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┌─────────────────┐
│  CSM – 17/17    │
├─────────────────┤
│   Chemistry     │
├─────────────────┤
│   Paper – II    │
└─────────────────┘
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Time : 3 hours

Full Marks : 300

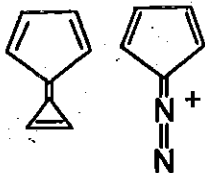*The figures in the right-hand margin indicate marks.*

*Candidates should attempt Q. No. 1 from
Section – A and Q. No. 5 from Section – B
which are compulsory and any **three** of
the remaining questions selecting
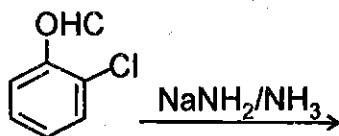at least **one** from each Section.*

SECTION – A

1. Answer any **three** of the following questions :

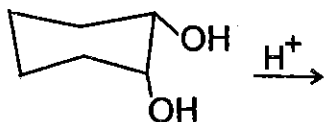$$20 \times 3 = 60$$

   (a) (i) The given compounds are aromatic or
            non-aromatics. Why ? Explain.

(Turn over)

(ii) Explain thermodynamic control reaction.

(iii) Write the product and mechanism of the given reaction :
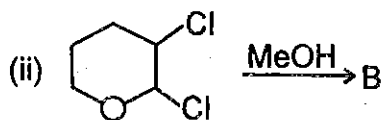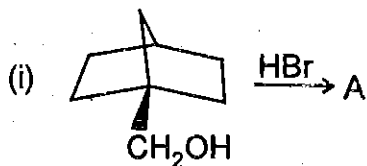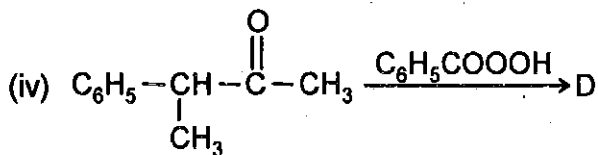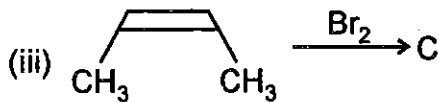

$$\xrightarrow{\text{NaNH}_2/\text{NH}_3}$$

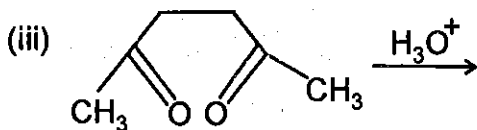(iv) Write the product and mechanism of the given reaction :

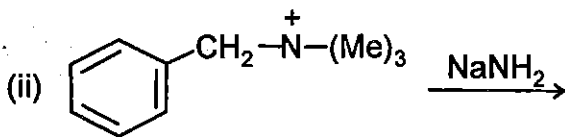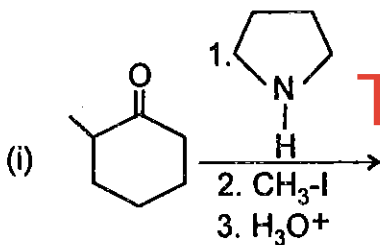$$\xrightarrow{\text{H}^+}$$

(b) Predict the product A, B, C, D of the given reaction :

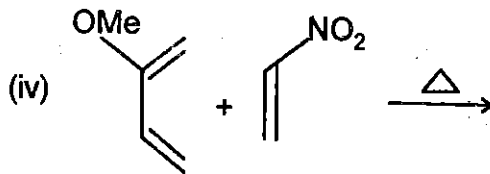Techofworld.In

(i)

$$\xrightarrow{\text{HBr}} A$$

(ii)

$$\xrightarrow{\text{MeOH}} B$$

(iii) $\xrightarrow{\text{Br}_2}$ C

(iv) $C_6H_5-CH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{C_6H_5COOOH} D$
$\qquad\qquad\quad |$
$\qquad\qquad CH_3$

(c) Predict the product with mechanism :

(i)

(ii) $\xrightarrow{NaNH_2}$

(iii) $\xrightarrow{H_3O^+}$

(iv)

(d) Predict the product and write the mechanism of the reaction :

(i)

(ii)

