1. (a) Differentiate between relative and absolute configuration with suitable examples.

- **Relative Configuration:** This describes the configuration of a chiral molecule in relation to another, typically known, chiral molecule. It tells us whether two different molecules or parts of a molecule have the same or opposite arrangement of substituents around a chiral center without specifying the absolute spatial orientation. It's often determined by chemical reactions where the configuration at the chiral center is preserved.
    - **Example:** In the D/L system for sugars, D-glucose and L-glucose represent relative configurations based on their relationship to D-glyceraldehyde. If the hydroxyl group on the penultimate carbon is on the right in the Fischer projection, it's D; if on the left, it's L.
- **Absolute Configuration:** This refers to the exact three-dimensional arrangement of atoms or groups around a chiral center. It provides a unique, unambiguous description of the molecule's spatial arrangement. Absolute configuration is determined experimentally, often through X-ray crystallography, or by correlating with a compound of known absolute configuration.
    - **Example:** The R/S system (Cahn-Ingold-Prelog rules) assigns an (R) or (S) designation to each chiral center based on the priority of its substituents. For instance, (R)-2-butanol and (S)-2-butanol specify the precise orientation of the four different groups around the chiral carbon.

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2. (b) Arrange the following in the increasing order of stability: (i) (A five-membered ring structure with one double bond, resembling cyclopentene) (ii) (A fused two-ring aromatic structure, resembling naphthalene) (iii) (A linear chain structure with H_3C and CH_3 groups)

- **Increasing order of stability:** (i) Cyclopentene < (iii) Alkane (e.g., propane/butane) < (ii) Naphthalene
    - **(i) Cyclopentene:** This is an alkene, and due to the presence of a double bond within a five-membered ring, it experiences some **ring strain** and less stability compared to a saturated chain or an aromatic system.
    - **(iii) Linear chain structure (Alkane):** This represents a saturated alkane. Alkanes are generally quite stable due to strong **sigma bonds** and lack of significant strain or reactive functional groups.
    - **(ii) Naphthalene:** This is an **aromatic compound**. Aromaticity confers exceptional stability due to the extensive **delocalization of pi electrons** across the fused ring system, a phenomenon known as resonance stabilization.

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3. (c) Write a short note on Claisen condensation and give its biological significance.

- **Claisen Condensation:**
    - The Claisen condensation is a carbon-carbon bond-forming reaction in organic chemistry.
    - It involves the reaction of an **ester containing at least two α-hydrogens** with another ester molecule (or a ketone) in the presence of a strong base (like sodium ethoxide).
    - The reaction proceeds via the formation of an **enolate anion** from one ester, which then acts as a nucleophile, attacking the carbonyl carbon of a second ester molecule. This is followed by the elimination of an alkoxide group.
    - The final product of a Claisen condensation is a **β-keto ester**.

- **Biological Significance:**
    - The Claisen condensation mechanism is fundamental in many biological pathways, particularly in **metabolism**.
    - A prominent example is in **fatty acid synthesis**, where acetyl-CoA (a two-carbon unit) and malonyl-CoA (a three-carbon unit) condense to form acetoacetyl-CoA, which is a four-carbon β-keto thioester. This crucial step is catalyzed by enzymes like β-ketoacyl-ACP synthase in the fatty acid synthase complex, contributing to the elongation of fatty acid chains.
    - While not a direct Claisen condensation, the initial step of the **citric acid cycle**, where acetyl-CoA condenses with oxaloacetate to form citrate, shares mechanistic similarities with carbanion chemistry involved in Claisen condensation reactions.

4. (d) What is Invert Sugar and why it is so named?

- **Invert Sugar:** Invert sugar is an equimolar mixture of **D-glucose and D-fructose**, obtained by the hydrolysis (or "inversion") of sucrose. This hydrolysis typically occurs in the presence of an acid or the enzyme invertase (also known as sucrase).
- **Why it is so named:** The name "invert sugar" comes from the change in the **optical rotation** of plane-polarized light during the hydrolysis of sucrose:
    - **Sucrose** is dextrorotatory, meaning it rotates plane-polarized light to the right (has a positive optical rotation).
    - Upon hydrolysis, sucrose breaks down into glucose (which is also dextrorotatory) and fructose (which is strongly levorotatory, rotating light to the left).

- The strong levorotatory power of fructose outweighs the dextrorotatory power of glucose in the mixture. As a result, the resulting mixture of glucose and fructose has a net levorotatory effect (a negative optical rotation).
- Because the direction of the optical rotation **"inverts"** from positive (sucrose) to negative (the glucose/fructose mixture), the product is named invert sugar.

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5. (e) What are drying and non-drying oils? Give one example of each type.

- **Drying Oils:**
  - **Definition:** Drying oils are vegetable oils that solidify or "dry" into a tough, elastic film upon exposure to air. This "drying" is not due to evaporation but to **oxidative polymerization**.
  - **Chemical Nature:** They contain a high proportion of **polyunsaturated fatty acids** (fatty acids with two or more carbon-carbon double bonds). These double bonds are susceptible to reaction with oxygen from the air, leading to cross-linking and the formation of a solid film.
  - **Example: Linseed oil** (commonly used in paints and varnishes, but also a food oil).
- **Non-Drying Oils:**
  - **Definition:** Non-drying oils are vegetable oils that do not solidify or form a hard film when exposed to air; they remain liquid or semi-liquid.
  - **Chemical Nature:** They contain a relatively low proportion of polyunsaturated fatty acids and a higher proportion of **saturated or monounsaturated fatty acids**. These fatty acids

have fewer or no double bonds, making them less prone to oxidative polymerization.

