1. (a) An alcohol A having molecular formula C_2H_6O, when treated with conc. H_2SO_4 gives an alkene B. When B is bubbled through bromine water (Br_2/H_2O) and the product obtained is dehydrohalogenated with an excess of strong base sodamide a new compound C is obtained. Compound C is also obtained by reacting calcium carbide with water. Compound C gives D when treated with dilute H_2SO_4 in presence of $HgSO_4$. Identify A to D. Write the sequence of chemical reactions involved.

- **Identification of A to D:**
    - **A: Ethanol (C_2H_6O)** - An alcohol with the given molecular formula.
    - **B: Ethene (C_2H_4)** - Formed by dehydration of ethanol.
    - **C: Ethyne (C_2H_2)** - Formed by dehydrohalogenation of 1,2-dibromoethane (product of B with Br_2/H_2O) and also by the reaction of calcium carbide with water.
    - **D: Ethanal (Acetaldehyde, CH_3CHO)** - Formed by hydration of ethyne.

- **Sequence of chemical reactions involved:**
    a. **Dehydration of Alcohol (A to B):**
        - C_2H_5OH (A) $\xrightarrow{\text{Conc. } H_2SO_4, \text{ Heat}}$ $CH_2=CH_2$ (B) + H_2O
    b. **Bromination of Alkene (B to 1,2-dibromoethane):**
        - $CH_2=CH_2$ (B) + $Br_2/H_2O \rightarrow BrCH_2\text{-}CH_2Br$ (1,2-dibromoethane)
        - (Note: While bromine water gives bromohydrin, in this context, for subsequent dehydrohalogenation with excess strong base to form an alkyne, it implies a dihalide or sufficient elimination to form the alkyne. Typically, Br_2/CCl_4 or direct halogenation would give the dibromide.

However, if Br_2/H_2O is strictly followed, it would give 2-bromoethanol. But to get an alkyne from it with excess sodamide, it implies a vicinal dihalide or a pathway that leads to it, or it could be implying the direct addition of bromine to the double bond.) Assuming it leads to 1,2-dibromoethane for the formation of C.

c. **Dehydrohalogenation with Sodamide (1,2-dibromoethane to C):**

- $BrCH_2\text{-}CH_2Br + 2NaNH_2$ (excess) $\rightarrow$ HC≡CH (C) + 2NaBr + $2NH_3$

d. **Reaction of Calcium Carbide with Water (formation of C):**

- $CaC_2 + 2H_2O \rightarrow$ HC≡CH (C) + $Ca(OH)_2$

e. **Hydration of Alkyne (C to D):**

- HC≡CH (C) + $H_2O \xrightarrow{\text{Dil. } H_2SO_4,\ HgSO_4} CH_3CHO$ (D)

(b) Out of following pairs, which is more stable ? Give reason.

- (i) Benzyl carbocation ; $CH_3CH_2^-$
- (ii) $(CH_3)_3C^+$; CF_3^+

- **(i) Benzyl carbocation vs. $CH_3CH_2^-$:**
  - **More Stable:** Benzyl carbocation
  - **Reason:** Benzyl carbocation is stabilized by resonance. The positive charge on the benzylic carbon can be delocalized over the ortho and para positions of the benzene ring through resonance, leading to greater stability. Ethyl carbanion ($CH_3CH_2^-$) is unstable due to the negative charge on a primary carbon and the electron-donating effect of the methyl group.
- **(ii) $(CH_3)_3C^+$ vs. CF_3^+:**

- **More Stable:** $(CH_3)_3C^+$ (tert-butyl carbocation)
- **Reason:** $(CH_3)_3C^+$ is stabilized by hyperconjugation and the positive inductive effect (+I effect) of the three methyl groups. Each methyl group has three alpha-hydrogens, contributing to hyperconjugation, which effectively disperses the positive charge. CF_3^+ is highly unstable because the highly electronegative fluorine atoms exert a strong electron-withdrawing inductive effect (-I effect), intensifying the positive charge on the carbon and destabilizing the carbocation.

(c) Define the terms racemic mixture. Demonstrate the chemical method for resolving a racemic mixture of an acid, using an example.

- **Racemic Mixture Definition:**
  - A racemic mixture (or racemate) is a mixture containing equal amounts of enantiomers (chiral molecules that are non-superimposable mirror images of each other).
  - It is optically inactive because the optical rotation of one enantiomer is exactly canceled out by the equal and opposite optical rotation of the other enantiomer.
- **Chemical Method for Resolving a Racemic Mixture of an Acid (Example):**
  - **Method:** Diastereomeric salt formation.
  - **Principle:** Enantiomers have identical physical properties (e.g., boiling point, melting point, solubility) and chemical properties when reacting with achiral reagents. However, they react differently with chiral reagents. By reacting a racemic acid with a chiral base, diastereomeric salts are formed. Diastereomers have different physical properties (e.g., different solubilities, melting points), which allows for their separation by techniques like fractional crystallization. Once separated, the individual

enantiomeric acids can be regenerated from their respective diastereomeric salts.

- **Example:** Resolution of a racemic carboxylic acid using a chiral amine.
  - **Step 1: Diastereomeric Salt Formation:**
    - Consider a racemic carboxylic acid, (R,S)-HA (where HA represents the acid).
    - React it with a pure enantiomeric chiral base, such as (R)-(-)-α-phenylethylamine.
    - (R,S)-HA + (R)-(-)-α-phenylethylamine → [(R)-HA · (R)-amine$^+$] + [(S)-HA · (R)-amine$^+$]
    - The products are two diastereomeric salts: (R)-acid-(R)-amine salt and (S)-acid-(R)-amine salt. These are diastereomers because they are stereoisomers that are not mirror images of each other (one has R,R configuration and the other has S,R configuration).
  - **Step 2: Separation of Diastereomeric Salts:**
    - Since diastereomers have different solubilities, they can be separated by fractional crystallization from a suitable solvent (e.g., ethanol, water). One diastereomeric salt will crystallize out preferentially, while the other remains in solution.
  - **Step 3: Regeneration of Enantiomeric Acids:**
    - Each separated diastereomeric salt is then treated with a strong mineral acid (e.g., dilute HCl). This protonates the amine part of the salt, regenerating the pure enantiomeric carboxylic acid and forming

the hydrochloride salt of the chiral amine, which can often be separated.

- [(R)-HA · (R)-amine$^+$] + HCl → (R)-HA (pure) + (R)-amine·HCl
- [(S)-HA · (R)-amine$^+$] + HCl → (S)-HA (pure) + (R)-amine·HCl

- This process yields the two pure enantiomers of the carboxylic acid.

2. (a) How many stereoisomers are possible for tartaric acid ? Draw their Fischer projection structures, describe the relationships between them and identify which are optically active and which are optically inactive.

- **Number of Stereoisomers:**
  - Tartaric acid has two chiral centers. The maximum number of stereoisomers for a molecule with 'n' chiral centers is 2^n. So, $2^2 = 4$ stereoisomers are possible in theory.
  - However, tartaric acid is a special case because it has a plane of symmetry when drawn in a specific conformation, leading to a meso compound. Therefore, there are actually **three** stereoisomers for tartaric acid.
- **Fischer Projection Structures:**
  - **L-(+)-Tartaric acid:**
    - COOH
    - |
    - H - C - OH
    - |
    - HO - C - H

        - |
        - COOH
    - **D-(-)-Tartaric acid:**
        - COOH
        - |
        - HO - C - H
        - |
        - H - C - OH
        - |
        - COOH
    - **Meso-Tartaric acid:**
        - COOH
        - |
        - H - C - OH
        - |
        - H - C - OH
        - |
        - COOH
        - (Note: For meso-tartaric acid, if you draw the top chiral center as R and the bottom as S, or vice versa, it will be the same meso compound due to the internal plane of symmetry.)

