PITHAPUR RAJAH'S GOVERNMENT COLLEGE

AN OUTCOME BASED AUTONOMOUS INSTITUTION
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AFFILIATED TO ADIKAVI NANNAYA UNIVERSITY, RAJAMAHENDRAVARAM
KAKINADA- 533 001

DEPARTMENT OF CHEMISTRY

Inspiring Tomorrow College Chemists

CLASS NOTES

II B.SC (Hons) CHEMISTRY

MAJOR/MINOR C-5- FUNDAMENTALS IN ORGANIC CHEMISTRY

UNIT-2

CLASS: SEMESTER-III B. Sc. (HONS) CHEMISTRY,
AQUA CULTURE,BIOTECHNOLOGY AND MICROBIOLOGY

NAME OF THE FACULTY: V.SANJEEVA KUMAR

COURSE 4: FUNDAMENTALS IN ORGANIC CHEMISTRY

UNIT-I STRUCTURAL THEORY IN ORGANIC CHEMISTRY (9 Hrs.)

Types of bond fission and organic reagents (Electrophilic, Nucleophilic, and free radical reagents).

Reaction intermediates – Carbocations, carbanions & free radicals. Bond polarization: Factors influencing the polarization of covalent bonds, inductive effect – Application of inductive effect (a)Basicity of amines (b) Acidity of carboxylic acids (c) Stability of carbonium ions. Resonance or Mesomeric effect, application to (a) acidity of phenol, and (b) acidity of carboxylic acids. Hyperconjugation and its application to stability of carbonium ions, Free radicals, and alkenes

Electrophiles and Nucleophiles: Detailed Notes

📘 1. Definitions

Electrophile (Electron-loving species):

- **Definition:** A species that seeks electrons and accepts an electron pair.
- **Nature:** Electron-deficient (positive charge or partial positive).
- **Function: Accepts** electron pairs during a chemical reaction.
- **Acts as: Lewis acid** (electron pair acceptor).

Nucleophile (Nucleus-loving species):

- **Definition:** A species that donates an electron pair to an electrophile.
- **Nature:** Electron-rich (negative charge or lone pairs).
- **Function: Donates** electron pairs during a chemical reaction.
- **Acts as: Lewis base** (electron pair donor).

Category	**Electrophiles**	**Nucleophiles**
Neutral	SO_3, BF_3, $AlCl_3$, CO_2	H_2O, NH_3, ROH (alcohols), RSH
Cations	H^+, NO_2^+, Br^+, Cl^+, CH_3^+	OH^-, CN^-, Cl^-, Br^-, I^-, RO^-

🧬 3. Mechanistic Roles in Organic Chemistry

🔹 ***Electrophiles* participate in:**

- **Electrophilic Addition Reactions**
    - Example: Alkene + HBr → Bromoalkene
- **Electrophilic Substitution Reactions**
    - Example: Benzene + Br_2 (with $FeBr_3$) → Bromobenzene

🔹 ***Nucleophiles* participate in:**

- **Nucleophilic Substitution Reactions**
    - SN1 and SN2 mechanisms
    - Example: $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$
- **Nucleophilic Addition Reactions**
    - Example: Aldehyde + CN^- → Cyanohydrin

⚛️ 4. Characteristics of Good Electrophiles and Nucleophiles

✅ **Electrophiles:**

- Positive or partially positive atoms ($\delta+$).
- Incomplete octet (e.g., carbocations, BF_3).
- Easily attacked by electron-rich species.

✅ **Nucleophiles:**

- Lone pair or π electrons.
- Negative charge often makes them stronger.
- Ability to form new bonds with electrophilic carbon.

📉 5. Factors Affecting Strength

🧲 ***Nucleophile Strength Depends on:***

1. **Charge:** Anions > neutral molecules.
2. **Electronegativity:** Less electronegative atoms donate electrons more easily.
3. **Solvent:**
    - **Polar protic solvent**: Weakens nucleophiles (hydrogen bonding).
    - **Polar aprotic solvent**: Enhances nucleophilicity.
4. **Steric hindrance:** Bulky nucleophiles are less reactive.

🔥 *Electrophile Strength Depends on:*

1. **Charge:** More positive = stronger electrophile.
2. **Leaving group:** Good leaving groups make carbon more electrophilic.
3. **Electron-withdrawing groups:** Increase electrophilicity by reducing electron density.

🧠 Conceptual Summary

Feature	**Electrophile**	**Nucleophile**
Electron status	Deficient	Rich
Type of species	Lewis acid	Lewis base
Action	Accepts electrons	Donates electrons
Charge	Often +ve or partial +ve	Often –ve or lone pair
Examples	H^+, NO_2^+, BF_3, carbocation	OH^-, NH_3, CN^-, alkene

UNIT-II SATURATED HYDROCARBONS (ALKANES AND CYCLOALKANES) (9 Hrs.)