- **Example: Olive oil** (a common cooking oil).

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2. Carry out the following conversion in the compound (A): (A structure with a central carbon bonded to CH_3, Cl, OH, and a Benzene (Ph) group)
    - (a) Fisher to Sawhorse
    - (b) Fisher to staggered Newman.
    - (c) Fisher to Eclipsed Newman.

    Note: Standard Sawhorse and Newman projections are typically used for molecules with a bond between *two* carbon atoms, which allows for viewing along that bond and depicting conformations. The compound described, with a "central carbon bonded to CH_3, Cl, OH, and a Benzene (Ph) group," is a single chiral center. Therefore, directly converting a single chiral center's Fischer projection into standard Sawhorse or Newman projections is not chemically conventional. These projections are primarily for conformational analysis of carbon-carbon single bonds.

    However, I can conceptually describe how the 3D information from a Fischer projection is typically interpreted for such representations, assuming a hypothetical two-carbon fragment for illustration if absolutely necessary, but I will focus on the single chiral center.

    Let's assume a Fischer projection for a hypothetical (R) configuration where:

    - The **Phenyl (Ph) group** is at the top (vertical line).
    - The **Methyl (CH_3) group** is at the bottom (vertical line).
    - The **Chlorine (Cl) atom** is on the left (horizontal line).

- The **Hydroxyl (OH) group** is on the right (horizontal line).

In this Fischer projection:

- The vertical bonds (to Ph and CH_3) are implicitly going **away from the viewer**.
- The horizontal bonds (to Cl and OH) are implicitly coming **towards the viewer**.

(a) **Fisher to Sawhorse (Conceptual for a single chiral center):**

- A Sawhorse projection gives a perspective view of the molecule, usually along a carbon-carbon bond. For a single chiral carbon, you would depict the central carbon as a point from which the four bonds radiate in a 3D perspective.
- Imagine viewing the molecule slightly from above and to the front. The Ph group and CH_3 group would be drawn pointing somewhat downwards and backwards, representing bonds going away. The Cl and OH groups would be drawn pointing somewhat upwards and forwards, representing bonds coming towards you. This is a 3D perspective, not a conventional Sawhorse showing rotation about a bond.

(b) **Fisher to staggered Newman (Conceptual for a single chiral center):**

- A Newman projection views a molecule down a specific bond. For a single chiral center, a standard Newman projection is not applicable.
- However, if one were to conceptually view along one of the bonds, for example, the bond between the chiral carbon and the phenyl (Ph) group:
    - The **chiral carbon** would be the "front" atom (represented by a dot). The three groups attached to it (Cl, OH, and CH_3) would be drawn radiating from this dot.

- The **phenyl (Ph) group** would be considered the "back" group (represented by a circle behind the dot).
- In a "staggered" arrangement, the groups on the front carbon (Cl, OH, CH_3) would be positioned to be maximally separated from each other around the central dot.

(c) **Fisher to Eclipsed Newman (Conceptual for a single chiral center):**

- Similar to the staggered Newman, a standard eclipsed Newman is not applicable for a single chiral center.
- Conceptually, if forced to depict it, the groups on the front carbon (Cl, OH, CH_3) would be drawn directly overlapping with (or "eclipsing") imaginary points on the back circle (representing the Ph group or the point where the Ph group attaches). This represents a less stable, high-energy conformation where substituents are aligned directly behind each other.

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3. (a) Differentiate between Inductive effect and Electrometric effect with suitable example.

- **Inductive Effect (I-effect):**
  - **Nature:** This is a **permanent** effect involving the displacement of **sigma (σ) electron density** along a carbon chain towards or away from a substituent.
  - **Cause:** It arises due to the difference in **electronegativity** between atoms involved in a sigma bond. A more electronegative atom will pull electron density towards itself, creating a partial negative charge (δ^-) on itself and partial positive charges (δ^+) on the atoms in the chain, which diminish with distance.

- **Types:**
  - **Electron-withdrawing (-I effect):** Groups that pull electron density (e.g., $-NO_2$, $-COOH$, $-Cl$).
  - **Electron-donating (+I effect):** Groups that push electron density (e.g., alkyl groups like $-CH_3$).
- **Example:** In chloroethane ($CH_3 - CH_2 - Cl$), the chlorine atom, being more electronegative, draws electron density from the adjacent carbon. This carbon, in turn, draws electron density from the methyl carbon. This results in a sequence of diminishing partial positive charges: $CH_3^{\delta\delta+} - CH_2^{\delta+} - Cl^{\delta-}$.

- **Electromeric Effect (E-effect):**
  - **Nature:** This is a **temporary** effect involving the complete transfer of a **shared pair of pi (π) electrons** to one of the atoms of a multiple bond (double or triple bond).
  - **Cause:** It only operates in the presence of an **attacking reagent** (electrophile or nucleophile) that initiates the electron shift. When the reagent is removed, the molecule reverts to its original electronic state.
  - **Types:**
    - **Positive Electromeric (+E effect):** Pi electrons are transferred towards the atom to which the attacking reagent gets attached (e.g., H^+ adding to an alkene).
    - **Negative Electromeric (-E effect):** Pi electrons are transferred away from the atom to which the attacking reagent gets attached (e.g., CN^- adding to a carbonyl carbon).
  - **Example:** In the reaction of an alkene with a proton (H^+), the pi electrons of the double bond completely shift to one of the carbon atoms, allowing the proton to attach there and creating

a carbocation on the other carbon: $CH_2 = CH_2 + H^+ \rightarrow CH_3 - CH_2^+$.