- **Relationships between them:**

- L-(+)-Tartaric acid and D-(-)-Tartaric acid are **enantiomers** (non-superimposable mirror images).
- Meso-Tartaric acid is a **diastereomer** of both L-(+)-Tartaric acid and D-(-)-Tartaric acid.
- Meso-Tartaric acid is also **superimposable on its own mirror image**, meaning it is achiral despite having chiral centers.

- **Optical Activity:**
  - **L-(+)-Tartaric acid:** Optically active (rotates plane-polarized light to the right, indicated by +)
  - **D-(-)-Tartaric acid:** Optically active (rotates plane-polarized light to the left, indicated by -)
  - **Meso-Tartaric acid:** Optically inactive (due to the presence of an internal plane of symmetry, the optical rotation caused by one chiral center is canceled out by the equal and opposite rotation caused by the other chiral center).

3. (a) Draw all conformations of n-butane resulting from rotation about the C2-C3 bond and arrange them in order of increasing stability, providing reasons for the stability order. Also, illustrate the potential energy diagram.

- **Conformations of n-Butane (Newman Projections looking down C2-C3 bond):**
  - Let's consider the methyl groups as the bulkier substituents.

  f. **Anti Conformation:**

    - Two methyl groups are 180° apart (farthest from each other).
    - H H
    - | /

- CH_3--C2---C3--CH_3
- | \
- H H
- (Front carbon H above, CH3 right, H left; Rear carbon H below, CH3 left, H right)

g. **Gauche Conformation:**

- Two methyl groups are 60° apart.
- H CH_3
- | /
- CH_3--C2---C3--H
- | \
- H H
- (There are two identical gauche conformations)

h. **Eclipsed Conformation (Methyl-Methyl Eclipsed):**

- Two methyl groups are directly opposite each other (0° torsion angle).
- H H
- | /
- CH_3--C2---C3--H
- | \
- H H
- (Front carbon CH3 right-up, H left-up, H down; Rear carbon CH3 directly behind front CH3, H directly behind H)

- (More specifically, a fully eclipsed conformation where CH_3 eclipses CH_3, and H eclipses H. This is the highest energy one).

i. **Partially Eclipsed Conformation (Methyl-Hydrogen Eclipsed):**

- Methyl group eclipses hydrogen.
- H CH_3
- | /
- CH_3--C2---C3--H
- | \
- H H
- (Front carbon CH3 right-up, H left-up, H down; Rear carbon H directly behind CH3, CH3 directly behind H)
- (There are two identical partially eclipsed conformations).

- **Order of Increasing Stability (Lowest Energy to Highest Energy):**

j. **Anti (Most Stable):**

- **Reason:** This conformation has the methyl groups (the largest substituents) as far apart as possible (180° dihedral angle). This minimizes steric strain (repulsion between electron clouds of non-bonded atoms) and torsional strain (repulsion between bonding electrons when bonds are eclipsed). It represents the global energy minimum.

k. **Gauche:**

- **Reason:** The methyl groups are 60° apart. There is some steric strain due to the close proximity of the methyl groups, known as gauche-butane interaction (a type of

van der Waals strain). However, there is no torsional strain. It is less stable than anti but significantly more stable than eclipsed conformations.

l. **Partially Eclipsed (Methyl-Hydrogen Eclipsed):**

- **Reason:** This conformation involves an eclipsing interaction between a methyl group and a hydrogen atom, and between two hydrogen atoms. This introduces torsional strain, making it less stable than gauche.

m. **Eclipsed (Methyl-Methyl Eclipsed) / Fully Eclipsed:**

- **Reason:** This is the least stable conformation. It has the greatest steric strain due to the direct eclipsing of the two methyl groups (the largest substituents), and also significant torsional strain due to all bonds being eclipsed. This represents the global energy maximum.

- **Potential Energy Diagram (Illustrative):** (Imagine a sine-wave like curve for energy vs. dihedral angle)
  - Y-axis: Potential Energy
  - X-axis: Dihedral Angle (rotation about C2-C3 bond from 0° to 360°)
  - **Points on the curve:**
    - 0° (Fully Eclipsed / CH_3-CH_3 Eclipsed): Highest Energy Peak
    - 60° (Gauche): Local Energy Minimum (higher than Anti)
    - 120° (Partially Eclipsed / CH_3-H Eclipsed): Local Energy Peak (lower than Fully Eclipsed)
    - 180° (Anti): Lowest Energy Minimum (Global Minimum)
    - 240° (Gauche): Local Energy Minimum (same as 60°)

        - 300° (Partially Eclipsed / CH_3-H Eclipsed): Local Energy Peak (same as 120°)
        - 360° (Fully Eclipsed / CH_3-CH_3 Eclipsed): Highest Energy Peak (same as 0°)
    - The diagram would show the energy fluctuating as the C2-C3 bond rotates, with minima at anti and gauche conformations and maxima at eclipsed conformations, with the fully eclipsed conformation being the highest energy.

(b) (i) Classify the following into Electrophiles or Nucleophiles with explanation. $AlCl_3$, BF_3, CN^-, NH_3, SO_3

- **$AlCl_3$ (Aluminum Chloride):**
    - **Classification:** Electrophile
    - **Explanation:** Aluminum in $AlCl_3$ has an incomplete octet (only 6 valence electrons). It is a Lewis acid, meaning it can accept a pair of electrons to complete its octet. Therefore, it is electron-deficient and seeks electron-rich centers.
- **BF_3 (Boron Trifluoride):**
    - **Classification:** Electrophile
    - **Explanation:** Similar to $AlCl_3$, Boron in BF_3 also has an incomplete octet (only 6 valence electrons). It is a strong Lewis acid and readily accepts a lone pair of electrons from electron-rich species to achieve a stable octet.
- **CN^- (Cyanide Ion):**
    - **Classification:** Nucleophile
    - **Explanation:** The cyanide ion has a negative charge and a lone pair of electrons on both carbon and nitrogen atoms. It is electron-rich and can donate this electron pair to an electron-deficient center (electrophile).

- **NH_3 (Ammonia):**
    - **Classification:** Nucleophile
    - **Explanation:** The nitrogen atom in ammonia has a lone pair of electrons. It is an electron-rich species and can donate this lone pair to form a new bond with an electrophile. It acts as a Lewis base.
- **SO_3 (Sulfur Trioxide):**
    - **Classification:** Electrophile
    - **Explanation:** Sulfur in SO_3 is highly oxidized and has a formal positive charge due to bonding with three highly electronegative oxygen atoms. Although sulfur has a complete octet (can expand it), the strong electron-withdrawing effect of oxygen makes the sulfur atom very electron-deficient and thus susceptible to nucleophilic attack. It can accept electron pairs, for example, in reactions like sulfonation.

(b) (ii) Define the terms optical rotation and specific rotation. Explain the factors on which they depend.

- **Optical Rotation:**
    - **Definition:** Optical rotation refers to the property of certain chiral substances to rotate the plane of plane-polarized light when it passes through a solution of the substance.
    - **Measurement:** It is measured in degrees using a polarimeter.
    - **Direction:** The rotation can be clockwise (dextrorotatory, denoted by '+') or counter-clockwise (levorotatory, denoted by '-').
- **Specific Rotation ($[\alpha]$):**
    - **Definition:** Specific rotation is a standardized physical constant that represents the observed optical rotation of a substance

under specific conditions, normalized for concentration and path length. It allows for comparison of the optical activity of different substances.

- **Formula:** $[\alpha]_D^T = \frac{\alpha}{c \times l}$
  - Where:
    - α = Observed optical rotation in degrees
    - T = Temperature in degrees Celsius
    - D = Wavelength of light (usually sodium D-line, 589 nm)
    - c = Concentration of the solution in grams per milliliter (g/mL) for solutions, or density in g/mL for neat liquids.
    - l = Path length of the sample cell in decimeters (dm).
- **Units:** Degrees (°) for neat liquids, or (°) mL g^{-1} dm^{-1} for solutions (often just stated as degrees, with units implied by context).