General methods of preparation of alkanes- Wurtz and Wurtz Fittig reaction, Corey House synthesis, physical and chemical properties of alkanes, Conformational analysis of alkanes (Conformations, relative stability and energy diagrams of Ethane, Propane, and butane). General molecular formulae of cycloalkanes and relative stability, Baeyer strain theory, Cyclohexane conformations with energy diagram, Conformations of monosubstituted cyclohexane

Wurtz Reaction:

The **Wurtz reaction** is a type of organic reaction in which two alkyl halides undergo coupling in the presence of sodium metal to form a new alkane. The reaction is commonly used to synthesize symmetrical alkanes.

Mechanism of the Wurtz Reaction:

1. **Formation of Radicals or Carbanions:**
    - Sodium metal donates electrons to the halogen in the alkyl halide, resulting in the halide ion leaving.
    - This produces a reactive alkyl radical or carbanion.

$$R–X + Na \rightarrow R\cdot + NaX$$

2. **Coupling of the Radicals or Carbanions:**
    - The alkyl radicals or carbanions generated from two molecules of alkyl halides will combine to form a new alkane.
    - The coupling forms a C–C bond.

$$R\cdot + R\cdot \rightarrow R–R$$

3. **Formation of the Product:**
    - The resulting product is a **symmetrical alkane** (R–R).

Example:

If **ethyl bromide (C_2H_5Br)** is used as the alkyl halide:

$$2\ C_2H_5Br + Na \rightarrow C_4H_{10} + NaBr_2$$

The product is **butane** (C_4H_{10}).

Wurtz–Fittig Reaction:

The **Wurtz–Fittig reaction** is a variation of the Wurtz reaction that involves the coupling of **alkyl halides** with **aryl halides** in the presence of sodium metal, leading to the formation of **alkylated aromatic compounds**.

Mechanism of the Wurtz–Fittig Reaction:

1. **Formation of Radicals or Carbanions:**
    - Sodium metal donates electrons to the halide (either alkyl halide or aryl halide), resulting in the formation of alkyl or aryl radicals or carbanions.

$Ar–X + Na \rightarrow Ar\cdot + NaX$

$R–X + Na \rightarrow R\cdot + NaX\backslash$

Coupling of the Radicals or Carbanions:

- The generated alkyl and aryl radicals/carbanions will couple to form a new C–C bond.
- This results in the formation of an **alkylated aromatic compound**.

$Ar\cdot + R\cdot \rightarrow Ar–R$

Formation of the Product:

- The product is an **alkylated aryl compound** (Ar–R), typically involving a simple alkyl group attached to an aromatic ring.

Example:

If **bromobenzene (C_6H_5Br)** and **ethyl bromide (C_2H_5Br)** are used:

$C_6H_5Br + C_2H_5Br + 2Na \rightarrow C_6H_5C_2H_5 + NaBr$

The product is **ethylbenzene** ($C_6H_5C_2H_5$).

Key Differences Between Wurtz and Wurtz-Fittig Reactions:

- **Wurtz Reaction**: Involves only **alkyl halides**, leading to the formation of symmetrical alkanes.
- **Wurtz–Fittig Reaction**: Involves **alkyl halides** and **aryl halides**, leading to the formation of **alkylated aromatic compounds**.

The mechanisms of both the **Wurtz reaction** and the **Wurtz–Fittig reaction** have been supported by various experimental observations and evidence, including reaction products, intermediates, and the nature of the reagents. Here's the evidence supporting the mechanisms of these reactions:

Evidence for Wurtz Reaction Mechanism:

1. **Formation of Free Radicals or Carbanions**:
   - **Radical formation** is supported by the use of **iodine** or **hydrogen peroxide**. These substances can inhibit the reaction, suggesting the involvement of free radicals.
   - **Intermediates**: The observation that the reaction works in the presence of **sodium metal** suggests that the metal is involved in electron donation, which facilitates the formation of alkyl radicals or carbanions. This has been observed in **electron paramagnetic resonance (EPR) spectroscopy** studies, which detect unpaired electrons typical of radicals.
2. **Reaction Conditions and Sodium's Role**:
   - The use of **sodium metal** as a reducing agent is essential for breaking the C–X bond of the alkyl halide. This is a well-established feature in many radical reactions, where **sodium** transfers an electron to the halide, producing a halide ion and an alkyl radical.

