3 & \rightleftharpoons \text{CH}_3 \\
& \rightarrow \cdot\text{CH}_3 & + \cdot\text{CH}_3 \\
\end{align*}
\]

Propagation:

\[
\begin{align*}
\cdot\text{CH}_3 & + \text{CH}_2 \rightleftharpoons \text{CH}_3 \\
& \rightarrow \text{CH}_4 & + \cdot\text{CH}_3 \rightleftharpoons \text{CH}_2 \\
\cdot\text{CH}_2 \rightleftharpoons \text{CH}_2 & \rightarrow \text{CH}_2 \rightleftharpoons \text{CH}_2 & + \cdot\text{H} \\
\cdot\text{H} & + \text{CH}_2 \rightleftharpoons \text{CH}_3 & \rightarrow \text{H}_2 & + \cdot\text{CH}_3 \rightleftharpoons \text{CH}_2 \\
\end{align*}
\]

You know that in propagation, each step has two products, one is a stable molecule and the other an unstable free radical.

Termination:

\[
\begin{align*}
\cdot\text{H} & + \cdot\text{H} \rightarrow \text{H}_2 \\
\cdot\text{CH}_3 \rightleftharpoons \text{CH}_2 & + \cdot\text{CH}_3 \rightarrow \text{CH}_3 \rightleftharpoons \text{CH}_2 \rightleftharpoons \text{CH}_3 \\
\end{align*}
\]
In each termination step, two radicals combine or disproportionate to form only stable product molecules. You find that cracking of ethane produces so many products out of which methane, ethene and H₂ are the major ones, others are minor byproducts.

Steam cracking is a part of thermal cracking where steam is used with the hydrocarbon undergoing cracking. This produces more alkenes in the product mixture. A mixture of ethylene, ethane, propylene, propane, butane and other components is formed by steam cracking of naphtha fraction of crude oil. Steam is used in the w/w 0.6kg steam per kg of naphtha feedstock to prevent the formation of coke at the cracking zone and make the process more efficient.

Naphtha + (steam) \[\xrightarrow{800-900^\circ C}\] C₂H₆ + CH₂=CH₂ + CH₄ + BTX + H₂ etc

(BTX = benzene, toluene and three xylenes, along with it some ethyl benzene, heavy oil (fuel oil) are also formed. A very small amount of acetylene is also formed. These chemicals are separated from each other by selective liquefaction and fractional distillation, the details of which will not be discussed here.

Catalytic Cracking: Cracking done in presence of catalysts like alumina-silica or zeolites which bring about the cracking process at lower pressure conditions with more efficiency.

The mechanisms in catalytic cracking is ionic. The catalyst abstracts a hydride ion from the alkane forming a carbocation. We are avoiding here to present a detailed mechanism for it.

Types:
(a) Fluidised Catalytic Cracking (FCC):
Naphtha fraction of crude oil is treated with silica-alumina catalyst or now zeolite catalyst used as powder (called Fluidised bed) at 600⁰C to convert into more useful petrol.
(b) Hydrocracking: In addition to catalyst, when H₂ gas is used, it called hydrocracking. Heavy oil is hydrocracked to more useful jet fuel, diesel and gasoline by this method. A molecule of tetradecane is cracked to two molecules of heptane in presence of H₂ and catalyst.

5. ISOMERIZATION:
* Straight chain alkanes on heating in presence of Lewis acids like anhydrous AlCl₃ at high pressure isomerise to a mixture of branched chain isomers. Isomerisation can also take place in presence of Pt catalyst.
Isomerisation of n-octane gives predominantly isooctane.
Similarly pentane on isomerisation gives a mixture of isopentane and neopentane.
N:B: Practically, this isomerisation is carried in presence HCl(gas) alongwith AlCl₃ at a high pressure of the gaseous alkane.

Mechanism:
(1) In presence of a Lewis acid, AlCl₃ alone, we can suggest simple mechanism involving carbocation.

This appears little unacceptable as, it is too difficult for the AlCl₃ to abstract a hydride ion, although the conversion of a more stable 20 carbocation to less stable 10 carbocation has to be acceptable at higher temperature conditions, which makes the free energy change negative.

(2) In presence of HCl(g) alongwith AlCl₃:

In reality, alkane always contains trace of alkene as impurity. For example, commercial n-butane always contains a trace quantity of but-1-ene and but-2-ene. Initiation step gives rise to the formation of carbocation in more easy way due to their presence. This is accompanied by a chain of propagations steps followed by termination step.
Initiation:

\[ \text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3 + \text{HCl} (\text{g}) \xrightarrow{\text{AlCl}_3} \text{CH}_3-\text{CH}==\text{CH}-\text{CH}_3 + [\text{AlCl}_4^-] \]

\[ \text{CH}_3-\text{CH}-\text{CH}_2 \xrightarrow{\text{Me}^+ \text{ shift}} \text{CH}_3-\text{CH}==\text{CH}_2 \]

Propagation:

\[ \text{CH}_3-\text{CH}-\text{CH}_2 + \text{CH}_3-\text{CH}==\text{CH}_2-\text{CH}_3 \rightarrow \text{CH}_3-\text{CH}==\text{CH}_2+ \text{CH}_3-\text{CH}==\text{CH}_2-\text{CH}_3 \]

\[ \text{CH}_3-\text{CH}-\text{CH}_2 \xrightarrow{\text{Me}^+ \text{ shift}} \text{CH}_3-\text{CH}==\text{CH}_2 \]

Termination:

\[ \text{CH}_3-\text{CH}==\text{CH}_2 + [\text{AlCl}_3]^- \rightarrow \text{CH}_3-\text{CH}-\text{CH}_2\text{Cl} + \text{AlCl}_3 \]

So in presence of HCl, a trace amount of alkyl chloride must be formed as byproduct.