- **Factors on which Optical Rotation and Specific Rotation Depend:**

n. **Nature of the Substance:**

- **Chirality:** Only chiral molecules (those lacking a plane of symmetry or center of inversion) can be optically active. Achiral molecules do not rotate plane-polarized light.
- **Molecular Structure:** The magnitude and direction of rotation are inherent properties of a specific chiral compound. Different enantiomers of the same compound

will rotate light by the same magnitude but in opposite directions.

o. **Concentration of the Solution (c):**

- **Effect:** For a given path length, a higher concentration of the optically active substance will result in a larger observed optical rotation. Specific rotation normalizes for this.

p. **Path Length of the Sample Cell (l):**

- **Effect:** A longer path length of the light through the solution will result in a larger observed optical rotation. Specific rotation normalizes for this.

q. **Temperature (T):**

- **Effect:** Temperature can influence specific rotation because it affects intermolecular interactions, solvation, and equilibrium between conformers, which in turn can affect how the molecules interact with plane-polarized light. Specific rotation is usually reported at a standard temperature (e.g., 20°C or 25°C).

r. **Wavelength of Light (λ):**

- **Effect:** The degree of rotation is dependent on the wavelength of the light used. This phenomenon is called optical rotatory dispersion (ORD). The sodium D-line (589 nm) is commonly used as a standard wavelength.

s. **Solvent (for solutions):**

- **Effect:** The nature of the solvent can affect specific rotation. Solvents can interact with the solute molecules (e.g., through hydrogen bonding, dipole-dipole interactions), influencing their conformation or aggregation, which can change the observed rotation.

(c) Assign the R/S nomenclature at all the chiral centre(s) present in the following molecules : (Do any two).

- (i) [Structure: Lactic Acid]
- (ii) [Structure: Glyceraldehyde]
- (iii) [Structure: Tartaric Acid]

(i) Lactic Acid:

- **Structure:**
  - COOH
  - |
  - H - C* - OH
  - |
  - CH_3
- **Chiral Center:** The carbon atom bonded to -H, -OH, -COOH, and -CH_3.
- **Prioritization of Groups (based on atomic number):**
  t. -OH (Oxygen, atomic number 8)
  u. -COOH (Carbon bonded to O,O,H) - C=O takes precedence over C-O.
  v. -CH_3 (Carbon bonded to H,H,H)
  w. -H (Hydrogen, atomic number 1)
- **Orientation:** The lowest priority group (-H) is on the horizontal line (towards the viewer) in the typical Fischer projection.
- **Assignment:**

- If -H is on horizontal, trace 1-2-3. If it's clockwise (R), the actual configuration is S. If it's counter-clockwise (S), the actual configuration is R.
- Tracing 1(-OH) → 2(-COOH) → 3(-CH_3) is clockwise.
- Since -H is on the horizontal, the configuration is **(S)** for the Lactic Acid shown. (If H were on vertical, it would be R).

(ii) Glyceraldehyde:

- **Structure:**
  - CHO
  - |
  - H - C* - OH
  - |
  - CH_2OH
- **Chiral Center:** The carbon atom bonded to -H, -OH, -CHO, and -CH_2OH.
- **Prioritization of Groups:**
  x. -OH (Oxygen, atomic number 8)
  y. -CHO (Carbon bonded to O,O,H; higher priority than -CH_2OH because of C=O)
  z. -CH_2OH (Carbon bonded to O,H,H)
  aa. -H (Hydrogen, atomic number 1)
- **Orientation:** The lowest priority group (-H) is on the horizontal line (towards the viewer).
- **Assignment:**
  - Tracing 1(-OH) → 2(-CHO) → 3(-CH_2OH) is clockwise.

- Since -H is on the horizontal, the configuration is **(S)** for the Glyceraldehyde shown. (This is generally D-Glyceraldehyde which is (R), so depending on how the structure is drawn, it can be R or S. The structure provided in text is H-C-OH which is S).

(iii) Tartaric Acid:

- **Structure (Assuming L-(+)-Tartaric acid from 2(a) structure):**
  - COOH (C1)
  - |
  - H - C* - OH (C2)
  - |
  - HO - C* - H (C3)
  - |
  - COOH (C4)
- **Chiral Centers:** C2 and C3.
- **For C2 (Top chiral carbon):**
  - **Groups:** -OH, -COOH (top), -CH(OH)COOH (bottom part), -H
  - **Prioritization:**
    i. -OH
    ii. -COOH (top group, as it's directly connected and is C=O)
    iii. -CH(OH)COOH (bottom part, carbon attached to OH,COOH)
    iv. -H
  - **Orientation:** -H is on the horizontal.

- **Assignment:** 1(-OH) → 2(-COOH) → 3(-CH(OH)COOH) is clockwise. Since H is horizontal, the configuration at C2 is **(S)**.

- **For C3 (Bottom chiral carbon):**
  - **Groups:** -OH, -CH(OH)COOH (top part), -COOH (bottom), -H
  - **Prioritization:**
    v. -OH
    vi. -CH(OH)COOH (top part)
    vii. -COOH (bottom group)
    viii. -H
  - **Orientation:** -H is on the horizontal.
  - **Assignment:** 1(-OH) → 2(-CH(OH)COOH) → 3(-COOH) is counter-clockwise. Since H is horizontal, the configuration at C3 is **(R)**.

- **Conclusion for L-(+)-Tartaric Acid:** The configuration is **(2S, 3R)**.
  - (Note: If the meso-tartaric acid structure from 2(a) was considered for C3 with H on left and OH on right, its configuration would be S, leading to (2R, 3S) or (2S, 3R) depending on drawing, confirming internal symmetry. For D-(-)-Tartaric acid, the configuration would be (2R, 3S).)

4. (a) Complete the following set of chemical reactions :
   - Cyclohexane $\xrightarrow{Br_2/hv}$ A $\xrightarrow{\text{Alcoholic KOH}}$ B $\xrightarrow{NBS}$ C

- **Reaction Sequence:**

  bb. **Cyclohexane** $\xrightarrow{Br_2/hv}$ **A**

  - **Reaction Type:** Free radical halogenation (bromination) of an alkane. Light (hv) initiates the reaction.

- **Product A:** Bromocyclohexane
  - (A: $C_6H_{11}Br$, Cyclohexyl bromide)

cc. **A** $\xrightarrow{\text{Alcoholic KOH}}$ **B**

- **Reaction Type:** Dehydrohalogenation (elimination reaction, E2) using a strong base (alcoholic KOH).
- **Product B:** Cyclohexene
  - (B: C_6H_{10}, Cyclohexene)

dd. **B** $\xrightarrow{\text{NBS}}$ **C**

- **Reaction Type:** Allylic bromination using N-Bromosuccinimide (NBS). NBS selectively brominates at the allylic position (carbon adjacent to a double bond) under radical conditions.
- **Product C:** 3-Bromocyclohexene (or Cyclohex-2-en-1-yl bromide)
  - (C: C_6H_9Br, 3-Bromocyclohexene)

(b) trans-2-Butene upon bromination gives meso-dibromo product, while cis-2-butene gives racemic mixture ?

- **Explanation:** This phenomenon is an example of **stereospecificity** in addition reactions to alkenes, specifically electrophilic addition of halogens. The key factor is the **anti-addition** mechanism.
- **Bromination of trans-2-Butene:**
  - **Starting Material:** trans-2-Butene (methyl groups on opposite sides of the double bond).
  - **Mechanism:** When Br_2 adds to trans-2-butene, it proceeds via a cyclic bromonium ion intermediate. The two bromine atoms add from opposite faces of the double bond (anti-addition).

- **Product:** The anti-addition to trans-2-butene (which is an achiral molecule) leads to a single, achiral product which is a **meso compound**. In this case, it's meso-2,3-dibromobutane.
- **Why Meso:** The two new chiral centers formed (C2 and C3) have opposite configurations (one R, one S), and the molecule possesses an internal plane of symmetry. Therefore, the overall molecule is achiral and optically inactive.

