Inductive Effect: Inductive effect is defined as permanent displacement of shared electron pair in a carbon chain towards more electronegative atom or group.
Types of Inductive effect:

1. Negative Inductive Effect: (—I effect, Electron withdrawing effect)
   when an electronegative atom or group (more electro negative than hydrogen) is attached to the terminal of the carbon chain in a compound, the electrons are displaced in the direction of the attached atom or group.

-NO₂ > -CN > -COOH > F > Cl > Br > I > OH > C₆H₅ > H
2. **Positive Inductive effect**: (+I effect, Electron releasing effect)

When an electro positive atom or group (more electro positive than hydrogen) is attached to the terminal of the carbon chain in a compound, the electrons are displaced away from the attached atom or group.

\[(\text{CH}_3)_3\text{C-} > (\text{CH}_3)_2\text{CH-} > -\text{C}_2\text{H}_5 > -\text{CH}_3.\]
Applications of Inductive effect:

Inductive effect is useful in explaining the strength of some organic acids and bases.

a) Effect of substituent on the acid strength of aliphatic acids.

\[
\text{HCOOH} > \text{CH}_3\text{COOH} > (\text{CH}_3)_2\text{CHCOOH}
\]

**Reason:** Acidic strength decreases as +I effect of the alkyl group increases.

b) \(\text{O}_2\text{NCH}_2\text{COOH} > \text{FCH}_2\text{COOH} > \text{CICH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH} > \text{CH}_3\text{COOH}\)

**Reason:** Acidic strength decreases as -I effect of the group or halogen decreases.
c) \( \text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH} \)

**Reason:** Acidic strength decreases as the number of halogen atoms decreases.

d) \( \text{CH}_3\text{CHClCOOH} > \text{CH}_2\text{ClCH}_2\text{COOH} \)

**Reason:** Acidic strength decreases as the distance of the halogen from carboxylic group increases.

e) i.e., Benzoic acid is stronger than acetic acid.

**Reason:** due to –I effect of phenyl group.
Relative basic strength of amines

1. All aliphatic amines are more basic than ammonia.  
   e.g. Methyl amine is more basic than ammonia.  
   **Reason**: Due to +I effect of methyl group.

2. Aniline is weaker base than Ammonia.  
   **Reason**: Due to +R effect and –I Effect of phenyl group.
Electromeric Effect

**Electromeric effect** is defined as the complete transfer of electrons of a multiple bond towards one of the bonded atoms at the demand of an attacking reagent.

**Note:**

a) It is shown by those compounds containing multiple bond

b) It is a purely temporary effect & is brought into play only at the requirement of attacking agent.
Types of Electromeric Effect

+E effect: When displacement of electrons is away from the atom or group.

E.g.: addition of $H^+$ to alkene.

-E effect: When displacement of electrons is towards the atom or group.

E.g.: addition of cyanide ion ($CN^-$) to the carbonyl group.
Mesomeric/ Resonance Effect

The flow of electrons from one part of a conjugated $\pi$ system to the other caused by phenomenon of resonance is called resonance effect or mesomeric effect.

-M or -R effect : When the electron displacement is towards the group.

E.g. :-NO$_2$, -CHO,

+M or +R effect : When the electron displacement is away from the group.

E.g. :-OH, -OR,-Cl
I. Conversion of Methane to Ethane (Ascent of Series):

Method - 1:

\[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{diffused sunlight}} \text{CH}_3\text{Cl} \xrightarrow{\text{Na, dry ether}} \text{C}_2\text{H}_6 \]

(a) Methane reacts with chlorine in the presence of diffused sunlight to give methyl chloride.

\[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{h\gamma} \text{CH}_3\text{Cl} + \text{HCl} \]

(b) Methyl chloride reacts with sodium in dry ether to give ethane. (Wurtz reaction).

\[ \text{CH}_3\text{Cl} + 2\text{Na} + \text{CH}_3\text{Cl} \xrightarrow{\text{dry ether}} \text{C}_2\text{H}_6 + 2\text{NaCl} \]