(iii) $\xrightarrow[\text{2. } H_3O^+, H_2O]{\text{1. } Ph_3P = CH-OCH_3}$
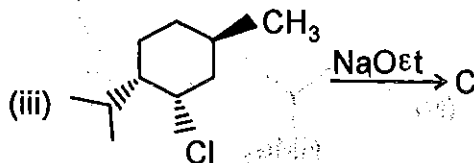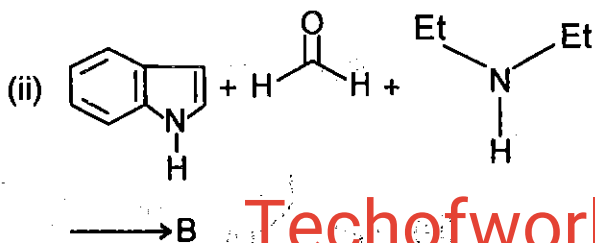

(iv) $\xrightarrow[H_2O]{H^+}$
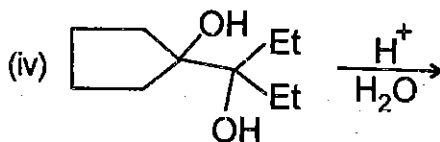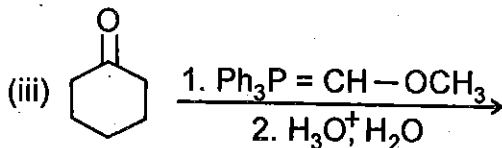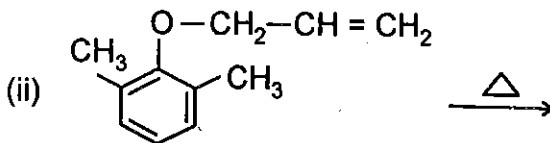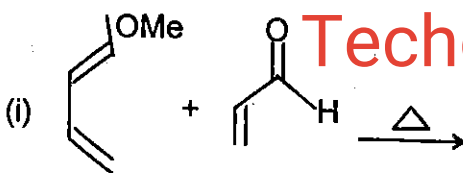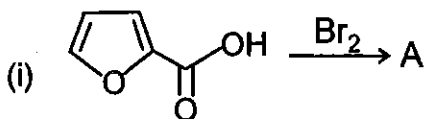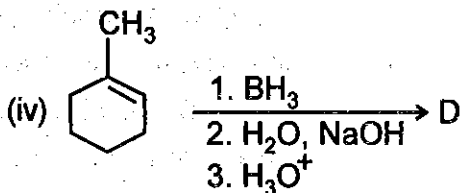
2. Answer the following :

(a) (i) With the help of molecular orbitals of annulenes, explain why annulenes having $(4n + 2)\pi$ electrons are more stable than one containing $4n\pi$ electrons. **10**

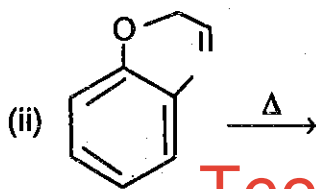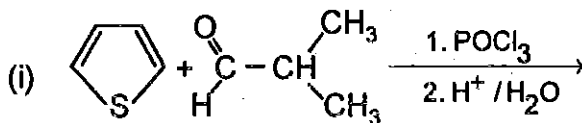(ii) Explain the mechanism of aromatic electrophilic substitution by the use of isotopes. **10**
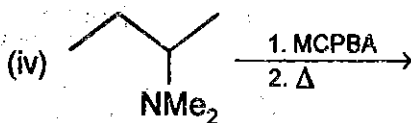
(b) Identify A, B, C, D with mechanism :

$$5+5+5+5 = 20$$

(i)

(ii)

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(iii)

(iv)

$$\underset{\text{(4-methylcyclohexene)}}{\text{CH}_3} \quad \xrightarrow[\begin{array}{c}\text{1. BH}_3 \\ \text{2. H}_2\text{O, NaOH} \\ \text{3. H}_3\text{O}^+\end{array}]{} \quad \text{D}$$

(c) Predicts the products :   5+5+5+5 = 20

(i) $+ \underset{H}{\overset{O}{\parallel}} C - \underset{CH_3}{\overset{CH_3}{CH}} \quad \xrightarrow[\text{2. H}^+/\text{H}_2\text{O}]{\text{1. POCl}_3}$