- **Bromination of cis-2-Butene:**
  - **Starting Material:** cis-2-Butene (methyl groups on the same side of the double bond).
  - **Mechanism:** Similar to trans-2-butene, bromination proceeds via a cyclic bromonium ion intermediate, and the two bromine atoms add from opposite faces of the double bond (anti-addition).
  - **Product:** The anti-addition to cis-2-butene (also an achiral molecule) leads to the formation of a **racemic mixture** of enantiomers. In this case, it's (2R,3R)-2,3-dibromobutane and (2S,3S)-2,3-dibromobutane.
  - **Why Racemic:** Since the cis-alkene is symmetrical, attack from either face is equally likely, leading to two enantiomeric products in equal amounts. Each product formed is chiral, and they are non-superimposable mirror images.

- **In summary:**
  - **trans-Alkene + Anti-addition → Meso Compound**
  - **cis-Alkene + Anti-addition → Racemic Mixture**

(b) 2-Methylpropane is brominated at 125°C in the presence of light. What % of product will be 2-bromo-2-methylpropane. The relative reactivity for 1°, 2°, 3° hydrogens are 1, 82 and 1600, respectively.

- **Analysis of 2-Methylpropane (Isobutane):**
    - **Structure:** $(CH_3)_3CH$
    - **Types of Hydrogens:**
        - **Primary (1°):** There are three methyl groups, each with three primary hydrogens. So, $3 \times 3 = 9$ primary hydrogens.
        - **Tertiary (3°):** There is one hydrogen attached to the tertiary carbon. So, 1 tertiary hydrogen.
        - (There are no secondary (2°) hydrogens in 2-methylpropane).
- **Relative Reactivity of Hydrogens:**
    - 1° H: 1
    - 2° H: 82 (not applicable here, but given)
    - 3° H: 1600
- **Calculate Relative Yields for each type of Hydrogen:**
    - **For 1° H:** (Number of 1° H) × (Relative reactivity of 1° H) = $9 \times 1 = 9$
    - **For 3° H:** (Number of 3° H) × (Relative reactivity of 3° H) = $1 \times 1600 = 1600$
- **Calculate Total Relative Yield:**
    - Total relative yield = (Relative yield from 1° H) + (Relative yield from 3° H) = $9 + 1600 = 1609$
- **Calculate Percentage of 2-bromo-2-methylpropane:**
    - 2-bromo-2-methylpropane is formed when the tertiary hydrogen is substituted.

- Percentage of 2-bromo-2-methylpropane = $\frac{\text{Relative yield from 3° H}}{\text{Total relative yield}} \times 100\%$
- Percentage = $\frac{1600}{1609} \times 100\%$
- Percentage $\approx 99.44\%$

- **Answer:** Approximately **99.44%** of the product will be 2-bromo-2-methylpropane.

(c) Bromination is more selective than chlorination of alkanes ?

- **Yes, bromination is indeed more selective than chlorination of alkanes.**
- **Explanation:**
  - **Selectivity vs. Reactivity:** This difference in selectivity is due to the difference in the reactivity of the halogen radicals (chlorine radical Cl• and bromine radical Br•). Bromine radical is less reactive but more selective, while chlorine radical is more reactive but less selective. This is often explained by the **Hammond Postulate**.
  - **Chlorination:**
    - The C-H bond breaking step (hydrogen abstraction by Cl•) is highly exothermic.
    - According to the Hammond Postulate, for an exothermic reaction, the transition state resembles the reactants. This means that bond breaking (C-H) has not proceeded very far, and the transition state has little radical character on carbon.
    - As a result, the energy differences between forming primary, secondary, or tertiary radicals are not very pronounced in the transition state. The reaction is fast,

and the chlorine radical attacks almost all types of C-H bonds with similar rates, leading to a mixture of products.

- Relative reactivities for 1°, 2°, 3° H are typically around 1:3.8:5.0 (at room temp).

- **Bromination:**
  - The C-H bond breaking step (hydrogen abstraction by Br•) is almost thermoneutral or slightly endothermic.
  - According to the Hammond Postulate, for a thermoneutral or endothermic reaction, the transition state resembles the products (the alkyl radical). This means that significant C-H bond breaking has occurred, and the carbon atom has developed considerable radical character in the transition state.
  - Consequently, the stability of the developing alkyl radical (3° > 2° > 1°) plays a much more significant role in determining the activation energy. The transition state leading to the more stable tertiary radical will have a much lower activation energy than that leading to a primary or secondary radical.
  - This leads to a much larger difference in reaction rates for abstracting different types of hydrogens, resulting in a highly selective formation of the most stable radical (and thus the most substituted bromoalkane).
  - Relative reactivities for 1°, 2°, 3° H are typically around 1:82:1600 (at 125°C, as seen in the previous question).

- **Conclusion:** Bromination is more selective because the rate-determining step (hydrogen abstraction) has a transition state that resembles the more stable alkyl radical, thus favoring the formation of the more substituted bromoalkane. Chlorination is less selective due

to its highly exothermic and reactant-like transition state, where radical stability differences are less influential.

(c) (i) Arrange the following in the decreasing order of their acidic strength and give suitable explanation.

- H-C≡C-H ; $H_2C=CH_2$; H_3C-CH_3

- **Compounds:**
  - H-C≡C-H (Ethyne / Acetylene)
  - $H_2C=CH_2$ (Ethene / Ethylene)
  - H_3C-CH_3 (Ethane)
- **Acidity Trend:** The acidity of C-H bonds in hydrocarbons is related to the stability of the conjugate base (carbanion) formed upon deprotonation. The stability of the carbanion depends on the hybridization of the carbon atom holding the negative charge.
- **Hybridization and s-Character:**
  - Ethyne (alkyne): sp hybridized carbon (50% s-character)
  - Ethene (alkene): sp^2 hybridized carbon (33.3% s-character)
  - Ethane (alkane): sp^3 hybridized carbon (25% s-character)
- **Explanation:**
  - **Electronegativity:** An orbital with a higher percentage of s-character is closer to the nucleus and therefore more electronegative (holds electrons more tightly).
  - **Carbanion Stability:** When a proton is removed from a C-H bond, a carbanion is formed with the negative charge on the carbon. If the carbon atom is more electronegative, it can better accommodate and stabilize the negative charge.

  - **Ethyne:** The sp hybridized carbon in ethyne is the most electronegative among the three. Therefore, the acetylide anion ($HC\equiv C^-$) formed by deprotonation of ethyne is the most stable carbanion, making ethyne the most acidic.
  - **Ethene:** The sp^2 hybridized carbon in ethene is less electronegative than sp but more electronegative than sp^3. Thus, the vinyl anion ($H_2C=CH^-$) is less stable than acetylide but more stable than alkyl anion.
  - **Ethane:** The sp^3 hybridized carbon in ethane is the least electronegative. The ethyl anion ($CH_3CH_2^-$) is highly unstable, making ethane the least acidic.

- **Decreasing Order of Acidic Strength: $H\text{-}C\equiv C\text{-}H > H_2C=CH_2 > H_3C\text{-}CH_3$** (Ethyne > Ethene > Ethane)

(c) (ii) How will you distinguish between 1-butyne and 2-butyne ? Provide the chemical reaction.

- **Distinction:** The key difference between 1-butyne and 2-butyne lies in the presence of a **terminal alkyne (acidic hydrogen)** in 1-butyne and its absence in 2-butyne.
- **1-Butyne (Terminal Alkyne):** $CH_3CH_2C\equiv CH$ (has an acidic hydrogen at the triple bond)
- **2-Butyne (Internal Alkyne):** $CH_3C\equiv CCH_3$ (does not have an acidic hydrogen at the triple bond)
- **Chemical Reaction for Distinction:**
  - **Reagent:** Tollens' reagent (ammoniacal silver nitrate solution, $Ag(NH_3)_2^+OH^-$) or ammoniacal cuprous chloride solution ($Cu(NH_3)_2^+Cl^-$). These reagents react with terminal alkynes to form insoluble metal acetylides, which precipitate out.
  - **Test with Tollens' Reagent:**

        - **1-Butyne:** Reacts with Tollens' reagent to form a white/gray precipitate of silver acetylide.
            - $CH_3CH_2C{\equiv}CH + Ag(NH_3)_2^+OH^- \rightarrow CH_3CH_2C{\equiv}CAg\downarrow$ (white/gray precipitate) + $2NH_3 + H_2O$
        - **2-Butyne:** Does not react with Tollens' reagent as it lacks an acidic terminal hydrogen. No precipitate will be formed.
    - **Test with Ammoniacal Cuprous Chloride Solution:**
        - **1-Butyne:** Reacts to form a red precipitate of copper(I) acetylide.
            - $CH_3CH_2C{\equiv}CH + Cu(NH_3)_2^+Cl^- \rightarrow CH_3CH_2C{\equiv}CCu\downarrow$ (red precipitate) + $2NH_3 + HCl$
        - **2-Butyne:** Does not react. No precipitate will be formed.
- **Conclusion:** The formation of a precipitate with Tollens' reagent or ammoniacal cuprous chloride distinguishes 1-butyne from 2-butyne.

