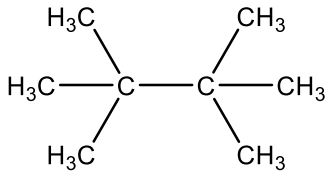
Unit-3

Structural elucidation of organic compounds using IR, NMR & mass spectral Data

1. 2,2,3,3-Tetramethylbutane:



2,2,3,3-tetramethyl butane

Key Properties:

1. Symmetry: Highly symmetric (identical methyl groups).
2. Branches: Four methyl groups attached to C2 and C3 of a butane chain.
3. No functional groups: Only C─C and C─H bonds**.**

a. Mass Spectrometry (MS):

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 114 ($C_8H_{18}^{+\cdot}$, weak intensity typical for alkanes).

Fragmentation Pattern:

Base peak at m/z = 57: Tert-butyl cation $(CH_3)_3C^+$ (stable tertiary carbocation).

Central C─C bond (quaternary-quaternary) is stable; fragmentation favors breaking bonds near branches to form stable tertiary carbocations.

Other peaks:

m/z 99: Loss of methyl radical $[M-15]^{+\cdot}$.

m/z 41/43: Common alkane fragments (e.g., $C_3H_5^+/C_3H_7^+$).

b. Infrared Spectroscopy (IR)

Key Absorptions:

2960–2870 cm^{-1}: Strong C─H stretch (sp^3 hybridized).

1380–1390 cm^{-1} & **~1465 cm^{-1}**: C─H bending (symmetrical/asymmetrical) of ─CH_3 groups.

No Peaks For:

O─H (3200–3600 cm^{-1}), C=O (1700 cm^{-1}), C─O (1000–1300 cm^{-1}), or C═C (1600–1680 cm^{-1}). This Confirms saturated alkane with no functional groups.

c. Nuclear Magnetic Resonance (^{1}H NMR)

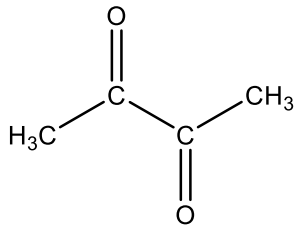
Single peak (singlet):

δ ≈ 0.9–1.0 ppm (integrates to **18H**).

All 18 hydrogens are identical (equivalent methyl groups due to symmetry).

No adjacent hydrogens → no splitting.

2. **Butane-2,3-dione:**



Butane-2,3-dione

Key Properties:

1. **Symmetry:** Symmetrical molecule with identical methyl groups and equivalent carbonyls.
2. **Functional Groups:** Two adjacent carbonyl groups (ketones).
3. **Conjugation:** Carbonyls are conjugated, affecting reactivity and spectral properties.

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 86 ($C_4H_6O_2^{+\cdot}$, moderate intensity).

Fragmentation Pattern:

Base peak at m/z = 43: Acetyl cation $CH_3C{\equiv}O^+$ (stable acylium ion).

Cleavage occurs adjacent to carbonyls, favoring resonance-stabilized acylium ions.

Key peaks:

m/z 15: Methyl cation $[CH_3]^+$ (weak).

m/z 29: $[CHO]^+$ or $[C_2H_5]^+$.

No significant M-15 peak (methyl loss unlikely due to carbonyl stabilization).

b. Infrared Spectroscopy (IR)

Key Absorptions:

1710–1720 cm^{-1}: Strong C═O stretch (lower than typical ketones ~1715-1750 cm^{-1} due to conjugation).

~3000 cm^{-1}: Weak C─H stretch (sp^3 hybridized, no acidic H).

~1360 cm^{-1} & 1420 cm^{-1}: C─H bending of ─CH_3 groups.

No Peaks For:

O─H (3200–3600 cm^{-1}), C═O above 1730 cm^{-1} (rules out esters/aldehydes). It confirms conjugated diketone.

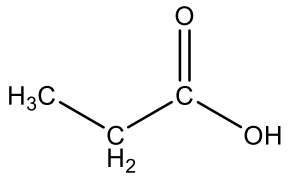
c. Nuclear Magnetic Resonance (^{1}H NMR)

Single peak (singlet):

δ ≈ 2.2–2.3 ppm (integrates to **6H**).

Methyl groups are equivalent and adjacent to quaternary carbonyl carbons (no adjacent H atoms).

3. Propionic acid:



propionic acid

Key Properties

1. **Functional Groups:** Carboxylic acid (–COOH).
2. **Polarity:** Forms hydrogen bonds (affects IR and NMR).
3. **Acidity:** Acidic proton (δ 11–12 ppm in NMR).

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 74 ($C_3H_6O_2^{+\cdot}$, weak due to instability).