(ii) $\xrightarrow{\Delta}$

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(iii) $\overset{}{\underset{OH}{}} \quad \xrightarrow[\text{CH}_3\text{I}]{\text{CS}_2-\text{NaOH}\Delta}$

(iv) $\underset{\text{NMe}_2}{} \quad \xrightarrow[\text{2. }\Delta]{\text{1. MCPBA}}$
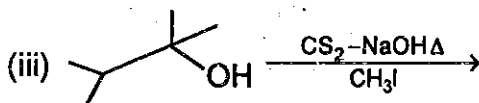
3. (a) Answer the following questions :

   (i) Sketch a suitable mechanism of the following transformation : 5

   (ii) Write the products of the following :

   $5+5+5 = 15$

   (A) $\xrightarrow{h\upsilon}$

   (B) $\xrightarrow{h\upsilon}$

   (C) $\xrightarrow{h\upsilon}$

(b) Predict the product of the following reactions with mechanism : 5+5+5+5 = 20

(i) + COOCH$_3$ / COOCH$_3$ →Δ

(ii) + →Δ

(iii) + C−COOCH$_3$ ‖ C−COOCH$_3$ →Δ

(iv) Ph / Ph →Δ
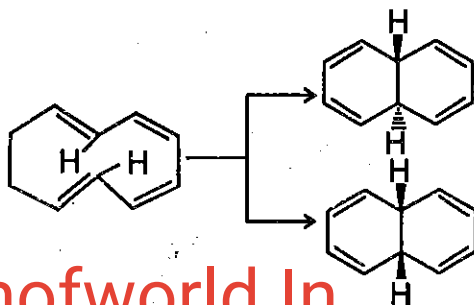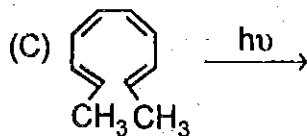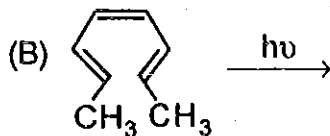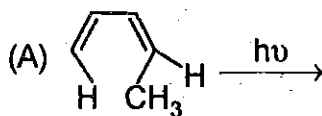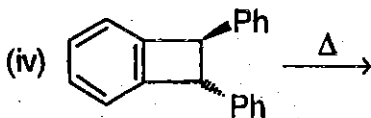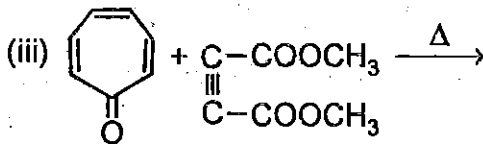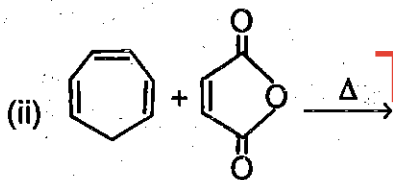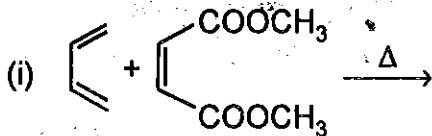
(c) Identify A, B, C, D with proper mechanism : 5+5+5+5 = 20

(i) $\xrightarrow[\text{ii. Proton transformation}]{\text{i. }\Delta}$ A

(ii) $\xrightarrow[1,5]{\Delta}$ B

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(iii) $\xrightarrow{\Delta}$ C

(iv) $\xrightarrow{\Delta}$ D
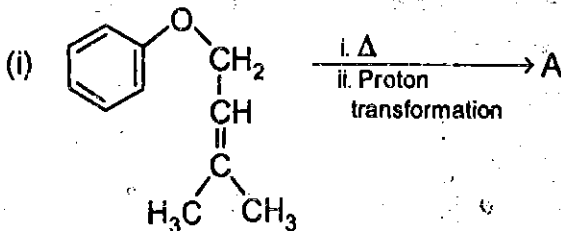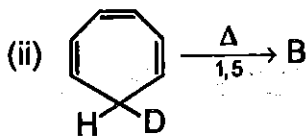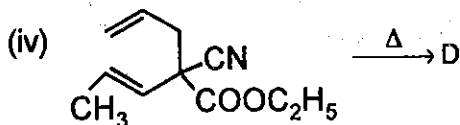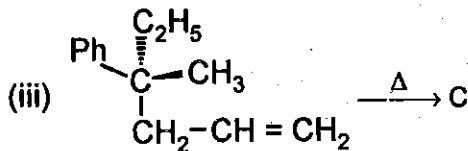
4. Predict the product(s) of any **ten** of the following reactions : 6×10 = 60