5. Give suitable explanations with mechanism (if involved).
    - (a) 3, 3, 3-Trifluoropropene when treated with HBr gives 3-bromo-1, 1, 1-trifluoropropane ?

- **Question:** Why does 3,3,3-Trifluoropropene (CF_3-$CH{=}CH_2$) react with HBr to give 3-bromo-1,1,1-trifluoropropane (CF_3-CH_2-CH_2Br) and not the Markovnikov product (e.g., CF_3-$CHBr$-CH_3)?
- **Explanation & Mechanism (Anti-Markovnikov Addition due to Electron-Withdrawing Group):**
    - This is an example of **regioselectivity** in electrophilic addition to alkenes, specifically when a strong electron-withdrawing group (like -CF_3) is present.
    - The reaction follows an **electrophilic addition mechanism**, where HBr adds across the double bond. The first step involves

the protonation of the alkene to form the most stable carbocation intermediate.

- **Step 1: Protonation to form Carbocation:**
  - The H^+ from HBr can add to either carbon of the double bond.
  - **Path A (Markovnikov Addition, leading to secondary carbocation):**
    - CF_3-CH=CH_2 + H^+ → CF_3-C^+H-CH_3 (Secondary carbocation)
  - **Path B (Anti-Markovnikov Addition, leading to primary carbocation):**
    - CF_3-CH=CH_2 + H^+ → CF_3-CH_2-C^+H_2 (Primary carbocation)

- **Stability of Carbocations:**
  - Normally, secondary carbocations are more stable than primary carbocations. However, the presence of the highly electron-withdrawing -CF_3 group drastically changes the stability.
  - **CF_3-C^+H-CH_3 (Secondary Carbocation from Path A):** The electron-withdrawing -CF_3 group is directly adjacent to the positive charge (on the α-carbon). This group strongly destabilizes the carbocation by pulling electron density away from an already electron-deficient center. This is a powerful destabilizing inductive effect (-I effect).
  - **CF_3-CH_2-C^+H_2 (Primary Carbocation from Path B):** Here, the electron-withdrawing -CF_3 group is further away from the positive charge (on the β-carbon). While it still exerts an electron-withdrawing effect, its destabilizing effect on the positive charge is significantly diminished

compared to when it is directly adjacent. Therefore, this primary carbocation, despite being primary, is relatively more stable than the highly destabilized secondary carbocation.

- **Step 2: Nucleophilic Attack by Bromide Ion:**
  - The more stable carbocation (CF_3-CH_2-C^+H_2) will be formed preferentially.
  - This carbocation is then attacked by the bromide ion (Br^-).
    - CF_3-CH_2-C^+H_2 + Br^- → CF_3-CH_2-CH_2Br (3-bromo-1,1,1-trifluoropropane)

- **Conclusion:** The strong electron-withdrawing inductive effect of the trifluoromethyl group (-CF_3) destabilizes the carbocation more when it is closer to the positive charge. As a result, the proton adds to the carbon atom that leads to a primary carbocation, placing the positive charge further away from the electron-withdrawing group, leading to an apparent **anti-Markovnikov** regioselectivity.

(b) (i) A 90° in the plane rotation is not allowed in a Fischer projection, while a 180° rotation is permitted. Justify this statement with a suitable example.

- **Fischer Projections Rules:** Fischer projections are a simplified way to represent the three-dimensional arrangement of groups around a chiral center, primarily for molecules with multiple chiral centers. They are subject to strict rules to preserve the correct stereochemistry.
- **Justification:**
  - **90° Rotation (Not Allowed):** A 90° rotation (or any odd multiple of 90°) of a Fischer projection, whether clockwise or counter-clockwise, **inverts the stereochemistry** (changes an R configuration to S, and vice versa). This is because it

interchanges the horizontal and vertical positions of groups. In a standard Fischer projection, horizontal lines represent bonds coming out of the plane of the page (towards the viewer), and vertical lines represent bonds going into the plane of the page (away from the viewer). A 90° rotation flips this convention for the central carbon, effectively creating the enantiomer. Therefore, it is not allowed as it represents a different molecule (enantiomer) and does not maintain the original stereochemistry.

- **180° Rotation (Allowed):** A 180° rotation of a Fischer projection, whether clockwise or counter-clockwise, **maintains the original stereochemistry**. This is because a 180° rotation simply exchanges the positions of the groups at the top and bottom, and the groups at the left and right, respectively. The relative orientation of the horizontal and vertical bonds remains consistent with the Fischer projection rules (horizontal still out, vertical still in). It represents the exact same molecule.

- **Suitable Example (Lactic Acid):**
  - **Original (S)-Lactic Acid Fischer Projection:**
    - COOH
    - |
    - H ---- C ---- OH
    - |
    - CH_3
  - **90° Clockwise Rotation (Not Allowed - Gives (R)-Lactic Acid):**
    - H
    - |

        - CH_3 ---- C ---- COOH
        - |
        - OH
        - (If you prioritize and assign R/S, this will be (R), which is the enantiomer of the original (S). Thus, a 90° rotation changes the molecule.)
    - **180° Rotation (Allowed - Gives Same (S)-Lactic Acid):**
        - CH_3
        - |
        - HO ---- C ---- H
        - |
        - COOH
        - (If you prioritize and assign R/S for this rotated structure, you will still find it to be (S), meaning it's the exact same molecule.)

- **Summary:** To preserve the absolute configuration represented by a Fischer projection, only even number of 90° rotations (i.e., 180°, 360°) are allowed, as they do not change the spatial relationship of the substituents relative to the chiral center.

  (b) (ii) Assign E/Z configuration at all the stereogenic centre(s) present in the following molecule : (Molecular structure provided)

- (Assuming the provided molecular structure for assignment is for a typical alkene, I will provide a general method for E/Z assignment. Since no specific structure is rendered, I will describe the procedure.)

- **E/Z Nomenclature:**

- E/Z nomenclature is used to describe the configuration of substituents around a double bond (geometrical isomerism). It is applied when the Cahn-Ingold-Prelog (CIP) priority rules cannot unambiguously assign 'cis' or 'trans' (e.g., when all four substituents on the double bond are different).
- **Steps for E/Z Assignment:**
    i. **Identify the Stereogenic Center:** This refers to the carbons involved in the double bond that can exhibit cis/trans isomerism (i.e., each carbon of the double bond must be bonded to two different groups).
    ii. **Assign Priorities on Each Carbon:** For each carbon atom of the double bond, assign priorities (1 and 2) to the two groups attached to it using the CIP rules (based on atomic number, higher atomic number gets higher priority).
    iii. **Compare Priorities:**
        - **Z (Zusammen = Together):** If the two higher priority groups (or the two lower priority groups) are on the **same side** of the double bond (either both above or both below the plane of the double bond).
        - **E (Entgegen = Opposite):** If the two higher priority groups (or the two lower priority groups) are on **opposite sides** of the double bond.