Evidence for Wurtz–Fittig Reaction Mechanism:

1. **Formation of Aryl and Alkyl Radicals**:
   - The mechanism involves the coupling of **alkyl** and **aryl radicals**. This has been supported by **EPR spectroscopy**, which has shown the formation of **alkyl** and **aryl radicals** when sodium metal reacts with alkyl or aryl halides.
   - The presence of these radicals is confirmed by reaction conditions (e.g., the reaction with sodium metal) and product analysis.
2. **Substituent Effects**:
   - The type of substituent on the aromatic ring (in the case of the Wurtz–Fittig reaction) affects the reaction. **Electron-withdrawing groups** (like nitro) on the aromatic ring typically **slow down** the reaction, whereas **electron-donating groups** (like methyl or methoxy) **facilitate** it. This is consistent with the idea that **radical formation** is crucial to the mechanism.
3. **Reaction with Mixed Halides**:
   - In the Wurtz–Fittig reaction, reactions between **different alkyl halides** (e.g., **ethyl bromide** and **methyl iodide**) and **aryl halides** lead to **mixed alkyl-aryl products**. This is further evidence that the reaction proceeds via **radical intermediates**, as the radicals can combine in different ways

Supporting Experiments:

- **Electron Paramagnetic Resonance (EPR) Spectroscopy**: EPR studies of reactions involving alkyl halides and sodium show **radical intermediates**, supporting the idea that the Wurtz and Wurtz–Fittig reactions proceed through radical or carbanion intermediates.
- **Control Reactions**: In some experiments, adding **radical inhibitors** (like **quinones**) or **oxygen** has been shown to suppress the reactions, which further supports the radical nature of the mechanism.

These various lines of experimental evidence, from **radical detection** to **product analysis**, strongly support the **Wurtz and Wurtz–Fittig reaction mechanisms** as outlined above.

Corey-House Synthesis for Alkanes

The **Corey-House synthesis**, developed by the American chemist **Robert E. Corey** in 1965, is a method used for the preparation of **alkanes** from **alkyl halides**. This reaction is particularly important because it allows the formation of a wide variety of alkanes using **organocuprates** (also known as **Gilman reagents**) in the presence of a **mild base**.

Overview:

The Corey-House synthesis involves the **coupling of two alkyl groups** via an **organocuprate** reagent (typically a **lithium dialkyl cuprate** or **Gilman reagent**), leading to the formation of **symmetrical or unsymmetrical alkanes**.

General Reaction:

$$R_2CuLi + R\text{-}X \rightarrow R\text{-}R + CuX + Li$$

Where:

- **R_2CuLi** = Organocuprate (Gilman reagent),
- **R-X** = Alkyl halide,
- **R-R** = Alkane product,
- **CuX** = Copper(I) halide,
- **Li** = Lithium ion.

Mechanism of the Corey-House Synthesis:

1. **Formation of Organocuprate**:
    - The first step involves the preparation of a **lithium dialkyl cuprate** (organocuprate) by reacting an **alkyl lithium reagent (R-Li)** with **copper(I) halide (CuX)**.
    - This reaction results in the formation of a **Gilman reagent** (R_2CuLi).

$$2R\text{-}Li + CuX \rightarrow R_2CuLi + LiX_2$$

Nucleophilic Substitution:

  - The **organocuprate (R_2CuLi)** is a **nucleophile** and will attack an **alkyl halide (R-X)** in an **S_N2 mechanism** (nucleophilic substitution), where the **organocuprate** displaces the halide ion (**X**) from the alkyl halide.
  - This results in the formation of a **new C–C bond** between the two **R groups**.

$$R_2CuLi + R\text{-}X \rightarrow R\text{-}R + CuX + Li$$

2. **Formation of the Alkane**:
    - The product is an **alkane (R-R)**, where the two alkyl groups have coupled to form a new carbon-carbon bond.
    - The by products include the **copper(I) halide** (**CuX**) and **lithium ion (Li)**.

Discussion of the Corey-House Synthesis:

1. **Advantages**:
    - **Selective Coupling**: The Corey-House synthesis is highly selective and allows the coupling of **different alkyl groups** to form **unsymmetrical alkanes**. This is a key advantage over older methods like the **Wurtz reaction**, which typically forms **symmetrical alkanes**.
    - **Milder Conditions**: The use of **organocuprates** allows for reactions to proceed under **milder conditions** than the Wurtz reaction, avoiding issues like side reactions or the formation of unwanted byproducts.
    - **Versatility**: The Corey-House reaction can be used with a variety of **alkyl halides** (both primary and secondary), making it versatile for synthesizing different alkanes.
2. **Limitations**:
    - **Steric Effects**: The reaction is less efficient when large groups are involved due to steric hindrance. Large alkyl groups on the cuprate can hinder the nucleophilic attack, reducing the reaction's efficiency.
    - **Reactivity of Alkyl Halides**: The Corey-House synthesis works best with **primary alkyl halides**. **Tertiary alkyl halides** are often less reactive due to their higher steric hindrance, and **vinyl** and **aryl halides** generally do not participate in the reaction.
    - **Formation of Byproducts**: Although the reaction is more selective than the Wurtz reaction, the formation of side products, such as **CuX** and **LiX**, still requires careful purification.
3. **Comparison to the Wurtz Reaction**:
    - **Symmetry of Products**: Unlike the **Wurtz reaction**, which typically forms **symmetrical alkanes**, the Corey-House reaction can form both **symmetrical and unsymmetrical alkanes**, depending on the combination of the alkyl halides used.