Method - 2:

\[ \text{CH}_4 + \text{Cl}_2 \xrightarrow{\text{diffused sunlight}} \text{CH}_3\text{Cl} \xrightarrow{\text{alc KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{Na / alcohol}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2 \text{0 - 5}\text{oC}} \]

\[ \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_5} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{Zn - Cu / alcohol}} \text{CH}_3\text{-CH}_3 \quad \text{i.e.,} \text{C}_2\text{H}_6. \]
II Conversion of Ethane to Methane:

\[ \text{CH}_3 - \text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{diffused sunlight}} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{aq.KOH}} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}^+ / \text{KMnO}_4, [O]} \text{CH}_4 \]

\[ \text{CH}_3\text{CHO} + [O] \xrightarrow{\text{soda lime (CaO / NaOH)}} \text{CH}_3\text{COOH} \xrightarrow{\text{soda lime}} \text{CH}_4 \]

iii) Conversion of Methanol to Ethanol:

\[ \text{CH}_3\text{OH} \xrightarrow{\text{PCl}_5} \text{CH}_3\text{Cl} \xrightarrow{\text{alc KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{Na / C}_2\text{H}_5\text{OH}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2, 0-5^\circ C} \text{CH}_3\text{CH}_2\text{OH} \]
**SYNTHETIC ORGANIC CHEMISTRY**

iv) **Ethanol to Methanol:** (Descent of Series)

**Method -1:**

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{aq.KOH} \rightarrow \text{CH}_3\text{Cl} \rightarrow \text{CH}_4
\]

\[
\text{CH}_3\text{CHO} + \text{[O]} \rightarrow \text{CH}_3\text{COOH} \quad \text{(K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4\text{)}
\]

**Method -2:**

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{[O]} \rightarrow \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COOH} \quad \text{(K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4\text{)}
\]

\[
\text{CH}_3\text{OH} \rightarrow \text{HNO}_2 \quad (0-5^\circ\text{C}) \quad \text{CH}_3\text{NH}_2 \rightarrow \text{Br}_2 / \text{KOH} \quad \text{CH}_3\text{CONH}_2 \rightarrow \Delta \rightarrow \text{CH}_3\text{COONH}_4^\text{•}
\]

\[
\text{CH}_3\text{CHO} + \text{[O]} \rightarrow \text{CH}_3\text{COOH} \quad \text{NH}_3
\]

**Additives:**
- 

**Reagents:**
- aq.KOH
- hγ , + Cl₂
- K₂Cr₂O₇ + H₂SO₄
- HNO₂
- Br₂ / KOH
- Δ
- Amm. acetate
Stereo isomerism: Compounds which have the same molecular formulae and same structural formulae but differ in spatial arrangement of the atoms or groups are known as stereoisomers and phenomenon is stereoisomerism.

1. Geometrical Isomerism
2. Optical Isomerism
1. Geometrical Isomerism: is due to restricted or hindered rotation around the double bond.

Conditions:
1. Molecule must have carbon-carbon double bond.
2. There must be two different atoms or groups attached to each carbon atom of the double bond.
2. **Optical Isomerism**: Compounds have same molecular & structural formulae but differ in action towards plane polarised light.

*E.g.*, Lactic acid (2-hydroxypropionic acid)

**Optical activity**: is the ability of chiral substance to rotate the plane of plane polarized light.

**Dextrorotatory Compounds**: Those compounds turn the plane of polarized light towards right (+).

**Laevorotatory Compounds**: Those compounds turn the plane of polarized light towards left (-).
Cause of Optical activity and Optical Isomerism:

**Chirality**: molecule and its mirror image must be non-superimposable.

**Chiral Carbon atom**: four different groups attached to carbon atom.

**Enantiomers**: The pair of molecules which are non-superimposable mirror images of each other.

**Racemic mixture**: when equal amounts of two enantiomers are mixed together it gives an optically inactive form.
Cycloalkanes: are saturated hydrocarbons in which the carbon atoms are joined by single covalent bonds to form a ring.

General formula $C_nH_{2n}$

Stability of cycloalkanes:
Stability of cycloalkanes increases with the size of ring up to cyclopentane and from cyclohexane onwards all cycloalkanes are quite stable.
This is explained by Adolf von Baeyer.
Postulates of Baeyer’s Strain Theory:

1. The atoms present in any cycloalkane molecule lie in same plane and thus all cycloalkanes are Co-planar. Carbon-Carbon angle is $109^\circ 28'1$.

2. The deviation of bond angle from the normal tetrahedral angle is called as angle strain ($109^\circ 28'1$).

3. The greater the angle strain, the greater is the instability of ring.

4. The higher the stability of the ring the greater would be its ease of formation.
Calculation of Angle strain

Angle strain = \( \frac{1}{2} [109^\circ 28' \text{-bond angle in cycloalkane}] \)