- **Example (Hypothetical Alkene):**
    - Consider a double bond with substituents:
        - Cl
        - \
        - C = C

        - / \
        - CH_3 Br
        - H
    - **Left Carbon (C1):**
        - Groups: Cl, H
        - Priorities: Cl (1, atomic number 17) > H (2, atomic number 1)
    - **Right Carbon (C2):**
        - Groups: Br, CH_3
        - Priorities: Br (1, atomic number 35) > CH_3 (2, Carbon, atomic number 6)
    - **Comparison:**
        - The higher priority group on C1 is Cl (above).
        - The higher priority group on C2 is Br (below).
        - Since the two higher priority groups (Cl and Br) are on **opposite sides** of the double bond, the configuration is **(E)**.

- **(To provide a concrete answer, the actual molecular structure would be needed for specific assignment.)**

(c) Define the term hyperconjugation effect and arrange the following free radicals in the increasing order of their stability, giving a suitable reason.

- (i) [Structure: tert-butyl radical]
- (ii) [Structure: isopropyl radical]
- (iii) [Structure: ethyl radical]

- **Hyperconjugation Effect Definition:**
    - Hyperconjugation is a stabilizing interaction that occurs when electrons in a filled sigma (σ) bond (typically C-H or C-C) are delocalized into an adjacent empty or partially filled non-bonding p-orbital, π-orbital, or anti-bonding $\pi *$ orbital.
    - It is often described as "no-bond resonance" because it involves the overlap of a filled sigma orbital with an adjacent empty p-orbital, similar to resonance but without the actual breaking of a bond.
    - In the context of carbocations and free radicals, it involves the delocalization of electron density from adjacent C-H σ bonds into the empty p-orbital (carbocation) or half-filled p-orbital (free radical) of the electron-deficient carbon. This delocalization helps to disperse the positive charge or the unpaired electron, leading to increased stability.
    - The more α-hydrogens (hydrogens on carbons adjacent to the electron-deficient center), the greater the number of hyperconjugative structures and thus the greater the stability.
- **Free Radicals and their Structures:**
    - (i) **tert-butyl radical:** $(CH_3)_3C\bullet$ (Tertiary radical)
        - Carbon with radical is bonded to 3 other carbons.
        - Number of α-hydrogens: $3 \times 3 = 9$ (from the three methyl groups)
    - (ii) **isopropyl radical:** $(CH_3)_2CH\bullet$ (Secondary radical)
        - Carbon with radical is bonded to 2 other carbons.
        - Number of α-hydrogens: $2 \times 3 = 6$ (from the two methyl groups)
    - (iii) **ethyl radical:** $CH_3CH_2\bullet$ (Primary radical)

    - Carbon with radical is bonded to 1 other carbon.
    - Number of α-hydrogens: $1 \times 3 = 3$ (from the one methyl group)

- **Arrangement in Increasing Order of Stability: Ethyl radical < Isopropyl radical < tert-Butyl radical** (Primary < Secondary < Tertiary)
- **Reason for Stability Order:**
    - The stability of free radicals (like carbocations) increases with increasing substitution, primarily due to the **hyperconjugation effect**.
    - More α-hydrogens allow for a greater number of hyperconjugative structures, leading to more extensive delocalization of the unpaired electron. This delocalization spreads out the spin density, effectively stabilizing the radical.
    - **tert-Butyl radical** has 9 α-hydrogens, allowing for maximum hyperconjugation, making it the most stable.
    - **Isopropyl radical** has 6 α-hydrogens, providing significant stabilization.
    - **Ethyl radical** has only 3 α-hydrogens, offering the least hyperconjugative stabilization among the three.
    - (Additionally, the positive inductive effect (+I effect) of alkyl groups also contributes to stabilizing electron-deficient species, but hyperconjugation is generally considered the more dominant factor for radical and carbocation stability.)

6. (a) What do you mean by inductive effect ? Arrange the following carboxylic acids in the increasing order of their acidity strength.
    - (i) CH_3COOH
    - (ii) F-CH_2-CH_2-COOH

- (iii) F_2CH-COOH
- (iv) F_3C-COOH

- **Inductive Effect Definition:**
  - The inductive effect is a permanent displacement of electron density along a sigma (σ) bond chain due to the difference in electronegativity between two bonded atoms or groups.
  - It is a relatively weak, short-range effect that diminishes rapidly with distance from the electronegative atom or electron-donating group.
  - **Electron-Withdrawing Inductive Effect (-I effect):** When an atom or group is more electronegative than carbon, it pulls electron density towards itself, creating a partial positive charge on the carbon chain. Examples: -F, -Cl, -NO_2, -COOH.
  - **Electron-Donating Inductive Effect (+I effect):** When an atom or group is less electronegative than carbon (or has lone pairs that can be effectively donated through polarization), it pushes electron density away from itself. Alkyl groups are often considered to have a weak +I effect.

- **Acidity of Carboxylic Acids and Inductive Effect:**
  - The acidity of a carboxylic acid (R-COOH) is determined by the stability of its conjugate base, the carboxylate anion (R-COO^-).
  - Factors that stabilize the carboxylate anion (by dispersing its negative charge) will increase the acidity of the parent carboxylic acid.
  - Electron-withdrawing groups (-I effect) near the carboxylate group pull electron density away from the negatively charged oxygen atoms, thereby dispersing the charge and stabilizing the anion. The stronger the -I effect and the closer it is to the

carboxylate group, the greater the stabilization and thus the stronger the acid.

- Electron-donating groups (+I effect) destabilize the carboxylate anion by intensifying the negative charge, thus decreasing acidity.

- **Analysis of Given Carboxylic Acids:**
  - (i) **CH_3COOH (Acetic acid):** Methyl group has a weak +I effect, slightly destabilizing the carboxylate anion compared to formic acid.
  - (ii) **F-CH_2-CH_2-COOH (3-Fluoropropanoic acid):** One fluorine atom is present, exerting a -I effect. However, it is two carbons away from the carboxyl group, so its effect is significantly diminished due to distance.
  - (iii) **F_2CH-COOH (Difluoroacetic acid):** Two fluorine atoms are present, both directly attached to the α-carbon (next to the carboxyl group). This exerts a strong combined -I effect, significantly stabilizing the carboxylate anion.
  - (iv) **F_3C-COOH (Trifluoroacetic acid):** Three fluorine atoms are present, all directly attached to the α-carbon. This is the strongest -I effect among all the given compounds, leading to maximum stabilization of the carboxylate anion.

- **Arrangement in Increasing Order of Acidity Strength: CH_3COOH < F-CH_2-CH_2-COOH < F_2CH-COOH < F_3C-COOH**

- **Reason:**
  - The acidity increases with the increasing number of electron-withdrawing fluorine atoms.
  - The -I effect of fluorine atoms stabilizes the conjugate base (carboxylate anion) by delocalizing the negative charge.

- More fluorine atoms mean a stronger overall -I effect.
- The closer the electron-withdrawing group is to the carboxylate group, the greater its impact on acidity. In (iii) and (iv), the fluorines are on the α-carbon, exerting a more significant effect than in (ii) where it is on the β-carbon.

(b) 2, 3-Dimethylbut-2-ene is more stable than 2-methylbut-1-ene. Explain.

- **Structures:**
  - **2,3-Dimethylbut-2-ene:** $(CH_3)_2C=C(CH_3)_2$ (Tetrasubstituted alkene)
  - **2-Methylbut-1-ene:** $CH_2=C(CH_3)CH_2CH_3$ (Disubstituted alkene)
- **Explanation (Stability of Alkenes):**
  - The stability of alkenes increases with increasing substitution of the double bond. This is primarily explained by two factors: **hyperconjugation** and **steric effects**.

ee. **Hyperconjugation:**

- **Definition:** As discussed before, hyperconjugation involves the delocalization of electron density from adjacent C-H σ bonds into the empty $\pi*$ antibonding orbital of the double bond.
- **2,3-Dimethylbut-2-ene:** This alkene has a highly substituted double bond. The two carbons of the double bond are each bonded to two methyl groups.
  - Number of α-hydrogens (hydrogens on carbons directly attached to the double bond): $4 \times 3 = 12$ α-hydrogens.

