DAY THIRTY TWO

Unit Test 5

(Organic Chemistry-I)

- 1 Which of the following species is paramagnetic in nature?
 - (a) Carbonium ion
- (b) Free radical
- (c) Carbene
- (d) Nitrene
- **2** Which of the following statement(s) is/are wrong?

→ NCERT Exemplar

- (a) Ozone is not responsible for greenhouse effect
- (b) Ozone can oxidise sulphur dioxide present in the atmosphere to sulphur trioxide
- (c) Ozone hole is thinning of ozone layer present in stratosphere
- (d) Ozone is produced in upper stratosphere by the action of UV-rays on oxygen
- **3** Among the following, the strongest nucleophile is
 - (a) C₂H₅SH

(b) CH₂COO

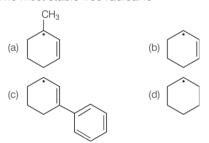
(c) CH₂NH₂

- (d) NCCH₂
- 4 Which of the following reactions represent the conversion of CH₄ into CH₃CI?
 - (a) Electrophilic substitution (b) Free radical addition
- - (c) Nucleophilic substitution (d) Free radical substitution
- 5 In the dehydration reaction,

 $CH_3CONH_2 \xrightarrow{P_2O_5} CH_3C \Longrightarrow N$, the hybridisation state of carbon changes from

- (a) sp^3 to sp^2
- (b) sp to sp^2
- (c) sp^2 to sp
- (d) sp to sp^3
- 6 The compound obtained when acetaldehyde reacts with dilute aqueous sodium hydroxide exhibits
 - (a) geometrical isomerism
 - (b) optical isomerism
 - (c) neither optical nor geometrical isomerism
 - (d) Both optical and geometrical isomerism

7 The most stable free radical is



8 Identify Z in the following series.

$$\operatorname{CH_2} = \operatorname{CH_2} \xrightarrow{\quad \operatorname{HBr} \quad} X \xrightarrow{\quad \operatorname{Hydrolysis} \quad} Y \xrightarrow{\quad \operatorname{Na}_2 \operatorname{CO}_3 \quad} Z$$

- (a) C_2H_5I
- (c) CH₂CHO
- (d) C₂H₅OH

9 Which of the following structures is enantiomeric with the molecule (A) given below. → NCERT Exemplar

$$H_5C_2$$
 H_5C_2
 H_5C_2
 H_5C_2
 H_5C_2
 H_5C_2
 H_5C_2
 H_5C_2

(a)
$$H_2C$$
 H_3C H_3C H_3C

(b)
$$CH_3$$
 H C_2H

- **10** Benzene vapours mixed with air when passed over V₂O₅ catalyst at 775 K gives
 - (a) glyoxal
- (b) oxalic acid
- (c) maleic anhydride
- (d) fumaric acid
- 11 Cyclopentene on treatment with alkaline KMnO₄ gives
 - (a) cyclopentanol
 - (b) trans -1, 2-cyclopentanediol
 - (c) cis-1, 2- cyclopentanediol
 - (d) 1: 1 mixture of cis and trans-1, 2-cyclopentanediol

$$\textbf{12} \ \, \text{CH}_{3} \text{C} \equiv \text{CH} \xrightarrow{\text{(i) NaNH}_{2}} A \xrightarrow{\text{H}_{2}} B$$

What is B in the above reaction?

(a)
$$^{\text{H}_3\text{C}}_{\text{H}}$$
 C= $^{\text{C}}_{\text{CH}_2\text{CH}_3}$

(b)
$$^{H_3C}_{H}$$
 C= $C < ^{CH_2CH_3}_{H}$

(c)
$$^{H_3C}_{H}$$
 $> C = C < ^{CH_3}_{H}$

$$(d) \stackrel{H_3C}{\longrightarrow} C = C \stackrel{C}{\searrow} H$$

13
$$CH_3CH_2CH_3 \xrightarrow{AICI_3} product$$

Product in the above reaction is

(a)
$$\operatorname{CH_3-CH-CH_2-CH_3}$$
 (b) $\operatorname{CH_3-CH-CH_3}$

- **14** Identify the reagent *X* in the following reaction.

$$H_3C$$
 CH_3
 X
 CH_3
 $CH_$

- (a) NaCl
- (b) SOCI₂
- (c) NaOCI
- (d) $KMnO_4/H^+$
- 15 Which of the following statements regarding the effect of trifluoromethyl, —CF₃ present on a benzene ring towards electrophilic substitution is correct?