Fragmentation Pattern:

Base peak at m/z = 45: $[COOH]^+$ or $[CH_3CH_2O]^+$ (carboxyl fragment).

Key peaks:

m/z 29: Ethyl cation $[CH_3CH_2]^+$ or formyl fragment $[CHO]^+$.

m/z 57: $[M–OH]^{+\cdot}$ (loss of hydroxyl radical).

m/z 73: $[M–H]^+$ (loss of hydrogen radical).

b. Infrared Spectroscopy (IR)

Key Absorptions:

2500–3300 cm^{-1}: *Very broad* O–H stretch (hydrogen-bonded carboxylic acid).

1710 cm^{-1}: Strong C═O stretch (carboxylic acid, lower than ketones due to resonance).

1410^{-1} & 1280 cm^{-1}: C–O stretch and O–H bend.
1411 ~2900 cm^{-1}: C–H stretches (alkyl group).

C═O above 1730 cm^{-1} rules out ester/aldehyde and Sharp O–H rules out alcohol. It Confirms carboxylic acid.

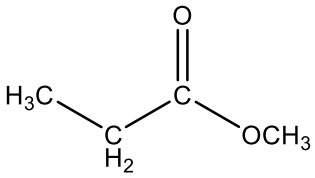
c. Nuclear Magnetic Resonance (^{1}H NMR)

Three distinct signals:

1. **δ ≈ 11.5–12.0 ppm**: Broad singlet (1H, –COOH).
2. **δ ≈ 2.3–2.5 ppm**: Quartet (2H, –CH_2– *alpha* to carbonyl).
3. **δ ≈ 1.1–1.3 ppm**: Triplet (3H, –CH_3).

Splitting:
–CH_2 and –CH_3 couple (J ≈ 7 Hz), confirming ethyl group.

4.Methyl Propionate



methyl propionate

Key Properties

1. **Functional Group:** Ester (–COOR).
2. **Polarity:** Polar but no O–H bonds (unlike carboxylic acids).
3. **Asymmetry:** Two distinct alkyl groups (ethyl from acid, methyl from alcohol).

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 88 ($C_4H_8O_2^{+\cdot}$, moderate intensity).

Fragmentation Pattern:

Base peak at m/z = 57: Propionyl cation $[CH_3CH_2C{=}O]^+$ (acylium ion from loss of $\bullet OCH_3$). This is due to esters fragment via α-cleavage i.e., loss of alkoxy group (–OR) forms stable acylium ions.

Key peaks:

m/z 59: Methoxycarbonyl cation $[CH_3OC{\equiv}O]^+$ (cleavage at C(alkyl)–C(carbonyl)).

m/z 29: Ethyl cation $[CH_3CH_2]^+$ or $[CHO]^+$.

m/z 31: Methoxy cation $[CH_3O]^+$.

b. Infrared Spectroscopy (IR)

Key Absorptions:

1735–1745 cm^{-1}: Strong C═O stretch (ester carbonyl, higher frequency than carboxylic acids).

1150–1250 cm^{-1}: Strong C–O stretch (asymmetric, ester-specific).

1050–1100 cm^{-1}: C–O stretch (symmetric).

~2980 cm^{-1}: C–H stretches (alkyl groups).

No Peaks For:

O–H (2500–3300 cm^{-1}; rules out carboxylic acids).

C═O below 1720 cm^{-1} (rules out conjugated ketones/acids).

This confirms ester functional group.

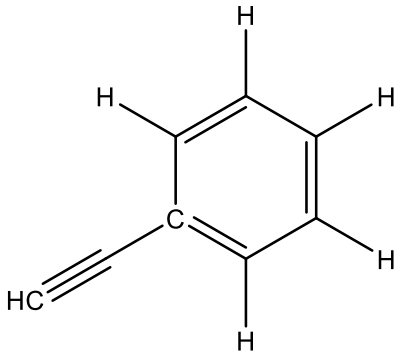
c. Nuclear Magnetic Resonance (^{1}H NMR)

Three distinct signals:

1. **δ ≈ 3.6–3.7 ppm**: Singlet (3H, $–OCH_3$).
2. **δ ≈ 2.3–2.5 ppm**: Quartet (2H, $–CH_2–$ *alpha* to carbonyl).
3. **δ ≈ 1.1–1.3 ppm**: Triplet (3H, $–CH_3$ of ethyl).

Splitting: $–CH_2$ (q) and $–CH_3$ (t) couple ($J \approx 7$ Hz), confirming ethyl group. $–OCH_3$ is singlet (no adjacent H).

5.Phenyl Acetylene



phenyl acetylene

Key Properties

1. **Functional Groups:** Terminal alkyne (–C≡C–H) + benzene ring.
2. **Acidity:** Alkyne proton is weakly acidic ($pK_a \approx 25$).
3. **Symmetry:** Monosubstituted benzene (no ring symmetry).