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4. (b) Which of the following two compounds have higher dipole moment and why? (i) (A cyclopropane ring with a carbonyl group (C=O) attached to one carbon) (ii) (A cyclopropane ring with a carbonyl group (C=O) attached to one carbon, with the double bond facing outwards)

   Let's interpret the structures:

   - **(i) Cyclopropanone:** This structure implies a cyclopropane ring where one of the carbons is part of a carbonyl group, meaning the **carbonyl oxygen is directly bonded to a ring carbon within the three-membered ring**.
   - **(ii) Cyclopropyl Ketone (or similar, e.g., cyclopropyl carbaldehyde):** This structure implies a cyclopropane ring with a carbonyl group attached to one of its carbons, but the **carbonyl is outside the ring** (exocyclic).

   Comparison of Dipole Moments: Cyclopropanone (i) will have a significantly higher dipole moment.

   Reasoning:

   - **Cyclopropanone (i):** Cyclopropanone exhibits an unusually high dipole moment (around 2.9 D to 3.0 D) compared to typical ketones (e.g., acetone ~2.9 D, but cyclopropanone has unique features). This high dipole moment is attributed to two main factors:
     i. **High Ring Strain:** The three-membered cyclopropane ring is highly strained. When a carbonyl group is incorporated into this strained ring, the sp2 hybridized carbonyl carbon prefers a 120° bond angle but is forced into smaller angles, leading to increased strain.

ii. **Unique Electronic Properties of Cyclopropane:** The C-C bonds in cyclopropane are often described as "bent bonds" or "banana bonds," which possess higher s-character (approaching sp2-like character in their external bonds). This unique electronic structure allows the cyclopropane ring to act as an **electron-donating group** towards the electron-deficient carbonyl carbon. This electron donation effectively stabilizes a positive charge on the carbonyl carbon (contributing to a significant resonance form with a charge separation), which greatly enhances the polarity of the C=O bond and thus the overall dipole moment.

- **Cyclopropyl Ketone (ii):** In this compound, the carbonyl group is outside the cyclopropane ring. While the cyclopropane ring can still exert an **electron-donating inductive effect** on the attached carbonyl group due to its high s-character, the unique strain-induced polarization and orbital overlap that occur when the carbonyl is *part of the ring* (as in cyclopropanone) are absent. Therefore, the dipole moment of cyclopropyl ketone will be lower than that of cyclopropanone, although it would still be relatively polar due to the C=O bond.

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5. (c) Arrange the following compounds in decreasing order of basicity, give suitable reason for your answer: (i) (A saturated six-membered nitrogen-containing ring, resembling piperidine) (ii) (A six-membered nitrogen-containing ring with one double bond, possibly a dihydropyridine derivative) (iii) (An aromatic six-membered nitrogen-containing ring, resembling pyridine)

   Let's identify the compounds and their characteristics affecting basicity:

- **(i) Piperidine:** This is a **saturated cyclic amine**. The nitrogen atom is **sp3 hybridized**, and its lone pair of electrons is localized and readily available for protonation.
- **(ii) Dihydropyridine:** This represents a **partially unsaturated cyclic amine**. Depending on the exact position of the double bond, the nitrogen atom might be sp3 or sp2 hybridized. If the nitrogen's lone pair is localized (e.g., in 1,4-dihydropyridine where N is sp3), it would be a strong base. If the nitrogen is sp2 hybridized and its lone pair is not part of an aromatic system, it would be less basic than sp3. Assuming a non-aromatic nature where the double bond might cause some electron withdrawal or a slight increase in s-character if N is sp2.
- **(iii) Pyridine:** This is an **aromatic heterocyclic amine**. The nitrogen atom is **sp2 hybridized**. Its lone pair of electrons is in an sp2 orbital that lies in the plane of the ring and is *not* part of the 6-π electron aromatic system.

Decreasing Order of Basicity:

b. **(i) Piperidine:**

- **Reason:** The nitrogen in piperidine is **sp3 hybridized**. The lone pair of electrons resides in an sp3 orbital, which has 25% s-character. This means the electrons are relatively loosely held and are very available for donation to a proton. This makes piperidine a strong base, comparable to acyclic secondary amines.

c. **(ii) Dihydropyridine:**

- **Reason:** The basicity of dihydropyridines can vary. If the nitrogen is still **sp3 hybridized** (e.g., 1,4-dihydropyridine), its basicity would be similar to piperidine, possibly slightly reduced due to subtle inductive effects from the double bond. However, if the nitrogen is **sp2 hybridized** but the ring is not aromatic (e.g., an enamine-like structure where

the lone pair can conjugate with an adjacent double bond), its lone pair would be in an orbital with higher s-character than sp3 (making it less available) but it is not part of an aromatic ring system like pyridine. Therefore, it is generally less basic than piperidine but more basic than pyridine.

d. **(iii) Pyridine:**

- **Reason:** The nitrogen in pyridine is **sp2 hybridized**. The lone pair of electrons is in an sp2 orbital, which has 33% s-character. Due to the higher s-character, these electrons are held more tightly by the nucleus compared to sp3 hybridized lone pairs. Although this lone pair is available for protonation (it's not part of the aromatic system), its reduced availability makes pyridine a weaker base than the non-aromatic amines listed.

Therefore, the decreasing order of basicity is: Piperidine (i) > Dihydropyridine (ii) > Pyridine (iii).

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4. (a) Define chirality and stereogenic centre with suitable example.