- More α-hydrogens lead to more hyperconjugative interactions, which effectively delocalizes electron density into the double bond and stabilizes it.

- **2-Methylbut-1-ene:** This alkene is less substituted. The carbon at C1 has two hydrogens, and the carbon at C2 has two methyl groups.
    - Number of α-hydrogens: The carbon at C2 has three α-hydrogens from the methyl group attached to it, and the CH_2CH_3 group has two β-hydrogens. Only the α-hydrogens contribute to hyperconjugation with the double bond. So, the methyl group attached to C2 contributes 3 α-hydrogens.
    - (For 2-methylbut-1-ene, the C2 of the double bond is attached to a methyl and an ethyl group. The number of alpha hydrogens are 3 (from the methyl on C2) + 2 (from the CH2 of the ethyl group, which is alpha to the double bond). So, 5 alpha hydrogens.)
    - Thus, 2,3-dimethylbut-2-ene has significantly more α-hydrogens (12) compared to 2-methylbut-1-ene (5).

ff. **Steric Strain (less significant but contributing):**

- In general, branched alkenes can have less steric strain if the substituents are arranged in a way that relieves crowding around the double bond. However, the primary reason for increased stability with substitution is hyperconjugation.

- **Conclusion:**

- **2,3-Dimethylbut-2-ene is more stable than 2-methylbut-1-ene** because it is a tetrasubstituted alkene with a much greater number of α-hydrogens (12 α-hydrogens) participating in hyperconjugation. This extensive hyperconjugation effectively delocalizes electron density into the double bond, lowering its energy and increasing its stability compared to 2-methylbut-1-ene (which has only 5 α-hydrogens).

(c) Draw and name various Conformations of Cyclohexane and arrange them in increasing order of their Stability. Draw their potential Energy diagram.

- **Conformations of Cyclohexane and their Names:**

gg. **Chair Conformation:**

- **Drawing:** Represented by parallel lines for the two pairs of C-C bonds. One set of parallel lines goes up to the right, and the other goes down to the right. The remaining two carbons form the "seat" and "backrest".
- **Description:** This is the most stable and common conformation. All bond angles are approximately 109.5°, and all adjacent bonds are staggered, minimizing torsional strain. Axial and equatorial hydrogens are distinct.

hh. **Half-Chair Conformation:**

- **Drawing:** One part of the ring is planar (like an alkene), and the other part is in a chair-like arrangement.
- **Description:** This is an unstable, high-energy transition state between the chair and twist-boat conformations. It has significant angle strain and torsional strain due to the planar portion.

ii. **Twist-Boat (or Skew-Boat) Conformation:**

- **Drawing:** Looks like a boat, but with one end twisted. The "flagpoles" are slightly offset.
- **Description:** Less stable than the chair but more stable than the pure boat. It reduces some of the flagpole interactions and torsional strain present in the boat by twisting.

jj. **Boat Conformation:**

- **Drawing:** Resembles a boat, with two "flagpole" hydrogens pointing upwards and two "bowsprit" hydrogens pointing inwards.
- **Description:** Less stable than the chair due to two main reasons:
  - **Flagpole Interactions:** Steric repulsion between the two "flagpole" hydrogens at C1 and C4.
  - **Torsional Strain:** Eclipsing interactions between hydrogens on C2-C3 and C5-C6 bonds.

- **Arrangement in Increasing Order of Stability (Lowest Energy to Highest Energy): Chair < Twist-Boat < Boat < Half-Chair**
- **Reason for Stability Order:**
  - **Chair (Most Stable):** All bonds are staggered, and bond angles are ideal (109.5°), minimizing both torsional strain and angle strain. No significant steric interactions.
  - **Twist-Boat (Intermediate Stability):** Slightly higher energy than the chair due to some torsional strain and minor steric interactions. It's a local minimum on the potential energy surface. It's more stable than the pure boat because the "twist" reduces both flagpole interactions and eclipsing interactions.

- **Boat (Less Stable):** Significantly higher energy than the chair due to flagpole steric interactions and full eclipsing interactions on four of the C-C bonds, leading to considerable torsional strain.
- **Half-Chair (Least Stable / Transition State):** This is the highest energy conformation and represents a transition state between interconverting forms. It has a planar segment with significant angle strain and torsional strain, making it very unstable.

- **Potential Energy Diagram (Illustrative):** (Imagine a curve showing energy fluctuations during ring inversion)
  - Y-axis: Potential Energy
  - X-axis: Reaction Coordinate (representing the conformational changes/ring inversion)
  - **Points on the curve:**
    - Start (Chair, global minimum)
    - Energy increases to a transition state (Half-Chair, highest peak)
    - Energy decreases to a local minimum (Twist-Boat)
    - Energy increases to another transition state (Boat, usually depicted as higher than Twist-Boat)
    - Energy decreases back to a local minimum (Twist-Boat)
    - Energy increases to another transition state (Half-Chair, highest peak)
    - Energy decreases to the Chair (global minimum)
  - The diagram would visually represent the Chair conformation as the lowest energy state, followed by the Twist-Boat as a higher local minimum. The Boat conformation would be a

higher energy state, and the Half-Chair would be the highest energy transition state that must be passed through during the interconversion of chair forms.

7. Write the structure of product(s) A to J :

- **(a) Propene** $\xrightarrow{\text{Cold alkaline } KMnO_4}$ **A**
    - **Reaction:** Syn-dihydroxylation (Baeyer's test)
    - **Product A:** Propane-1,2-diol (Vicinal diol)
        - A: CH_3-CH(OH)-CH_2OH
- **(b) CH_3-CH=CH-CH_3** $\xrightarrow{BH_3.THF}$ **B** $\xrightarrow{H_2O_2,\ NaOH}$ **C**
    - **Reaction:** Hydroboration-oxidation (Anti-Markovnikov hydration)
    - **Product B (Intermediate):** Organoborane (e.g., $(CH_3CH_2CH(CH_3))_2BH$ or trialkylborane)
    - **Product C:** Butan-2-ol (Alcohol)
        - C: $CH_3CH_2CH(OH)CH_3$
- **(c) $H_3C{\equiv}CH_3$** $\xrightarrow{Na,\ Liq\ NH_3}$ **D**
    - **Reaction:** Reduction of alkyne using Sodium in liquid ammonia (Birch Reduction). This specifically converts internal alkynes to trans-alkenes.
    - **Product D:** trans-But-2-ene
        - D: H_3C
        - \
        - C=C
        - / \

    - H CH_3

- **(d) CH_2=CH-CH=CH_2 $\xrightarrow{1 \text{ mole } Br_2}$ E (-80 °C) / F (+80 °C)**
    - **Reaction:** Electrophilic addition to conjugated diene (kinetic vs. thermodynamic control)
    - **E (-80 °C, Kinetic Product):** 1,2-addition product (lower activation energy, formed faster)
        - E: CH_2Br-CHBr-CH=CH_2 (3,4-Dibromobut-1-ene)
    - **F (+80 °C, Thermodynamic Product):** 1,4-addition product (more stable, formed at higher temperatures allowing for equilibration)
        - F: CH_2Br-CH=CH-CH_2Br (1,4-Dibromobut-2-ene, likely predominantly trans)
- **(e) Propene $\xrightarrow{\text{(i) } Hg(OAc)_2 \text{ (ii) } NaBH_4}$ G**
    - **Reaction:** Oxymercuration-demercuration (Markovnikov hydration without rearrangement)
    - **Product G:** Propan-2-ol (Alcohol)
        - G: CH_3-CH(OH)-CH_3
- **(f) Cyclopentene + $COOC_2H_5$ $\xrightarrow{\triangle}$ H**
    - **Reaction:** Diels-Alder Reaction (Cycloaddition of a diene and a dienophile)
    - **(Assuming the dienophile is diethyl maleate or fumarate, or just a generic ester in a specific context. The structure $COOC_2H_5$ alone is ambiguous. Assuming it reacts as a dienophile, e.g., diethyl maleate or fumarate which is typically used for Diels-Alder.)**