    - **Milder Conditions**: The Corey-House reaction is less prone to unwanted side reactions and is more efficient, especially when dealing with **secondary alkyl halides**, than the Wurtz reaction.
4. **Synthesis of Unsymmetrical Alkanes**:
    - By using **two different alkyl halides** (R-X and R'-X), the Corey-House synthesis can generate **unsymmetrical alkanes**. This is a significant advantage, as it allows for greater diversity in the types of alkanes that can be synthesized.
5. **Reactivity of Organocuprates**:
    - Organocuprates, such as **lithium dialkyl cuprates (R_2CuLi)**, are less reactive than organolithium reagents (R-Li), making them more selective and reducing the risk of undesired reactions. This reduced reactivity allows the Corey-House synthesis to work efficiently with a wider range of substrates.

Example of Corey-House Synthesis:

Let's consider the reaction between **ethyl iodide (C_2H_5I)** and **methyl iodide (CH_3I)**:

1. **Preparation of Organocuprate**:
   $2CH_3Li + CuI \rightarrow (CH_3)_2CuLi + LiI$
2. **Coupling with Alkyl Halide**:
   $(CH_3)_2CuLi + C_2H_5I \rightarrow C_7H_{16} + CuI + Li$

   The product is **heptane (C_7H_{16})**, formed by the coupling of methyl and ethyl groups.

Conclusion:

The **Corey-House synthesis** is a powerful method for the preparation of alkanes, especially unsymmetrical alkanes, from alkyl halides using **organocuprates**. It is more selective and milder than traditional methods like the **Wurtz reaction**, allowing for the formation of a diverse range of alkanes under controlled conditions. Its utility in forming both symmetrical and unsymmetrical alkanes makes it a key tool in organic synthesis.

Physical and Chemical Properties of Alkanes

Alkanes are **saturated hydrocarbons** that consist only of carbon (C) and hydrogen (H) atoms, with single bonds between the carbon atoms. They follow the general molecular formula CnH2n+2C_nH_{2n+2} for straight-chain alkanes. Alkanes are widely used as fuels and solvents due to their abundance and non-polar nature.

1. Physical Properties of Alkanes:

1. **State and Molecular Size**:
    - **Lower alkanes (C1 to C4)** such as **methane (CH_4)**, **ethane (C_2H_6)**, **propane (C_3H_8)**, and **butane (C_4H_{10})** are **gases** at room temperature.
    - **Medium-sized alkanes (C5 to C17)**, such as **pentane (C_5H_{12})** and **heptane (C_7H_{16})**, are typically **liquids**.
    - **Larger alkanes (C18 and above)** are usually **solids** or **waxes** at room temperature.
2. **Boiling and Melting Points**:
    - Alkanes have relatively **low boiling and melting points**, but these increase with the size of the molecule (i.e., as the number of carbon atoms increases).
    - **Boiling points**: Generally, alkanes with longer carbon chains have **higher boiling points** due to **greater van der Waals forces** (induced dipole-induced dipole interactions) between molecules.
    - **Melting points**: Similar to boiling points, the melting points of alkanes increase with the molecular size. However, branching in alkanes tends to lower the melting point compared to their straight-chain counterparts
    - .
3. **Density**:
    - Alkanes are typically **less dense than water** (less than 1 g/cm³) and hence **float on water**.
    - The density increases with the molecular size but remains lower than that of water for most alkanes.
4. **Solubility**:
    - Alkanes are **insoluble in water** due to their **non-polar nature**.
    - However, they are **soluble in organic solvents** like ether, benzene, and chloroform because they are **also non-polar** and can form **van der Waals interactions** with similar non-polar molecules.
5. **Refractive Index**:
    - The refractive index increases with the size of the alkane molecules. Larger alkanes generally have a higher refractive index.
6. **Odour**:
    - **Lower alkanes** (e.g., methane, ethane, propane, and butane) are **odorless** in their pure form.
    - Larger alkanes, especially **gasoline** (a mixture of C5 to C12 hydrocarbons), can have a characteristic **petrol-like odor**.
7. **Flammability**:
    - Alkanes, especially **lower molecular weight alkanes**, are highly **flammable**.
    - They burn with a **blue, non-sooty flame**, making them efficient fuels.

2. Chemical Properties of Alkanes:

Alkanes are relatively **inert chemically** due to the strong C–H and C–C single bonds, which make them resistant to reactions. However, they do undergo certain types of reactions under specific conditions.

1. **Combustion**:
   - Alkanes undergo **complete combustion** in the presence of excess oxygen to form **carbon dioxide (CO_2)** and **water (H_2O)**.
     $CH_4+2O_2 \rightarrow CO_2+2H_2O$
2. **Halogenation (Substitution Reaction)**:
   - Alkanes can react with **halogens** (like chlorine or bromine) under **light (UV radiation)** or **heat** to undergo **free radical halogenation**. In this reaction, one or more hydrogen atoms are replaced by a halogen atom.
     - **Chlorination of methane**:
       $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$
       The reaction proceeds via a **free radical mechanism**.