Angle strain in various cycloalkane rings

<table>
<thead>
<tr>
<th>Cycloalkane</th>
<th>C-C-C bond angle</th>
<th>Angle strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Cyclopropane</td>
<td>60°</td>
<td>( \frac{1}{2} (109^\circ 28' - 60^\circ) = +24^\circ 44' )</td>
</tr>
<tr>
<td>2) Cyclobutane</td>
<td>90°</td>
<td>( \frac{1}{2} (109^\circ 28' - 90^\circ) = +9^\circ 44' )</td>
</tr>
<tr>
<td>3) Cyclopentane</td>
<td>108°</td>
<td>( \frac{1}{2} (109^\circ 28' - 108^\circ) = 0^\circ 44' )</td>
</tr>
<tr>
<td>4) Cyclohexane</td>
<td>120°</td>
<td>( \frac{1}{2} (109^\circ 28' - 120^\circ) = -5^\circ 16' )</td>
</tr>
<tr>
<td>5) Cycloheptane</td>
<td>128° 34'</td>
<td>( \frac{1}{2} (109^\circ 28' - 128° 34') = -9° 33' )</td>
</tr>
</tbody>
</table>
Rings with six or more carbon atoms in cycloalkanes are **NOT planar but puckered.**

They exist in two strain less forms **boat form** and **Chair form**

**Note:** the chair conformation of cyclohexane has been found more stable than boat conformation
Mechanism of Electrophilic Substitution Reactions of Benzene

Benzene undergoes Electrophilic Substitution Reactions

Reason: due to the presence of $\pi$ electron cloud above and below the plane of carbon atoms of the ring.

Electrophilic Substitution Reactions are of the following types:

- Halogenation,
- Nitration,
- Sulphonation & Friedel-Craft reaction
Halogenation

The substitution of ‘H’ atom of benzene ring by halogen atom.

**Conditions**: presence of halogen carrier. (FeCl₃ or Fe)

**Electrophile**: $X^+$ (halonium ion)

where $X =$ Halogen atom
Nitration

The substitution of ‘H’ atom of benzene ring by –NO₂ group.

To carry out nitration, nitrating mixture is used.

Nitrating Mixture: it is a mixture of

\[ \text{Conc.} \text{HNO}_3 + \text{Conc. } \text{H}_2\text{SO}_4 \]

Electrophile: \( \text{NO}_2^+ \) (nitronium ion)
Sulphonation

The substitution of ‘H’ atom of benzene ring by –SO₃H group.

To carry out Sulphonation, Conc. sulphuric acid is used.

Electrophile : SO₃ (Neutral electrophile)
Friedel-Craft Reaction

Friedel-Craft alkylation

The substitution of ‘H’ atom of benzene ring by ‘alkyl’ group.
To carry out alkylation, alkyl halide is used.

Condition: ‘anhydrous AlCl₃’ as catalyst (Lewis acid)

Electrophile: \(^{+}\text{CH}_3\) (Methyl Carbocation)
General Mechanism of Aromatic Electrophilic Substitution

Step 1: Generation of electrophile

\[ E - B \rightarrow E^+ + B^- \]

electrophile

Step 2: Formation of intermediate carbocation.

Electrophile attacks benzene ring to form carbocation which is stabilised due to resonance.

\[
\begin{align*}
\text{H} & \quad + \quad E^+ \quad \xrightarrow{\text{Slow}} \quad \text{I} \\
\text{II} & \quad \text{III} \\
& \quad \equiv
\end{align*}
\]

Step 3: Loss of Proton (to form substitution product)

\[
\begin{align*}
\text{H} & \quad E \\
& \quad + \quad A^- \quad \xrightarrow{} \quad \text{H} + \text{HA}
\end{align*}
\]
Elucidation of structure of Benzene


2. Possibility of Open Chain Structure: it is highly unsaturated, it contains 8 hydrogen atoms less than corresponding alkane ($C_6H_{14}$). Formation of Cyclohexane, benzene hexachloride, benzene triozonide shows that it contains 3 carbon-carbon double bonds.
Elucidation of structure of Benzene

3. Failure of Open Chain Structure:
   benzene does not decolourise colour of alk. KMNO$_4$, colour of Br$_2$ water.
   It undergoes substitution reaction readily compared to addition reactions,
   It forms only one type of monosubstituted product.

4. Kekule’s Ring Structure:
5. Objections against Kekule’s structure:

Objection-1: there should exist two ortho isomers for similar substituents.

Overcome this objection; Kekule suggest that benzene is a mixture of two forms in rapid equilibrium.
Elucidation of structure of Benzene

5. Objections against Kekule’s structure:
   Objection-2: Structure of benzene possesses three double bonds which suggests that it should be highly reactive. But this is against the observed fact. Benzene is found to be stable unlike alkenes (i.e., does not undergo the addition reaction easily).
Elucidation of structure of Benzene

Modern view: Structure of benzene can be explained by Valence bond theory & Molecular Orbital Theory.

Valence bond theory:
Elucidation of structure of Benzene

Molecular Orbital Theory.
Questions?

Thank you

ALL THE BEST