(a) $\xrightarrow{\text{dil. NaOH}}$

(b) $\xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{KCN}}$

(c)

$$\xrightarrow[\text{2. } H_2O, H^+]{\text{1.} Ph_3P=CH-COOEt}$$

(d)

$$\xrightarrow[\substack{\text{2.KOH} \\ \text{3.} H^+, H_2O}]{\text{1. } NH_2NH_2}$$

(e)

$$\xrightarrow[C_6H_5NO_2]{H_2SO_4}$$

(f)

$$\xrightarrow[\text{KOH}]{CHCl_3}$$

(g)

$$\xrightarrow[\Delta]{POCl_3, \text{ toluene}}$$

(h)

$$\xrightarrow{CuCl}$$

(i) $\xrightarrow[\text{HCl}]{\text{Zn – Hg}}$

(j) $C_6H_5 - CHO + H$ $H + \xrightarrow{\text{conc. NaOH}}$

(k) $\xrightarrow[\text{H}_3\text{O}^+]{\text{NaOEt}}$

(l) $\xrightarrow[\Delta]{\text{ZnCl}_2}$
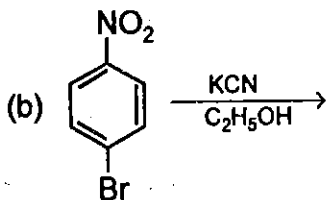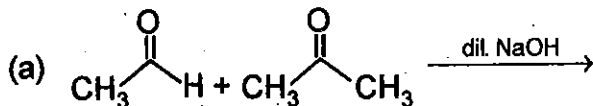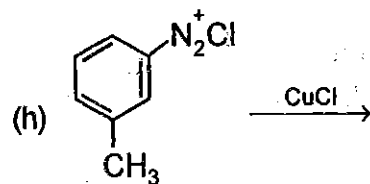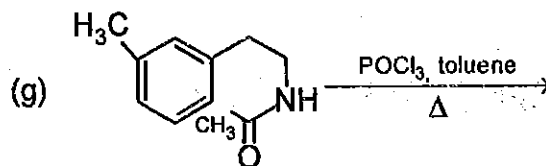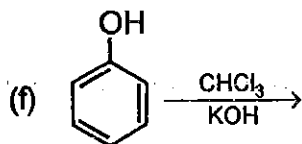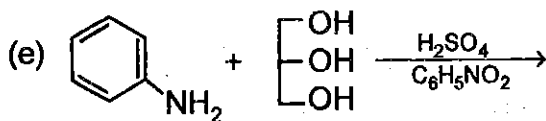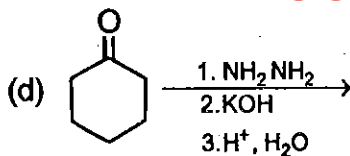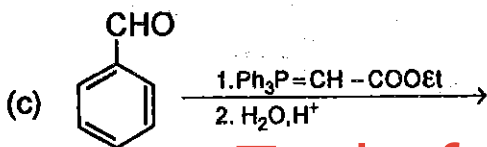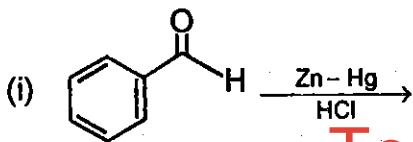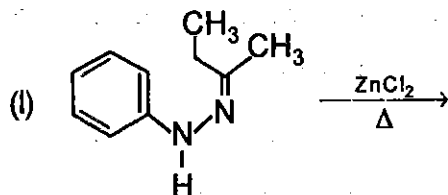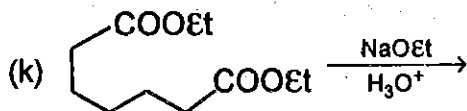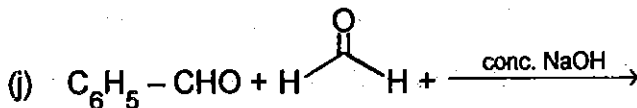
SECTION – B