     Halogenation is commonly used to **make chlorinated compounds** (e.g., **chloroform, $CHCl_3$**.

3. **Reaction with Oxygen**:
   - **Partial oxidation** of alkanes leads to the formation of **alcohols**, **aldehydes**, and **ketones**. This reaction generally requires the presence of a **catalyst** orhigh temperatures

     $CH_4+O_2 \rightarrow CH_3OH$

   - This is used in processes like the **synthesis of methanol**.
4. **Nitration** :
   - Alkanes reacts with Nitric acid in vapour state to form Nitro Alkanes

     $CH_3\text{-}CH_3 + HNO_3 \xrightarrow{400^{o}C} CH_3CH_2NO_2$

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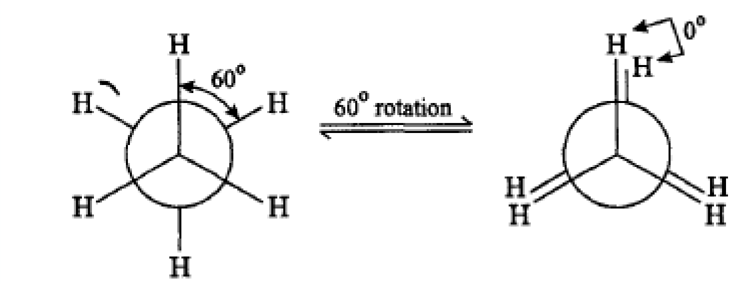
CONFORMATIONAL ANALYSIS OF ALKANES ;

The different spatial arrangements of atoms in a molecule which are readily inter convertible by rotation about single bonds are called conformations. Determinations of relative stabilities of the conformations of a compound and interpretations of its physical and chemical properties in terms of conformations is called conformation analysis

Conformations Analysis of ethane:

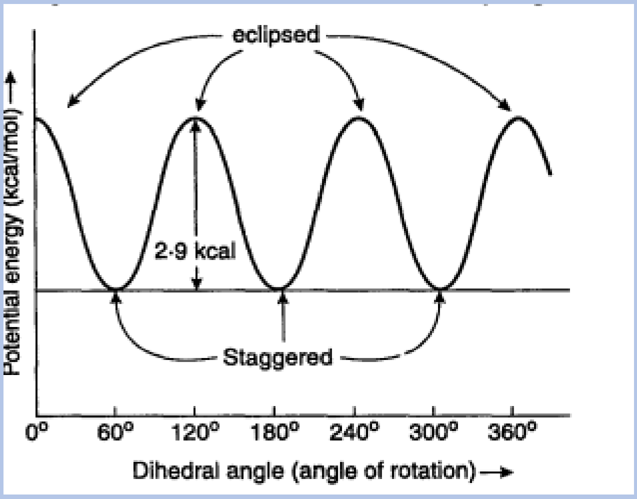
Ethane consists of two carbon atoms connected by a single bond with six hydrogen atoms attached (three on each carbon). The molecule can rotate around the C-C bond, leading to different conformers.

- **Conformers**: Ethane has two main types of conformers:
    - **Eclipsed Conformation**: In this conformation, the hydrogen atoms on adjacent carbons are aligned, leading to maximum steric hindrance. This is the **least stable** conformation due to the torsional strain caused by eclipsing interactions.
    - **Torsional Strain** : The electrons in a carbon-hydrogen bond will repel the electrons in another carbon-hydrogen bond if the bonds get too close to each other. This is called torsional Strain
    - **Staggered Conformation**: In this conformation, the hydrogen atoms are spaced as far apart as possible, minimizing steric hindrance. This is the **most stable** conformation.



Newman projections of ethane

- **Energy Profile**: The staggered conformation is more stable by about 12.6 kJ/mol compared to the eclipsed conformation.

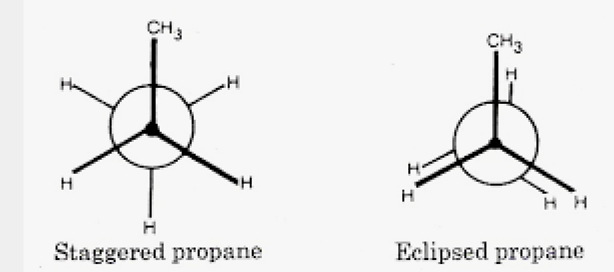


Conformations Analysis of Propane:

Propane (C_3H_8)

Propane consists of three carbon atoms connected by single bonds, with hydrogen atoms attached to the carbons. The rotational barrier around the C-C bonds in propane is similar to that of ethane but involves an additional carbon.