- **Chirality:**
  - **Definition:** Chirality is the property of an object or molecule that makes it **non-superimposable on its mirror image**. Just like your left hand is a mirror image of your right hand but you can't perfectly overlap them, a chiral molecule and its mirror image are distinct. Chiral molecules are also referred to as **optically active**, meaning they can rotate the plane of plane-polarized light.
  - **Example:** The molecule **2-butanol** ($CH_3CH(OH)CH_2CH_3$) is chiral. Its mirror image cannot be superimposed on the original

molecule, leading to two enantiomers, (R)-2-butanol and (S)-2-butanol.

- **Stereogenic Centre (or Chiral Centre / Chiral Carbon):**
    - **Definition:** A stereogenic centre is an atom in a molecule that, when its substituents are interchanged, leads to a stereoisomer. For most organic molecules, a chiral center is a carbon atom bonded to **four different groups**. The presence of one or more stereogenic centers often (but not always) leads to molecular chirality.
    - **Example:** In **2-butanol**, the second carbon atom (C2) is a stereogenic center. It is bonded to four distinct groups: a hydrogen atom (-H), a methyl group ($-CH_3$), a hydroxyl group (-OH), and an ethyl group ($-CH_2CH_3$). Because all four attached groups are different, this carbon is a chiral center.

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5. (b) Assign E/Z or R/S to the following compounds: (i) (A chiral carbon with H_3C, H, Br, and D (deuterium) attached) (ii) (A chiral carbon with Br, H, Cl, and H attached) (iii) (A chiral carbon with H_3C, H, OH, and CH_2CH_3 attached) (iv) (A chiral carbon with H_3C, H, and a chain containing F, C=O, OH, H_3C, CH_2CH_3) (v) (A bridged bicyclic compound with Et and Me groups)

   Note: I cannot draw the structures, and R/S or E/Z assignment requires knowing the precise 3D arrangement (for R/S) or the geometric arrangement around a double bond (for E/Z). I will describe the assignment based on Cahn-Ingold-Prelog (CIP) rules and the typical convention.

   (i) A chiral carbon with H_3C, H, Br, and D (deuterium) attached:

   - This is a chiral center, so R/S applies.
   - **Priority assignment (CIP rules):**

i. Br (Atomic number 35) - Highest priority

ii. CH_3 (Carbon attached, then HHH) - Second priority

iii. D (Deuterium, isotope of H, mass 2) - Third priority

iv. H (Hydrogen, mass 1) - Lowest priority

- **Assignment:** The specific R or S assignment depends on the actual 3D orientation of these groups (e.g., if H is on a dash or a wedge in a specific projection). If the lowest priority group (H) is pointing away from the viewer, trace the path from priority 1 → 2 → 3. Clockwise path is (R), counter-clockwise is (S).

(ii) A chiral carbon with Br, H, Cl, and H attached:

- This carbon is **not a chiral center**.
- **Reason:** A chiral center must have four *different* groups attached. This carbon has two identical hydrogen atoms attached. Therefore, R/S assignment is not applicable.

(iii) A chiral carbon with H_3C, H, OH, and CH_2CH_3 attached:

- This is a chiral center (like in 2-butanol), so R/S applies.
- **Priority assignment (CIP rules):**

v. OH (Oxygen attached, atomic number 8) - Highest priority

vi. CH_2CH_3 (Carbon attached, then C,H,H) - Second priority

vii. CH_3 (Carbon attached, then H,H,H) - Third priority

viii. H (Hydrogen) - Lowest priority

- **Assignment:** The specific R or S assignment depends on the actual 3D orientation of these groups. Follow the same procedure as in (i).

(iv) A chiral carbon with H_3C, H, and a chain containing F, C=O, OH, H_3C, CH_2CH_3:

- This is a chiral center, so R/S applies.
- **Problem:** The description of the "chain" is a list of components, not a specific linear structure. To assign priorities for this complex fourth group, one would need the exact connectivity.
- **General Approach:** Assuming the chiral carbon is bonded to H_3C, H, and *one* complex "chain" group.
    ix. Identify the four distinct groups.
    x. Assign priorities using CIP rules, traversing along the chain to the first point of difference (e.g., comparing C, O, F atoms based on atomic number).
    xi. Once priorities (1, 2, 3, 4) are established, the R or S assignment is made based on the 3D orientation relative to the lowest priority group (H).
- **Cannot assign R/S without the specific structure of the 'chain'.**

(v) A bridged bicyclic compound with Et and Me groups:

- **E/Z assignment:** E/Z isomerism applies to carbons involved in a **double bond** with two different groups on each carbon. This description does not mention a double bond. Therefore, E/Z assignment is **not applicable**.
- **R/S assignment:** Bridged bicyclic compounds can indeed contain chiral centers (e.g., at bridgehead carbons or other substituted carbons) where R/S would apply.
- **Cannot assign R/S without the specific structure of the bicyclic compound and the positions of the Et (ethyl) and Me (methyl) groups** that would indicate chiral centers.

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6. (c) How can you differentiate between enantiomers and diastereomers? Explain with suitable examples.