5. Answer any **three** of the following questions :

$$20 \times 3 = 60$$

(a) Write the synthesis of the following polymer with chemical equation :

Nylon 66, terylene, Bakelite, Polystyrene, SBR

(b) Write two synthetic uses of the following reagents with mechanism :

$$OsO_4, CrO_3, B_2H_6, LiAlH_4$$
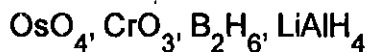
(c) What is Coupling Constant ? Discuss the factors affecting Coupling Constant.

The Proton NMR spectra of an organic compound with molecular formula $C_3H_3Cl_5$ exhibits a triplet with $\delta\,4.52$ ppm and a doublet with $\delta\,6.67$ ppm, what is the structural formula of the compound ?

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(d) The first line in the rotational spectrum of carbon monoxide has a frequency of 3.8424 cm^{-1}. Calculate rotational constant and C – O bond length in carbon monoxide (reduced mass of CO is 1.1385 × 10^{-23} g).

Though rotational energy levels of a diatomic molecules are unequal spaced but the spacing between rotational lines are equal — explain.

6. Answer any **five** of the following : 12×5 = 60

(a) How molecular weight of polymer is determined by light scattering method ?

   A polymer sample contains 100 polymers of molecular mass 10^3, 200 molecules of molecular mass 10^4, 300 molecules of molecular mass 10^5, calculate number average $\bar{M}n$ and weight average $\bar{M}w$ molecular mass of polymer.

(b) Write notes on the following :

   (i) Silicates

   (ii) Biopolymers

   (iii) Photo-Fries reaction

(c) The molecular mass of a compound shows two strong peaks at m/z 91 and 65 and a broad peak at 46.4. Justify the origin of the signal and identify the compound.

   How would you distinguish among ethylamine, diethylamine and triethylamine on the basis of their mass spectral studies ?

(d) Write three high temperature polymers and their formula and use.

What is intrinsic viscosity ? How it helps in determining molecular mass of polymer ?

What is relative rate of sedimentation for two spherical particles of same density but which differ in radius by a factor 10 ?

(e) What is the expression of chemical shift ? Discuss the factors affecting chemical shift.

An organic compound with molecular formula C_8H_8O gives the following protein NMR spectrum :

(i) Multiplet (δ 7.28)5H
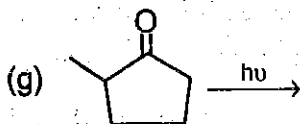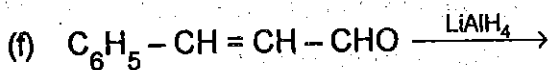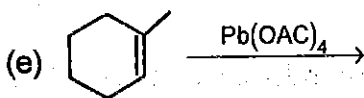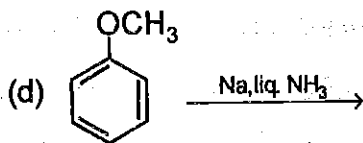
(ii) Doublet (δ 2.8)2H

(iii) Triplet (δ 9.78)1H
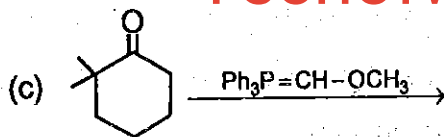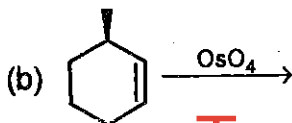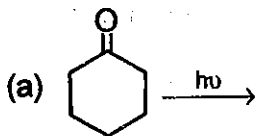
Predict the structure of the compound.

(f) What is the most characteristic feature of mass spectra of compounds containing one bromine atom ? Do fluorine and iodine containing compounds display the same feature in their mass spectra ?