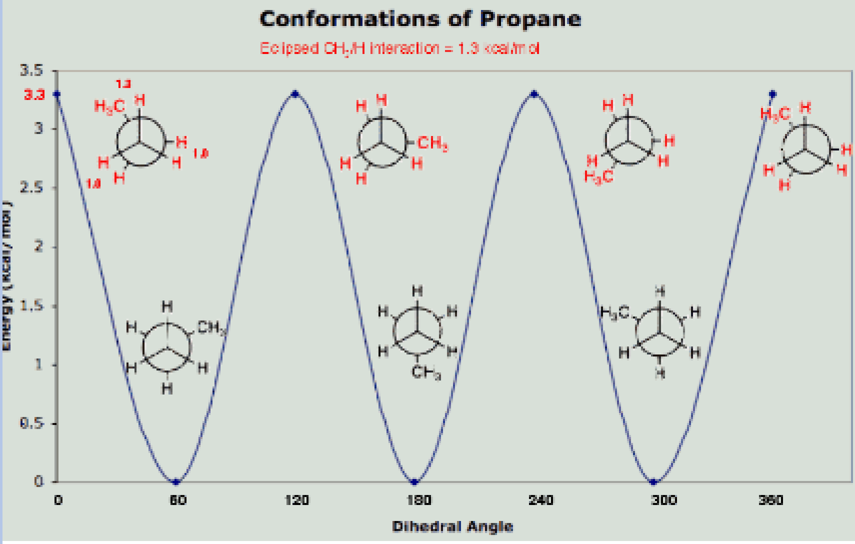
- **Conformers**: Propane can adopt several conformations:
    - **Eclipsed Conformation**: Similar to ethane, the hydrogen atoms on adjacent carbons are aligned, creating steric strain.
    - **Staggered Conformation**: Here, the hydrogen atoms are spaced as far apart as possible, minimizing steric repulsion.



Staggered propane   Eclipsed propane

Fig. Newman projections of propane

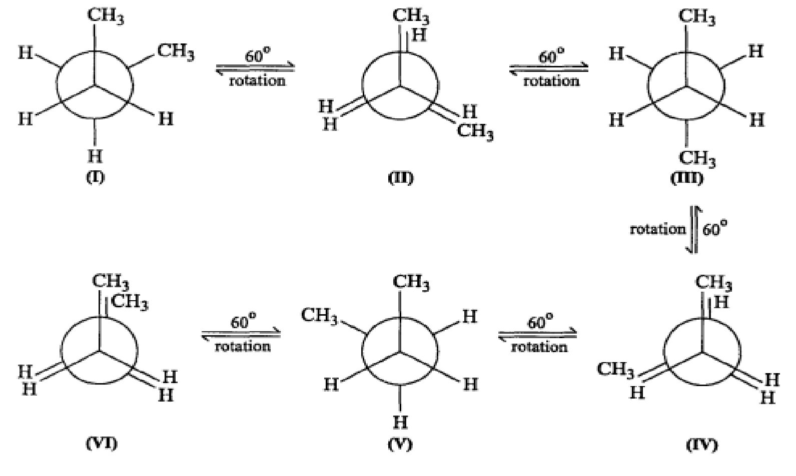
- **Energy Profile**: The anti conformation is the most stable, followed by staggered, and finally, the eclipsed conformation is the least stable.



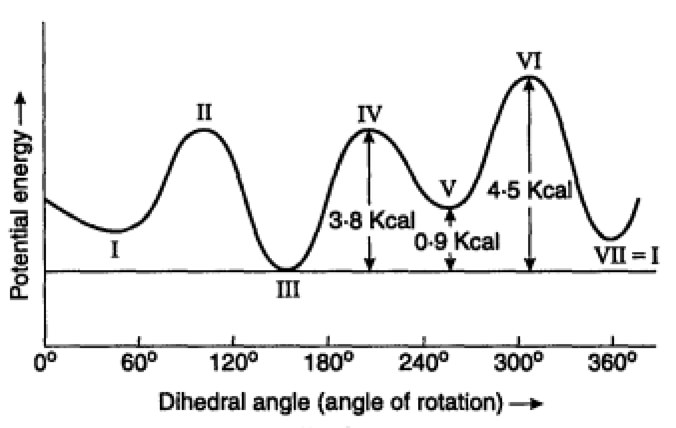
Conformations of n-butane:

Butane consists of four carbon atoms connected by single bonds. The rotational flexibility around the C-C bonds is more significant here than in ethane or propane.

- **Conformers**:
    - **Eclipsed Conformation**: Similar to ethane and propane, this is a high-energy conformation due to steric strain from the eclipsing of hydrogens or methyl groups. Fig No II,IV,IV
    - **Staggered Conformation**: In the staggered conformation, the hydrogens and methyl groups are spread out, minimizing steric interactions. Also called Gauche Conformation The two methyl groups are adjacent to each other, causing steric strain but still lower in energy than the eclipsed conformation Fig No I,V
    - **Anti Conformation**: This is the most stable conformation, where the two large methyl groups are opposite each other, minimizing steric clash. **Fig No III**



Energy Profile: The anti conformation is the most stable, followed by the gauche conformation (which has some steric strain between the methyl groups), and the eclipsed conformation is the least stable .The two gauche conformers have the same energy but each is 0.9 kcal/mole less stable than the anti-conformer. Anti and gauche conformers do not have the same energy because of the steric strain. All these eclipsed conformers VI have both torsional and steric strain.