6. Aromatization:

* Hexane and heptane undergo dehydrocyclisation to form benzene and toluene respectively. When hexane OR heptane is treated with Cr\text{O}_3/Al\text{O}_3 mixed catalyst at 600°C and about 15 atm pressure (of alkane vapour) this reaction takes place. This is called aromatization of alkanes.

\[ \text{CH}_2=\text{CH}==\text{CH}_2+ \xrightarrow{\text{Al}_{2}\text{O}_3/\text{Cr}_2\text{O}_3 \text{ 600°C/ 15 atm}} \text{benzene} + 4\text{H}_2 \]

\[ \text{CH}_2=\text{CH}==\text{CH}_2+ \xrightarrow{\text{Al}_{2}\text{O}_3/\text{Cr}_2\text{O}_3 \text{ 600°C/ 15 atm}} \text{toluene} + 4\text{H}_2 \]

* Modified Pt can be used as catalyst for this reaction. Nowadays zeolites(ZSM-5) is used as catalyst for aromatization.

* n-octane on aromatisation gives a mixture of xylenes and ethyl benzene. In presence of other catalyst like Ni-Al\text{O}_3, a mixture of toluene and methane is formed by the decomposition of ethyl benzene. Still higher alkanes can also be aromatized, but there will be many decomposition byproducts.

Dr. S. S. Tripathy
ORGANIC CHEMISTRY: Alkanes

REFORMING:
Reforming means aromatisation of hydrocarbons, particularly used in petroleum fractions.

OCTANE NUMBER OF GASOLINE:
* Gasoline (petrol) consists primarily of a mixture of pentane, hexane, heptane and octane (and their isomers).
* Petrol engine has the demerit of producing explosive combustion called KNOCKING, which is damaging to the engine. Hence anti-knocking additives are added to gasoline to reduce the knocking effect.
* To grade gasolines in terms of its knocking effect, the term “Octane Number” is used.
* Isooctane produces the minimum knocking effect and has been arbitrarily assigned the Octane Number = 100.
* n-heptane produces the maximum knocking effect and has been assigned the octane number = 0
* The commercial gasoline has Octane Number between 0 – 100.

Definition: It is the percentage of isooctane present in a mixture of isooctane and n-heptane which produce the same knocking effect as the commercial gasoline under study.
* For example, you have sample of petrol from some petrol pump which produces the same knocking effect of a petrol-engine as a synthetic mixture of 80% isooctane and 20% n-heptane, then the Octane Number of the commercial petrol under study is 80.

Anti-knock Additives:
Previously Ethyl Fluid [A mixture of TEL(tetraethyl lead i.e Et Pb and 1,2-dibromoethane and 1,2-dichloroethane] was used as anti-knock additive in gasoline(called leaded petrol). But due lead pollution in air it caused, the leaded petrol is almost banned in most countries. The unleaded petrol contain aromatic compounds like benzene, toluene as ant-knock compounds to reduce knocking. Tert-butyl alcohol, methyl tert-butyl ether are also used as anti-knock additives.

Isomerisation and aromatization(reforming) during the formation of gasoline by a cracking process increase % of isooctane and hence Octane Number.

CETANE NUMBER OF DIESEL:
* The quality of diesel oil is measured by one of the parameters called CETANE NUMBER. It is similar to Octane number. Here knocking is not a factor. The combustion speed of diesel oil and the compression needed for ignition are important parameters in a diesel engine. There is always an ignition delay for the engine. Less this delay, more efficient is the fuel. Hence greater the Cetane Number, less is the ignition delay and hence more efficient is the diesel.

Definition:
It is percentage of n-hexadecane(cetane) present in a mixture of n-hexadecane and α-methyl naphthalene which give the same ignition delay as the diesel fuel under study.
Cetane Number of cetane = 100; and that of α-methylnaphthalene = 0

More about Methane:
* Natural Gas: The most important natural source of methane is Natural Gas which is obtained during mining of crude oil. The upper gaseous part in an oil well is this gas. This gas contains 70% methane, 10% ethane and 15% propane and rest other hydrocarbons. It was previously used as house hold fuel. But now compressed natural gas(CNG) is mostly used as fuel in automobiles.
* It is called Marsh gas, as it is found in marshy lands, in sewage sludge by the fermentation of organic matter by bacteria.
* It can be prepared from coal gas or synthesis gas by the following

\[ \text{CO} + 3 \text{H}_2 \xrightarrow{\text{Ni}, 300^\circ\text{C}} \text{CH}_4 + \text{H}_2\text{O} \]

(Note that the opposite reaction is possible at 1000°C.