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 102 ($C_8H_6^{+\cdot}$, moderate intensity).

Fragmentation Pattern:

Base peak at m/z = 76: $[M–C_2H_2]^{+\cdot}$ (loss of acetylene → benzene ion $C_6H_4^{+\cdot}$).

Terminal alkynes easily lose H• or C_2H_2 due to weak C(sp)–H bond.

Key peaks:

m/z 101: $[M–H]^+$ (loss of alkyne proton).

m/z 50: $[C_4H_2]^+$ (alkyne chain fragment).

m/z 51/77: Benzene ring fragments.

b.Infrared Spectroscopy (IR)

Key Absorptions:

~3300 cm^{-1}: Sharp ≡C–H stretch (terminal alkyne).

2100–2140 cm^{-1}: Weak C≡C stretch (alkyne).

3030–3080 cm^{-1}: Aromatic C–H stretch.

1500–1600 cm^{-1}: Aromatic C=C stretches.

690–710 cm^{-1} & 730–770 cm^{-1}: Monosubstituted benzene C–H bends.

No Peaks For:

O–H/N–H (3200–3500 cm^{-1}), C=O (1700 cm^{-1}).

This Confirms terminal alkyne + monosubstituted benzene.

c. Nuclear Magnetic Resonance (^{1}H NMR)

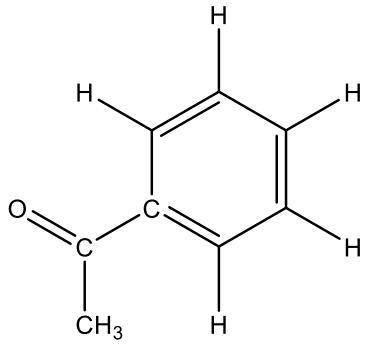
Two key regions:

1. **δ ≈ 2.8–3.1 ppm**: Singlet (1H, ≡C–H).
2. **δ ≈ 7.2–7.8 ppm**: Multiplet (5H, aromatic H).

Aromatic pattern:

Complex multiplet (no symmetry → all 5H distinct).

6. acetophenone



acetophenone

Key Properties

1. **Functional Groups:** Ketone conjugated to aromatic ring.
2. **Conjugation:** Carbonyl group directly attached to benzene ring.
3. **Asymmetry:** Monosubstituted benzene (no ring symmetry).

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 120 ($C_8H_8O^{+\cdot}$, strong intensity).

Fragmentation Pattern:

Base peak at m/z = 105: Benzoyl cation $[C_6H_5C{\equiv}O]^+$ (loss of $\bullet CH_3$).

α-cleavage favors benzoyl cation (resonance-stabilized). McLafferty rearrangement not possible (no γ-hydrogens).

Key peaks:

m/z 77: Phenyl cation $[C_6H_5]^+$ (loss of CO from benzoyl).
m/z 43: Acetyl cation $[CH_3C{\equiv}O]^+$.
m/z 51: Cyclopentadienyl fragment.

b. Infrared Spectroscopy (IR)

Key Absorptions:

1680–1700 cm^{-1}: C═O stretch (lower than aliphatic ketones due to conjugation).
1590–1600 cm^{-1} & 1580 cm^{-1}: Aromatic C═C stretches.
3000–3100 cm^{-1}: Aromatic C─H stretch.
690–710 cm^{-1} & 750–770 cm^{-1}: Monosubstituted benzene C─H bends.

No Peaks For:

O─H (3200–3600 cm^{-1}), C═O above 1720 cm^{-1} (rules out aliphatic ketones).

This confirms a conjugated aromatic ketone.

c. Nuclear Magnetic Resonance (^{1}H NMR)

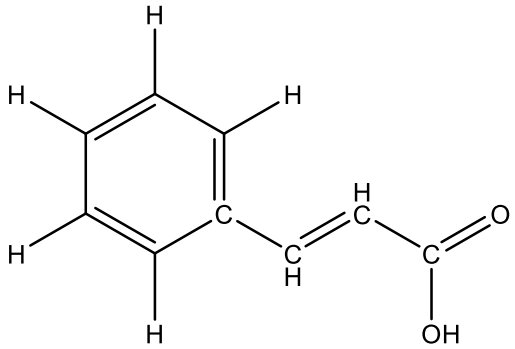
Two key regions:

1. **δ ≈ 2.5–2.6 ppm**: Singlet (3H, $–COCH_3$).
2. **δ ≈ 7.4–8.0 ppm**: Multiplet (5H, aromatic H).

Ortho protons most deshielded (δ ≈ 7.8–8.0 ppm).

No aldehyde proton: δ 9–10 ppm absent.