Cyclo Alkanes: the carbon atoms are arranged to form a ring; these are called cyclic compounds. These compound have cyclic structures but resemble aliphatic (open chain) compounds in fll.my properties, hence are called alicyclic compounds. the general formula C_nH2_n

Baeyer's Strain Theory

Baeyer's Strain Theory (1885) explains the relative stability of cycloalkanes in terms of angle strain—the deviation of internal bond angles from the ideal tetrahedral angle of 109.5° for sp^3 hybridized carbon

All cycloalkanes are planar (flat rings).

Maximum stability is found when bond angles are exactly 109.5° (the tetrahedral angle).

Any deviation from this ideal angle is called Angle strain when Angle strain increases, Potential energy increases and stability decreases making more reactive (especially true for smaller rings like cyclopropane and cyclobutane)

Angle Strain Calculation

- Cycloalkane ring angle = $180 \times (n-2)/n$ where n = number of ring atoms.
- Angle strain = ½(109°.28"- Cycloalkane ring angle)

Cycloalkane	**Bond Angle**	**Angle Strain (from 109.28°)** ½(109°.28"- Cycloalkane ring angle)	**Relative Stability (predicted)**
Cyclopropane	60°	+24.64°	Least (most strained)
Cyclobutane	90°	+9.64°	Less stable
Cyclopentane	108°	+.64°	Most stable
Cyclohexane+	120°+	-5.36°	Predicted as less stable

Predicted order of stability **:** Cyclopentane > Cyclobutane > Cyclopropane**.**

Observations and Limitations

Cyclohexane and larger rings are actually **much more stable** than Baeyer predicted because they adopt non-planar (*puckered*) conformations (e.g., chair form for cyclohexane) that relieve angle strain entirely.

- Real ring compounds are not always planar—this is a major limitation of the original theory.
- For larger rings (7+ carbons), Baeyer incorrectly expected high instability due to “negative strain,” but such rings do exist and can be quite stable

Conformational Analysis of Cyclohexane

Introduction

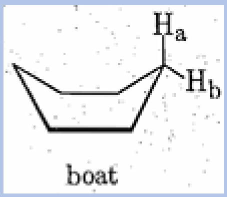
Cyclohexane, a six-membered carbon ring (C_6H_{12}), does **not remain planar** due to angle and torsional strain. Instead, it adopts non-planar conformations to minimize these strains and achieve **greater stability**[1][2].

1. Chair Conformation

- **Most stable** conformation due to minimal angle (109.5°) and torsional strain.
- All carbon atoms are sp^3 hybridized.
- All C–C bond angles approach the ideal tetrahedral value (~111°).
- All C–H bonds are staggered, eliminating eclipsing interactions.
- **Prevalent form:** At room temperature, almost all (99.99%) cyclohexane molecules are in the chair conformation

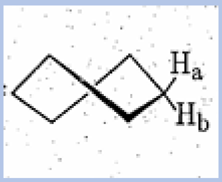
2. Boat Conformation

- Created by lifting two opposite carbon atoms out of the plane.
- **Less stable** than the chair conformation.
- Features steric repulsion between flagpole hydrogens (1,4 interactions).
- Exhibits some torsional strain due to eclipsed C–H bonds



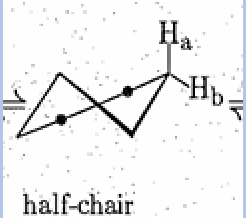
3. Twist-Boat (Skew-Boat) Conformation

- Derived by distorting the boat conformation.
- **More stable** than the pure boat, but less stable than the chair.
- Torsional and steric interactions are lower compared to the boat form



4. Half-Chair Conformation

- The highest energy and **least stable** conformation.
- Results from lifting one carbon atom completely out of plane.
- Contains high angle and torsional strain[2].