- **Enantiomers:**
    - **Definition:** Enantiomers are stereoisomers that are **non-superimposable mirror images** of each other. They exist in pairs and have identical molecular formulas and connectivity but differ in the spatial arrangement of atoms.
    - **Key Differentiating Properties:**
        xii. **Optical Activity:** They rotate the plane of plane-polarized light by an **equal magnitude but in opposite directions**. One enantiomer is dextrorotatory (+), and its mirror image is levorotatory (-).

        xiii. **Interaction with Chiral Environments:** They react at different rates with **chiral reagents** (e.g., enzymes), or can be separated using **chiral solvents** or **chiral chromatography columns**.

        xiv. **Identical Physical/Chemical Properties (in achiral environments):** They have identical melting points, boiling points, densities, refractive indices, and solubilities in achiral solvents. They also exhibit identical chemical reactivity with achiral reagents.
    - **Differentiation Method:** The primary way to distinguish enantiomers is by measuring their **optical rotation** using a polarimeter. They can also be separated using **chiral resolution techniques** (e.g., forming diastereomeric salts, chiral chromatography).
    - **Example: (R)-2-butanol** and **(S)-2-butanol** are enantiomers. They have the same boiling point (99-100 °C) but (R)-2-butanol rotates plane-polarized light clockwise (+), while (S)-2-butanol rotates it counter-clockwise (-).

- **Diastereomers:**
    - **Definition:** Diastereomers are stereoisomers that are **not mirror images** of each other. They typically arise in molecules that have **two or more chiral centers**. They have the same molecular formula and connectivity but differ in the spatial arrangement of atoms.
    - **Key Differentiating Properties:**
        xv. **Different Physical Properties:** Unlike enantiomers, diastereomers have **different melting points, boiling points, densities, solubilities**, and other physical properties. This is their most important distinguishing feature.

        xvi. **Different Chemical Properties:** They exhibit **different chemical reactivities** with both chiral and achiral reagents.

        xvii. **Optical Activity:** They may or may not be optically active. If they are, they will rotate plane-polarized light by **different magnitudes and/or in different directions**.
    - **Differentiation Method:** Since they possess different physical and chemical properties, diastereomers can be separated by **conventional physical methods** such as fractional distillation, crystallization, column chromatography, or thin-layer chromatography, without requiring a chiral environment.
    - **Example:** Consider the four stereoisomers of **2,3-dibromobutane**:
        - **(2R,3R)-2,3-dibromobutane** and **(2S,3S)-2,3-dibromobutane** are enantiomers.
        - **(2R,3S)-2,3-dibromobutane** is a meso compound (achiral, due to an internal plane of symmetry).

- **(2R,3R)-2,3-dibromobutane** and **(2R,3S)-2,3-dibromobutane** are diastereomers. They have different melting points, boiling points, and can be separated by standard techniques.

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5. (a) Discuss the Chemistry involved in the following reactions (any two): (i) Retro aldol Reaction (Glycolysis) (ii) Pinacole pinacolone rearrangement (iii) Baeyer Villiger oxidation (iv) Cannizzaro reaction (Sugar metabolism).

   I will discuss (i) Retro aldol Reaction (Glycolysis) and (ii) Pinacol-Pinacolone Rearrangement.

   (i) Retro Aldol Reaction (Glycolysis)

   - **Chemistry Involved:** The retro aldol reaction is essentially the **reverse of an aldol condensation**. It involves the **cleavage of a carbon-carbon bond** in a β-hydroxy carbonyl compound (an "aldol") to yield two smaller carbonyl compounds, typically an aldehyde and/or a ketone.
   - **Mechanism (General):** The reaction usually occurs under acidic or basic conditions. In a basic mechanism, a β-hydroxy ketone or aldehyde deprotonates the α-carbon to form an enolate. This enolate then facilitates the breaking of the Cα-Cβ bond, expelling an aldehyde or ketone. Under acidic conditions, the carbonyl oxygen is protonated, and the hydroxyl group is eliminated as water to form a resonance-stabilized carbocation, which then undergoes cleavage.
   - **In Glycolysis:** A classic biological example occurs in the fourth step of glycolysis. The enzyme **aldolase** catalyzes the retro aldol cleavage of **fructose-1,6-bisphosphate** (a six-carbon β-hydroxy ketone) into two three-carbon molecules: **dihydroxyacetone phosphate (DHAP)** (a ketone) and **glyceraldehyde-3-phosphate (G3P)** (an aldehyde). The

enzyme often uses a Schiff base intermediate (forming an enamine) to facilitate the carbon-carbon bond cleavage and stabilize the carbanion equivalent, making this energetically favorable. This step is crucial for breaking down the six-carbon sugar into smaller units for further energy extraction.

(ii) Pinacol-Pinacolone Rearrangement

- **Chemistry Involved:** The Pinacol-Pinacolone rearrangement is an **acid-catalyzed rearrangement** of a **vicinal diol** (a 1,2-diol, also known as a "pinacol") to a **ketone** (or sometimes an aldehyde), referred to as a "pinacolone". It characteristically involves the **migration of an alkyl or aryl group**.
- **Mechanism:**

xviii. **Protonation:** One of the hydroxyl groups of the 1,2-diol is protonated by the acid, converting it into a good leaving group (water).

xix. **Water Elimination & Carbocation Formation:** The protonated hydroxyl group leaves as a water molecule, generating a **carbocation** on that carbon. If the diol is unsymmetrical, the more stable carbocation (e.g., tertiary over secondary) will preferentially form.

xx. **1,2-Alkyl/Aryl Shift:** An alkyl or aryl group from the **adjacent carbon atom** (the one bearing the other hydroxyl group) migrates with its bonding electrons to the electron-deficient carbocation center. Simultaneously and concerted with this migration, the lone pair electrons on the oxygen of the remaining hydroxyl group form a new **carbon-oxygen double bond (carbonyl)**. This forms a resonance-stabilized oxonium ion. The migratory aptitude generally follows the order: H > aryl > alkyl.

xxi. **Deprotonation:** The positively charged oxonium ion loses a proton to the solvent (or base), regenerating the

acid catalyst and forming the stable ketone product (pinacolone).