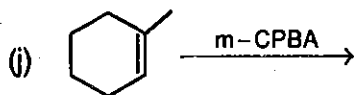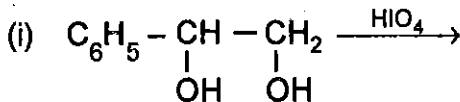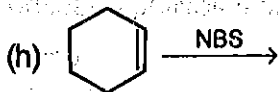How will you account for the prominent peaks at m/z 31, 42, 70 in the mass spectrum of n-pentanol ?

7. Answer any **ten** from the following questions :

$$6×10 = 60$$

(a) $\xrightarrow{h\upsilon}$

(b) $\xrightarrow{OsO_4}$

(c) $\xrightarrow{Ph_3P=CH-OCH_3}$

(d) $\xrightarrow{Na, liq. NH_3}$

(e) $\xrightarrow{Pb(OAC)_4}$

(f) $C_6H_5 - CH = CH - CHO \xrightarrow{LiAlH_4}$

(g) $\xrightarrow{h\upsilon}$

(h) $\xrightarrow{\text{NBS}}$

(i) $C_6H_5 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{OH}{|}}{CH_2} \xrightarrow{\text{HIO}_4}$

(j) $\xrightarrow{\text{m-CPBA}}$

(k) Write note on Norrish-Type-I cleavage.

(l) Explain Wittig reaction with suitable example and mechanism.

8. Answer any **six** of the following : 10×6 = 60

(a) Outline the effect of isotopic substitution on the rotational spectra of diatomic molecule.

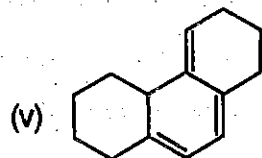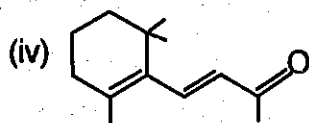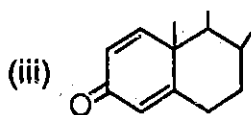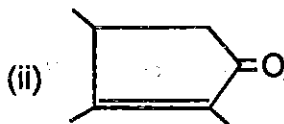What is the change in rotational constant B when hydrogen is replaced by deuterium in the hydrogen molecule ?

(b) One of the fundamental vibration mode of water occurs at 3652 cm^{-1}. What is the frequency of corresponding mode in D_2O ?

How many translational, rotational, vibrational modes of vibrations are there for the following molecules ?

C_6H_6, $HC = C - C \equiv C - H$, C_2H_4, H_2O_2, CH_2Cl_2
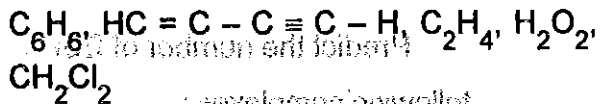
(c) Calculate λ_{max} of the following molecules using Woodward-Fieser rule :

(i)

(ii)

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(iii)

(iv)

(v)
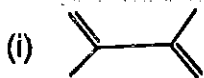
(d) The ESR spectrum of unpaired electron interacting with two equivalent protons show three lines with intensities $1 : 2 : 1$. Why ?

Predict the number of ESR lines in the following complexes :

(i) Magnetic dilute Cu(II) complex and magnetic concentrate Cu(II) complex

(ii) Cu(glicinato)$_2$

(iii) Na$_2$[PtCl$_6$]

(iv) bis (salicylaldiminato) Cu(II)

(v) K$_3$[Fe(CN)$_6$]

(e) Calculate the number of double bonds present in molecular formula $C_6H_8O_2N_2$.

A compound molecular formula $C_4H_{10}O$ gave PMR spectrum consisting of two group of lines (multiplets) with relative intensities in the ratio of $3 : 2$. The PMR spectra of another compound having same formula exhibited two lines with relative area of $9 : 1$. Identify these substances.

(f) Distinguish the following compounds on the basis of their mass spectrum :

    (i) Cyclohexanol and n-pentanol

    (ii) Acetaldehyde and benzaldehyde

    (iii) Benzene and Toluene

(g) Predict the number of lines in proton NMR of the following compounds :

    (i) Benzyl alcohol

    (ii) 2-chloropropanoic acid

    (iii) Vinyl acetate

    (iv) Methyl cyclopropane

    (v) 2, 3-dibromopropene

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