- **If dienophile is Ethylene ($CH_2=CH_2$) with ester group (e.g., $CH_2=CHCOOC_2H_5$):**
  - This reaction would form a six-membered ring with a bridge.
  - **Product H:** A bicyclic adduct, specifically an ester-substituted bicyclo[2.2.1]heptene derivative if it's reacting as a dienophile. For cyclopentene to react, it must act as a diene. But it's an alkene. This setup looks more like an intramolecular Diels-Alder or a specific example.
  - **Re-evaluating (f):** Cyclopentene is an alkene. $COOC_2H_5$ implies an ester group. If this is a reaction of cyclopentene with an α,β-unsaturated ester as dienophile, it would be a Diels-Alder.
  - Let's assume the question meant a diene, or that cyclopentene somehow acts as a diene (which it doesn't in a typical Diels-Alder). If it is a cycloaddition, and considering the structure implies a general addition, then a common reaction with an alkene and a specific ester could be a [2+2] cycloaddition (if photochemically initiated, not just $\triangle$) or a Michael addition if it's a specific enolate.
  - Given the context of general organic reactions, and assuming a typo or simplification, let's consider **if it meant a maleate/fumarate derivative (a dienophile) reacting with a cyclic diene (not cyclopentene).**
  - **If it's Cyclopentadiene (not cyclopentene) and diethyl maleate/fumarate:**
    - H: A bicyclic compound (e.g., bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate).

- **If it's really Cyclopentene as a dienophile with a diene like Buta-1,3-diene:**
    - This is not the usual way it's written.
- **Best interpretation for "Cyclopentene + $COOC_2H_5 \xrightarrow{\triangle}$ H" as a Diels-Alder:** This suggests an intramolecular Diels-Alder or a specific named reaction.
- **Without a clearer structure for $COOC_2H_5$ as a dienophile or a diene, this is ambiguous.**
- **Common interpretation of such notation for Diels-Alder:** Usually, a diene and a dienophile are shown explicitly. If $COOC_2H_5$ is part of a dienophile, it could be something like CH_2=CH-$COOC_2H_5$ (ethyl acrylate) or H_5C_2OO C-CH=CH-$COOC_2H_5$ (diethyl maleate/fumarate).
- **Assuming the intent is a Diels-Alder and "Cyclopentene" is the dienophile (which is less common without a strong electron-withdrawing group or if it acts as a diene):** No, Cyclopentene usually acts as a dienophile only if activated.
- **Let's reconsider this. If Cyclopentene is the diene (not possible for D.A.) or dienophile. The only way it makes sense with just $COOC_2H_5$ (an ester group) as a reactant without a double bond specified, is if it is a specific reaction for which the user must infer the dienophile. However, given the other examples, it's likely a standard reaction of cyclopentene.**
- **If it's an alkylation reaction in context of alkene reactions, but $\triangle$ usually implies Diels-Alder or high temp rearrangement.**
- **Let's consider if it's the addition of an ester to an alkene, which is rare for just heat.**

- **Alternative interpretation: If it's a reaction like a carbene insertion or other special cycloaddition. Given no other information, this question part (f) is unanswerable precisely without clarification on the structure of the reactant involving $COOC_2H_5$.**
- **However, if "$COOC_2H_5$" implicitly refers to "diethyl maleate" (H_5C_2OOC-CH=CH-$COOC_2H_5$), and this is meant to be a Diels-Alder reaction where Cyclopentene is the DIENE. This implies "Cyclopentene" is a typo for "Cyclopentadiene".**
- **Assuming "Cyclopentene" is a typo and should be "Cyclopentadiene":**
  - If diene is Cyclopentadiene and dienophile is diethyl maleate/fumarate, then H is:
  - **H:** Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (endo/exo mixture, but often endo is preferred kinetically).
    - (This is the most plausible interpretation for a Diels-Alder type question when '△' is used).

- **(g) 1-Bromopropane** $\xrightarrow{\text{Alcoholic KOH}}$ **I**
  - **Reaction:** Dehydrohalogenation (E2 elimination)
  - **Product I:** Propene
    - I: CH_3-CH=CH_2
- **(h) Propyne** $\xrightarrow{HgSO_4 + \text{dil } H_2SO_4}$ **J**
  - **Reaction:** Acid-catalyzed hydration of alkyne (Markovnikov addition of water, followed by tautomerization).
  - **Product J:** Acetone (Propan-2-one)

- J: CH_3-C(=O)-CH_3

8. Write short note on the following (attempt any three) :
    - (a) Wurtz-Fittig reaction
    - (b) Elcb reaction

- **(a) Wurtz-Fittig Reaction:**
    - **Definition:** The Wurtz-Fittig reaction is a coupling reaction in organic chemistry that is used to synthesize alkyl-substituted aromatic compounds (alkylarenes) from an aryl halide, an alkyl halide, and sodium metal in a dry ether solution. It is a variation of the Wurtz reaction.
    - **Mechanism (Proposed):** The reaction is believed to proceed via a free radical mechanism involving organosodium intermediates. Sodium first reacts with the alkyl halide and aryl halide to form alkyl sodium and aryl sodium intermediates, respectively. These then couple to form the desired alkylarene.
    - **General Reaction:**
        - $Ar\text{-}X + R\text{-}X + 2Na \xrightarrow{\text{Dry Ether}} Ar\text{-}R + 2NaX$
        - Where:
            - Ar-X = Aryl halide (e.g., Chlorobenzene, Bromobenzene)
            - R-X = Alkyl halide (e.g., Methyl bromide, Ethyl bromide)
            - Ar-R = Alkylarene
    - **Example:**
        - Bromobenzene + Methyl bromide + $2Na \xrightarrow{\text{Dry Ether}}$ Toluene + 2NaBr

- **Limitations:**
  - Side reactions can occur, such as the Wurtz coupling of two alkyl halides (forming R-R) and Fittig coupling of two aryl halides (forming Ar-Ar), reducing the yield of the desired mixed product.
  - Not suitable for preparing alkylarenes where the alkyl halide is highly hindered.
  - Often gives poor yields for complex or highly substituted products.

- **(b) E1cB Reaction:**
  - **Definition:** E1cB stands for "Elimination, Unimolecular, Conjugate Base". It is an elimination reaction mechanism that proceeds in two steps, where the first step is the deprotonation of a carbon atom to form a carbanion (a conjugate base), and the second step is the loss of a leaving group from this carbanion, leading to the formation of a π (pi) bond.
  - **Key Characteristics:**
    - **Two-Step Process:**
      1. **Deprotonation:** A strong base removes an acidic β-hydrogen (proton) from the substrate, generating a carbanion (the conjugate base). This step is often reversible and slow.
      2. **Loss of Leaving Group:** The lone pair on the carbanion rapidly displaces the leaving group (LG) from the adjacent carbon, forming a double bond.
    - **Rate-Determining Step:** The first step (deprotonation) is typically the rate-determining step.
    - **Substrate Requirements:**

- The substrate must have a relatively acidic β-hydrogen. This acidity is often enhanced by the presence of an electron-withdrawing group (EWG) adjacent to the β-carbon (e.g., C=O, CN, NO_2).
- It must also have a poor leaving group, or a leaving group that is not easily removed in an E2 or E1 reaction. This ensures that the carbanion has time to form before the leaving group departs.

- **General Reaction Scheme:**
  - H-C-C-LG + Base ⇌ C^--C-LG + Base-H (Formation of carbanion)
  - C^--C-LG → C=C + LG^- (Elimination of leaving group)
- **Example:** The elimination of water from β-hydroxy carbonyl compounds (aldol condensation dehydration step) under basic conditions often proceeds via an E1cB mechanism.
  - (Example: Dehydration of 3-hydroxybutanal to but-2-enal under basic conditions.)
- **Distinction from E1/E2:** Unlike E1 and E2, which typically involve good leaving groups and are often sensitive to carbocation stability or steric hindrance, E1cB is favored by acidic β-hydrogens and poorer leaving groups.