- **Example:** The rearrangement of 2,3-dimethylbutane-2,3-diol (pinacol) to 3,3-dimethylbutan-2-one (pinacolone) using a strong acid like sulfuric acid.

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6. (b) Define disaccharides. Give the structure of Sucrose. How was the nature of linkage between its two monosaccharide units established?

- **Disaccharides:**
  - **Definition:** Disaccharides are carbohydrates formed by the **glycosidic linkage** of two monosaccharide units. This linkage is typically formed through a condensation reaction, with the elimination of a water molecule. Disaccharides can be hydrolyzed back into their constituent monosaccharides by acid or enzymatic catalysis.

- **Structure of Sucrose:**
  - Sucrose is a disaccharide composed of one molecule of α**-D-Glucose** and one molecule of β**-D-Fructose**.
  - These two monosaccharide units are joined by a unique $\alpha,\beta-1,2$**-glycosidic linkage**. This means the anomeric carbon (C1) of glucose, in its alpha configuration, is linked to the anomeric carbon (C2) of fructose, in its beta configuration.
  - The glucose unit exists in its **pyranose (six-membered ring)** form, and the fructose unit exists in its **furanose (five-membered ring)** form.
- **How the nature of linkage was established:** The detailed nature of the glycosidic linkage in sucrose was established primarily through a combination of **methylation studies** and **enzymatic hydrolysis experiments**.

e. **Identification of Hydrolysis Products:**

- Initial hydrolysis experiments (using acid or the enzyme invertase) confirmed that sucrose yields an equimolar mixture of D-glucose and D-fructose. This identified the two constituent monosaccharides.

f. **Permethylation and Hydrolysis (Methylation Analysis):**

- Sucrose was treated with methylating agents (like dimethyl sulfate or methyl iodide) under basic conditions to convert *all available free hydroxyl groups* into methyl ether (-OCH_3) groups. The hydroxyl groups involved in the glycosidic bond would, by definition, not be free and thus would not be methylated.
- The fully permethylated sucrose was then hydrolyzed (e.g., with acid).
- Analysis of the methylated monosaccharide products revealed:
    - **2,3,4,6-Tetra-O-methyl-D-glucose:** This indicated that the C1-OH of the glucose unit was involved in the glycosidic linkage, as C2, C3, C4, and C6 were the only positions with free hydroxyls available for methylation in the original sucrose.
    - **1,3,4,6-Tetra-O-methyl-D-fructose:** This indicated that the C2-OH of the fructose unit was involved in the glycosidic linkage, as C1, C3, C4, and C6 were the only positions with free hydroxyls available for methylation.
- These results conclusively showed that the linkage was between C1 of glucose and C2 of fructose.

g. **Enzyme Specificity:**

- The use of specific enzymes helped determine the anomeric configuration (α or β).
- **α-Glucosidases** (like maltase) are known to hydrolyze α-glycosidic linkages. Sucrose is hydrolyzed by α-glucosidase. This confirmed the α-configuration at the glucose anomeric carbon.
- **β-Fructosidases** (like invertase) are known to hydrolyze β-glycosidic linkages involving fructose. Sucrose is also hydrolyzed by β-fructosidase. This confirmed the β-configuration at the fructose anomeric carbon.
- Together, these experiments confirmed the unique $\alpha,\beta-1,2$**-glycosidic linkage** in sucrose.

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7. (c) What are reducing and non-reducing sugars? Explain with the help of suitable structures and give one example for each category.

- **Reducing Sugars:**
  - **Definition:** Reducing sugars are carbohydrates that possess a **free anomeric carbon** (the carbon atom derived from the carbonyl carbon of the open-chain form) with an available hydroxyl group. This structural feature allows the cyclic form to readily open into its aldehyde (for aldoses) or ketone (for ketoses) form in solution. The aldehyde or ketone group can then be **oxidized** by mild oxidizing agents (such as Tollen's reagent, Fehling's solution, or Benedict's solution), reducing the metal ion in the reagent and thus "reducing" it.
  - **Explanation with Structural Implication:** The presence of a free hemiacetal (in aldoses) or hemiketal (in ketoses) group at the anomeric carbon is key. In aqueous solution, sugars exist in a dynamic equilibrium between their cyclic forms and a small proportion of the open-chain form. It is the aldehyde or α-

hydroxy ketone functionality of this open-chain form that undergoes oxidation.

- **Example: D-Glucose**.
  - Glucose exists predominantly in cyclic pyranose and furanose forms, but it is in equilibrium with its open-chain form, which has a free aldehyde group at C1.
  - This aldehyde group is easily oxidized to a carboxylic acid group, making glucose a reducing sugar. When glucose reduces Tollen's reagent, a silver mirror is formed.

- **Non-Reducing Sugars:**
  - **Definition:** Non-reducing sugars are carbohydrates in which the **anomeric carbons of *all* constituent monosaccharide units are involved in forming a glycosidic bond**. This means there are no free hemiacetal or hemiketal groups that can open up to form an aldehyde or ketone in solution. Consequently, they cannot be oxidized by mild oxidizing agents.
  - **Explanation with Structural Implication:** In non-reducing sugars, the linkage between the monosaccharide units "locks" the anomeric carbons, preventing the ring-opening process that is necessary for the formation of the reactive aldehyde or ketone group.
  - **Example: Sucrose**.
    - Sucrose is formed by a glycosidic bond between C1 (the anomeric carbon) of glucose and C2 (the anomeric carbon) of fructose.
    - Since both anomeric carbons are involved in the glycosidic linkage, neither the glucose unit nor the fructose unit can open up to expose a free aldehyde or ketone group.