* Methane can also be prepared by heating methanide type of carbides (Al\(_4\)C\(_3\), Be\(_2\)C) in water.

**CYCLOALKANES**

**General Methods of Preparation:**

1. **Intramolecular Wurtz reaction of terminal dihalides:**
   1,3-dichloropropane on treatment with sodium metal in the presence of anhydrous ether produces cyclopropane.

\[
\begin{align*}
\text{Cl} & \quad \text{CH} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{Cl} \\
& \xrightarrow{\text{ether}} \\
\text{1,3-dichloropropane} & \xrightarrow{2\text{Na}} \\
& \xrightarrow{\text{ether}} \text{cyclopropane}
\end{align*}
\]

(Zn can be used in place of Na)

1,5-dichloropentane gives cyclopentane. Similarly 1,4-dihalobutane and 1,6-dihalohexane gives cyclobutane and cyclohexane respectively. Higher cycloalkanes cannot be prepared by this method, as terminal dihaloheptanes and higher members undergo intermolecular Wurtz reaction to give higher terminal dihalides.

2. **From Ca salt of dicarboxylic acids:**
   Calcium adipate on dry distillation gives cyclopentanone, which subjected to Clemmensen reduction gives cycloalkane. In the chapter “Aldehydes and Ketones” you shall study how calcium salt of carboxylic acids on dry distillation gives ketones.
3. Cyclopropane from alkenes:
Alkenes undergo addition of CH₂ group by reacting with CH₂N₂ in presence of UV light or with CH₂I₂/Zn-Cu (IZn–CH₂I : a carbenoid) to form cyclopropane derivatives, via carbene intermediates. We shall discuss this in details in the chapter “Alkenes”.

\[ \text{CH}_2\text{=CH}_2 + \text{CH}_2\text{N}_2 \xrightarrow{\text{hv}} \text{CH}_3\text{CH}_2\text{CH}_2\text{NH} \]

\[ \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{CHCl}_3 \xrightarrow{\text{Et}, \text{t-BuOK}} \text{ClCl} \]

4. Hydrogenation of Aromatic Compounds:
Benzene or other aromatic compounds on hydrogenation give cyclohexanes.

\[ \text{benzene} + 3\text{H}_2 \xrightarrow{\text{Ni/300°C}} \text{cyclohexane} \]

5. Diels Alder Reaction:
A conjugated diene and an alkene or alkyne (dienophile) add up in presence of heat to form cyclohexene which on catalytic hydrogenation gives cycloalkane. The details of Diels Alder reaction will be taken up in the chapter ‘alkenes’.

(N.B: Other methods like Dieckmann condensation etc. we shall know gradually. Let us not hurry).

**Properties:**
* From Baeyer’s strain theory we know that cyclopropane has the highest angle strain and cyclohexane has NO angle strain. Then angle strain slightly increases in cycloheptane (same as cyclopentane) and then decreases with increase in ring size and finally vanishes in cyclododecane. The heat of combustion per CH₂ group is highest for cyclopropane and lowest for cyclohexane and cyclododecane onwards, which is due to relative strains present in the molecules.
* Cyclopropane and cyclobutane are gases, next three members are liquids and higher members are solids.
* The boiling point are also higher than their corresponding alkenes and alkanes.

**Addition Reactions:**
Cyclopropane, due to its highest angle strain is unstable and undergo addition reaction easily like alkenes.
Cyclobutane is less reactive to addition reactions. However, under restricted conditions does undergo addition reactions.

\[
\begin{align*}
\text{Cyclopropane} & \quad \xrightarrow{Br_2} \quad \text{BrH}_2\text{CCH}_2\text{CH}_2\text{Br} \\
& \quad \xrightarrow{HBr} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \\
& \quad \xrightarrow{(i) \text{H}_2\text{SO}_4} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
& \quad \xrightarrow{(ii) \text{H}_2\text{O}} \quad \text{CH}_3\text{CH}_2\text{CH}_3 \\
& \quad \xrightarrow{800 \text{GC}} \quad \text{(propane)}
\end{align*}
\]

* **Substitution Reaction:**
Cycloalkanes can be halogenated (chlorinated) in presence of sunlight like alkanes by free radical mechanism.

\[
\text{Cyclohexane} \quad \xrightarrow{\text{Cl}_2, \text{hv}} \quad \text{chlorocyclohexane (cyclohexyl chloride)} + \text{HCl}
\]

* **Oxidation:**
Cycloalkanes are oxidised by strong OAs like conc. HNO\textsubscript{3} or alkaline KMnO\textsubscript{4} to form open chain dicarboxylic acids by ring opening.

\[
\text{Cyclohexane} \quad \xrightarrow{\text{conc. HNO}_3} \quad \text{HOOC-(CH}_2)_4\text{COOH (adipic acid)}
\]

(Later we shall know that cyclohexanol and cyclohexanone also will produce the same adipic acid on oxidation)
E-CONCEPT IN CHEMISTRY

For Class XI (+2 1st Year Science)

Chemistry
of
Alkanes

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