7. cinnamic acid



cinnamic acid

Key Properties

1. **Functional Groups:** Carboxylic acid + conjugated *trans*-alkene + phenyl ring.
2. **Conjugation:** Extended π-system (phenyl–CH=CH–COOH).
3. **Geometry:** Typically isolated as *trans* isomer (higher stability).

a.Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\bullet}$):

m/z = 148 ($C_9H_8O_2^{+\bullet}$, weak due to instability).

Fragmentation Pattern:

Base peak at m/z = 131: $[M–OH]^{+\bullet}$ (loss of hydroxyl radical).

Carboxylic acids favour loss of –OH or –COOH.

Key peaks:

m/z 103: due to loss of carboxyl radical to form styrene ion.

m/z 77: Phenyl cation $[C_6H_5]^+$.

m/z 51: Cyclopentadienyl fragment.

b. Infrared Spectroscopy (IR)

Key Absorptions:

2500–3300 cm^{-1}: *Broad* O–H stretch (H-bonded carboxylic acid).

1680–1700 cm^{-1}: C═O stretch (lower than aliphatic acids due to conjugation).

1630–1650 cm^{-1}: C═C stretch (conjugated alkene).

1590–1610 cm^{-1} & 1500 cm^{-1}: Aromatic C═C stretches.

985–995 cm^{-1}: Strong =C–H bend (*trans* alkene).

No Peaks For:

O–H above 3300 cm^{-1} (rules out alcohols).

Cis alkene bends (690 cm^{-1} absent).

c.Nuclear Magnetic Resonance (^{1}H NMR)

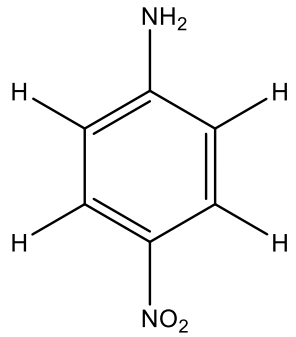
Four key signals:

1. **δ ≈ 12.0–12.5 ppm**: Broad (1H, –COOH).
2. **δ ≈ 7.6–7.8 ppm**: Doublet (1H, =CH–CO; $J \approx 16$ Hz).
3. **δ ≈ 6.4–6.5 ppm**: Doublet (1H, Ph–CH=; $J \approx 16$ Hz).
4. **δ ≈ 7.2–7.5 ppm**: Multiplet (5H, aromatic H).

Coupling:

$J \approx 16$ Hz confirms *trans* alkene (large coupling constant).

8. p-nitroaniline



para-nitroaniline

Key Properties

1. **Functional Groups:** Electron-donating amino (–NH_2) + electron-withdrawing nitro (–NO_2) in *para* positions.
2. **Conjugation:** Strong push-pull resonance between groups.
3. **Symmetry:** *Para* substitution creates mirror plane (simplifies NMR).

a. Mass Spectrometry (MS)

Molecular Ion Peak ($M^{+\cdot}$):

m/z = 138 ($C_6H_6N_2O_2^{+\cdot}$, moderate intensity).

Fragmentation Pattern:

Base peak at m/z = 92: $[M–NO_2]^{+\cdot}$ (loss of nitro group → aniline ion).

–NO_2 group cleaves easily due to weak C–N bond; resonance stabilizes aniline fragment.

Key peaks:

m/z 65: $[C_5H_5]^+$ (cyclopentadienyl fragment).
m/z 108: $[M–NO]^{+\cdot}$ (loss of nitric oxide, weak).
m/z 39/51: Benzene ring fragments.

b. Infrared Spectroscopy (IR)

Key Absorptions:

3360–3480 cm^{-1}: Doublet N–H stretches (asymmetric/symmetric; primary amine).

1330–1350 cm^{-1} & **1510–1560 cm^{-1}**: N–O stretches (nitro group).

1600 cm^{-1}: Aromatic C═C stretch (enhanced by conjugation).

1270 cm^{-1}: C–N stretch (amine).

830–850 cm^{-1}: *Para*-disubstituted benzene C–H bends.

No Peaks For:

C═O (1700 cm^{-1}), O–H (3200–3600 cm^{-1}).

c. Nuclear Magnetic Resonance (NMR)

(a) ^{1}H NMR:

- **Three distinct signals:**
  1. **δ ≈ 6.5–6.7 ppm**: Doublet (2H, H-3/H-5 *ortho* to –NH_2).
  2. **δ ≈ 7.9–8.1 ppm**: Doublet (2H, H-2/H-6 *ortho* to –NO_2).
  3. **δ ≈ 4.5–5.5 ppm**: Broad singlet (2H, –NH_2; concentration-dependent).
- **Coupling:**

  $J \approx 9$ Hz between H-2/H-3 (meta coupling negligible).