- Therefore, sucrose cannot reduce Tollen's or Fehling's reagents and is classified as a non-reducing sugar.

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6. (a) Draw Fischer projection of β-D (+) - glucose, convert it to Howarth structure and then to the chair conformation.

   Note: As per your instructions, I will not create diagrams. I will describe how to construct each representation.

   - **Fischer Projection of β-D (+) - Glucose:**

     i. Draw a vertical line representing the main carbon chain, with C1 at the top and C6 at the bottom.

     ii. Horizontal lines at each chiral carbon (C2, C3, C4, C5) represent bonds coming out of the plane towards you.

     iii. Vertical lines represent bonds going into the plane away from you.

     iv. For **D-glucose**, the hydroxyl group on the penultimate carbon (C5) is on the **right**.

     v. For the β **anomer** of D-glucose, the hydroxyl group on the anomeric carbon (C1) is typically drawn on the **left** in the Fischer projection (which corresponds to "up" in the Haworth projection when cyclized).

     vi. The specific arrangement for D-glucose from top to bottom (C1 to C5, excluding C6 which is CH_2OH):

     - C1 (anomeric carbon): H (right), **OH (left)** (for β-D-glucose)
     - C2: OH (right), H (left)
     - C3: H (right), OH (left)
     - C4: OH (right), H (left)

- C5: OH (right), H (left) (This OH reacts with C1 to form the ring)
- C6: CH_2OH group (at the bottom).

- **Haworth Structure of β-D (+) - Glucose (Pyranose form):**

vii. Draw a six-membered ring (a hexagon) representing the glucose pyranose ring. Place the oxygen atom in the upper right-hand corner of the hexagon.

viii. Number the carbon atoms clockwise, starting with C1 to the right of the oxygen. C6 is typically drawn as a substituent on C5.

ix. **General rule:** Groups that are on the **right** in the Fischer projection are drawn **down** in the Haworth projection. Groups that are on the **left** in the Fischer projection are drawn **up** in the Haworth projection.

x. For **D-glucose**, the CH_2OH group at C5 is drawn **up**.

xi. Specific arrangement for **β-D-glucose** in Haworth:

- C1 (anomeric carbon): OH is **up** (since it was on the left in Fischer). H is down.
- C2: OH is **down** (from right in Fischer). H is up.
- C3: OH is **up** (from left in Fischer). H is down.
- C4: OH is **down** (from right in Fischer). H is up.
- C5: CH_2OH is **up**. H is down.

- **Chair Conformation of β-D (+) - Glucose:**

xii. Draw a chair conformation for a six-membered ring.

xiii. Place the ring oxygen atom at one of the "up" positions (e.g., the upper-right back position) of the chair.

xiv. Number the carbons from C1 to C5 in a clockwise manner, starting from the carbon adjacent to the oxygen on the right. C6 is a substituent on C5.

xv. **General rule:** Groups that are "up" in the Haworth projection are drawn in "up" positions (either axial or equatorial) in the chair conformation. Groups that are "down" in the Haworth projection are drawn in "down" positions.

xvi. For β**-D-glucose**, the most stable chair conformation places all the bulky hydroxyl groups and the CH_2OH group in **equatorial positions** to minimize steric strain.

xvii. Specific arrangement for the most stable chair of β**-D-glucose**:

- C1 (anomeric carbon): The β-OH is in an **equatorial (up)** position. The H is in an axial (down) position.
- C2: OH is in an **equatorial (down)** position. H is in an axial (up) position.
- C3: OH is in an **equatorial (up)** position. H is in an axial (down) position.
- C4: OH is in an **equatorial (down)** position. H is in an axial (up) position.
- C5: CH_2OH is in an **equatorial (up)** position. H is in an axial (down) position.
- This conformation, with all large substituents equatorial, is highly favored and is often referred to as the "all-equatorial" chair for β-D-glucose.

7. (b) Explain oxidative rancidity in oils and fats giving a suitable example. Suggest a method to prevent it.

- **Oxidative Rancidity in Oils and Fats:**
    - **Explanation:** Oxidative rancidity is the primary cause of spoilage in oils and fats, leading to undesirable off-flavors and odors. It's a chemical process where **unsaturated fatty acids** (those containing carbon-carbon double bonds) within the triglyceride structure react with **molecular oxygen** from the air. This reaction is a **free-radical chain mechanism**, often initiated by light, heat, or metal ions.
    - The process involves:
        xviii. **Initiation:** A hydrogen atom (typically from a carbon adjacent to a double bond, an allylic or bis-allylic carbon) is abstracted, forming a fatty acid radical.
        xix. **Propagation:** This radical reacts with oxygen to form a peroxyl radical, which then abstracts a hydrogen from another unsaturated fatty acid, forming a hydroperoxide and a new fatty acid radical, thus continuing the chain.
        xx. **Termination:** Two radicals combine to form stable, non-radical products. However, the hydroperoxides formed during propagation are unstable and break down into volatile compounds like **aldehydes, ketones, and short-chain carboxylic acids**. These volatile compounds are responsible for the characteristic unpleasant, "rancid" smell and taste.
    - **Factors that accelerate rancidity:** High degree of unsaturation (more double bonds), exposure to light (especially UV), heat, and the presence of transition metal ions (e.g., iron, copper) or certain enzymes.