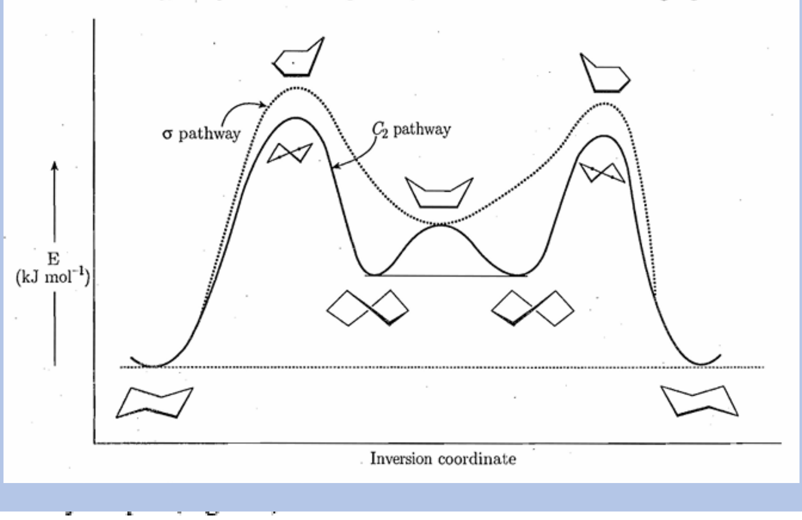
Energy Diagram Overview

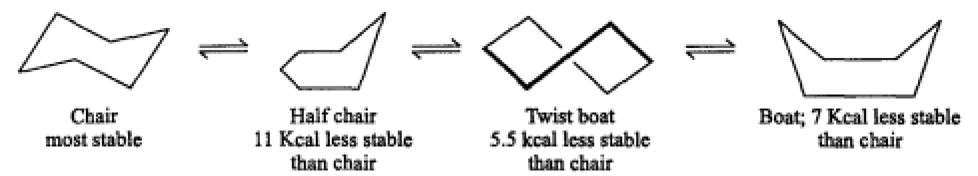
- The energy profile starts with the most stable **chair** conformation.
- Moving from chair to boat, the molecule passes through a **half-chair** transition state (highest energy point) and a **twist-boat** intermediate (energy minimum between half-chair and boat).
- The **boat** form is a local maximum, higher in energy than twist-boat, but not as high as half-chair.
- Completing the transition, the molecule passes through another twist-boat and half-chair before returning to the alternate chair conformation.

Features of the Energy Profile

- **Energy Barrier:** The energy required to go from one chair to another via ring-flipping is about **10–11 kcal/mol**. This modest barrier explains why cyclohexane rapidly interconverts between two chair forms at room temperature[3][1].
- **Populations:** At room temperature, virtually all cyclohexane exists in the chair form due to its much lower energy. Twist-boat and boat populations are extremely low, and half-chair forms exist only fleetingly as transition states[3][1].
- **Order of Stability:**
  Chair > Twist-Boat > Boat > Half-Chair

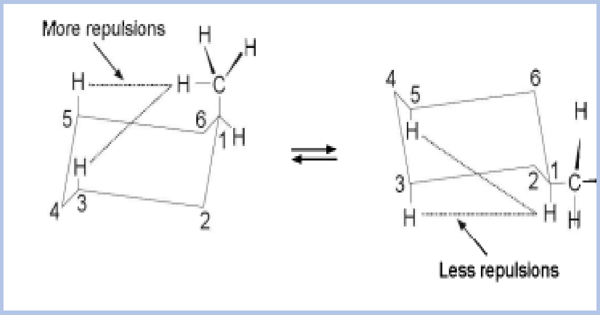
The energy diagrams of these pathways are shown in the following figure.

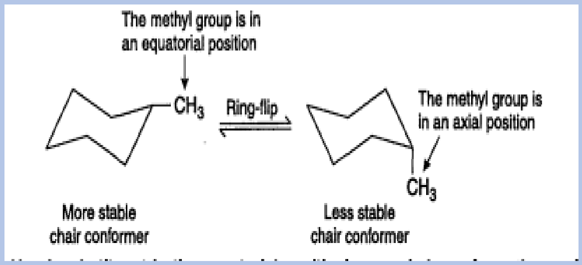




CONFORMATIONS OF MONO SUBSTITUTED CYCLOHEXANES

A methyl group is bulkier than a hydrogen atom. When the methyl group in methylcyclohexane is in the axial position, the methyl group and the axial hydrogens of the ring repel each other. These interactions are called Axial-Axial Interactions. When the methyl group is in the equatorial position, the repulsions are minimum. Thus, the energy of the conformation with equatorial methyl group is lower. At room temperature, about 95% methylcyclohexane molecules are in the conformation in which the methyl group is equatorial. The bulkier the group, the greater is the energy difference between equatorial and axial conformations. In other words, a cyclohexane ring with a bulky substituent (e.g., t-Butyl group) is more likely to have that group in the equatorial position.





Unit 2: Saturated Hydrocarbons (Alkanes and Cycloalkanes)

Long Answer Questions (10 Marks)

1. Discuss the methods of preparation of alkanes with a focus on the Wurtz and Wurtz-Fittig reactions.
2. Explain the conformational analysis of alkanes, including the energy diagrams of ethane, propane, and butane.
3. Discuss the molecular structure and stability of cycloalkanes, highlighting Baeyer’s strain theory.
4. What are the properties of alkanes, and how do they influence the chemical reactions they undergo?
5. Compare the stability of different conformations of cyclohexane.

Short Answer Questions (5 Marks)

1. Write a short note on the physical properties of alkanes.
2. What is the Corey House synthesis?
3. Explain Baeyer’s strain theory and its relevance to cycloalkanes.
4. What is the significance of the conformational analysis of ethane?
5. How does the molecular formula affect the stability of cycloalkanes?