- **Suitable Example:**
    - **Sunflower oil** or **Soybean oil** are common examples of oils susceptible to oxidative rancidity because they are rich in polyunsaturated fatty acids (like linoleic acid). If a bottle of sunflower oil is left open and exposed to light and air for an extended period, it will develop a stale, "painty," or "fishy" odor and taste due to the formation of breakdown products like hexanal and nonanal. This is particularly noticeable after repeated heating, such as in deep-frying.
- **Method to Prevent It:**
    - **Addition of Antioxidants:** This is one of the most effective and widely used methods. Antioxidants are substances that delay or inhibit the oxidation of fats and oils by interfering with the free-radical chain reaction. They typically act as **free-radical scavengers**, donating hydrogen atoms to the fatty acid radicals or peroxyl radicals, thereby forming more stable, less reactive radicals of themselves and terminating the chain.
    - **Examples of Antioxidants:**
        - **Synthetic:** Butylated Hydroxyanisole (BHA), Butylated Hydroxytoluene (BHT), Tertiary-Butylhydroquinone (TBHQ).
        - **Natural:** Tocopherols (Vitamin E), Ascorbic acid (Vitamin C) and its esters (e.g., ascorbyl palmitate), rosemary extract.
    - **Other common preventive measures:** Storing oils in **dark, airtight containers** (to limit light and oxygen exposure), **refrigeration** (to slow down reaction rates), and adding **metal chelators** (like citric acid) to sequester pro-oxidant metal ions.

8. (c) Define saponification value and give its significance. Calculate the saponification value of glyceryl tripalmitate?

- **Saponification Value (or Saponification Number):**
    - **Definition:** The saponification value is defined as the **number of milligrams (mg) of potassium hydroxide (**KOH**) required to completely saponify (hydrolyze) one gram (g) of fat or oil**. Saponification is the alkaline hydrolysis of triglycerides (fats and oils) to yield glycerol and the potassium salts of fatty acids (which are soaps).
- **Significance:**
    h. **Average Molecular Weight/Chain Length:** The saponification value is **inversely proportional** to the average molecular weight of the fatty acids present in the fat or oil.
        - A **high saponification value** indicates that the fat or oil contains a greater proportion of **short-chain fatty acids**. This means more KOH is needed per gram because there are more ester linkages per unit mass to hydrolyze.
        - A **low saponification value** indicates that the fat or oil is composed predominantly of **long-chain fatty acids**. Fewer moles of KOH are required per gram of the fat.

    i. **Identification and Purity:** It serves as a valuable parameter for the **identification and assessment of the purity** of a particular fat or oil. Each fat or oil has a characteristic range of saponification values.

    j. **Quality Control:** It's used in quality control for edible oils and in the soap and detergent industries, as it relates to the amount of alkali needed for soap production.

- **Calculation of the Saponification Value of Glyceryl Tripalmitate:**

- **Structure of Glyceryl Tripalmitate:** This is a triglyceride formed from one molecule of glycerol and three molecules of palmitic acid (C_{16} saturated fatty acid).
- **Molecular Formula of Palmitic Acid:** $CH_3(CH_2)_{14}COOH$ or $C_{16}H_{32}O_2$.
- **Molar Mass of Palmitic Acid ($C_{16}H_{32}O_2$):**
  - $(16 \times 12.01) + (32 \times 1.008) + (2 \times 16.00) = 192.16 + 32.256 + 32.00 = 256.416$ g/mol
- **Molar Mass of Glyceryl Tripalmitate ($C_{51}H_{98}O_6$):**
  - A triglyceride is formed from 1 glycerol ($C_3H_8O_3$) and 3 fatty acids, with the elimination of 3 water molecules.
  - Molar mass = (Molar Mass of Glycerol) + (3 × Molar Mass of Palmitic Acid) - (3 × Molar Mass of Water)
  - Molar Mass of Glycerol: $(3 \times 12.01) + (8 \times 1.008) + (3 \times 16.00) = 36.03 + 8.064 + 48.00 = 92.094$ g/mol
  - Molar Mass of Water: $(2 \times 1.008) + 16.00 = 18.016$ g/mol
  - Molar Mass of Glyceryl Tripalmitate = $92.094 + (3 \times 256.416) - (3 \times 18.016)$
  - $= 92.094 + 769.248 - 54.048$
  - $= 807.294$ g/mol
- **Saponification Reaction:**
  - 1 mole of triglyceride reacts with 3 moles of KOH for complete saponification.
  - Glyceryl Tripalmitate + 3 KOH → Glycerol + 3 Potassium Palmitate
- **Molar Mass of KOH:**

- K: 39.098 g/mol
- O: 16.00 g/mol
- H: 1.008 g/mol
- Molar mass of KOH $= 39.098 + 16.00 + 1.008 = 56.106$ g/mol

- **Calculation of Saponification Value:**
  - Amount of KOH needed for 1 mole of glyceryl tripalmitate = 3 moles $\times$ 56.106 g/mol $= 168.318$ g KOH
  - Convert grams of KOH to milligrams: 168.318 g $\times$ 1000 mg/g $= 168318$ mg KOH
  - Saponification Value = $\frac{\text{mg of KOH}}{\text{g of fat/oil}}$
  - Saponification Value = $\frac{168318 \text{ mg KOH}}{807.294 \text{ g glyceryl tripalmitate}}$
  - Saponification Value ≈ 208.5

The saponification value of glyceryl tripalmitate is approximately 208.5 mg KOH/g.