[NCERT Exemplar]

- (a) CF₃ group activates the ring
- (b) CF₃ group renders the ring basic
- (c) CF₃ group is a *meta*-directing group, therefore, deactivates the ring
- (d) CF₃ group is an ortho, para-directing group

- **16** HBr reacts with $CH_2 = CHOCH_3$ under anhydrous conditions at room temperature to give
 - (a) CH₂CHO and CH₂Br
- (b) BrCH₂CHO and CH₂OH
- (c) BrCH₂— CH₂— OCH₂
 - (d) H₂C— CHBr— OCH₂
- 17 2-methylbutane on reacting with bromine in the presence of sunlight gives mainly
 - (a) 1-bromo-3-methylbutane
 - (b) 2-bromo-3-methylbutane
 - (c) 2-bromo-2-methylbutane
 - (d) 1-bromo-2- methylbutane
- **18** Elimination of bromine from 2-bromobutane results in the formation of
 - (a) predominantly 2-butyne
 - (b) predominantly 1-butene
 - (c) predominantly 2-butene
 - (d) equimolar mixture of 1-butene and 2-butene
- 19 Reaction of one molecule of HBr with one molecule of 1,3-butadiene at 40°C gives predominantly
 - (a) 1-bromo-2-butene under kinetically controlled
 - (b) 3-bromobutene under thermodynamically controlled conditions
 - (c) 1-bromo-2-butene under thermodynamically controlled conditions
 - (d) 3-bromobutene under kinetically controlled conditions
- 20 The compound formed as a result of oxidation of ethyl benzene by KMnO₄ is
 - (a) benzophenone
- (b) acetophenone
- (c) benzoic acid
- (d) benzyl alcohol
- **21** Among the following, the one that gives positive iodoform test upon reaction with I₂ and NaOH is
 - (a) CH₃CH₂CH(OH)CH₂CH₃ (b) C₆H₅CH₂CH₂OH

- (d) PhCHOHCH₃
- 22 The increasing order of the rate of HCN addition to compound A-D is
 - A HCHO
- B. CH₃COCH₃
- C. PhCOCH₃
- D. PhCOPh
- (a) A < B < C < D (b) D < B < C < A (c) D < C < B < A (d) C < D < B < A
- 23 Acid catalysed hydration of alkenes except ethene leads to the formation of
 - (a) mixture of secondary and tertiary alcohols
 - (b) mixture of primary and secondary alcohols
 - (c) both secondary or tertiary alcohol
 - (d) only primary alcohol
- 24 The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is
 - (a) pyridinium chlorochromate
 - (b) chromic acid in aqueous acetone
 - (c) acidic dichromate
 - (d) acidic permanganate

- 25 Which one of the following undergoes reaction with 50% sodium hydroxide solution to give corresponding alcohols and acids?
 - (a) Phenol
 - (b) Benzaldehyde
 - (c) Butanol
 - (d) Benzoic acid
- 26 Ethyl isocyanide on hydrolysis in acidic medium generates
 - (a) ethylamine salt and methanoic acid
 - (b) propanoic acid and ammonium salt
 - (c) ethanoic acid and ammonium salt
 - (d) methylamine salt and ethanoic acid
- 27 In the chemical reaction,

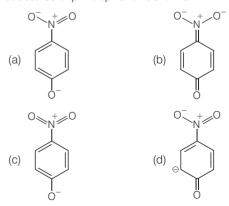
$$CH_3CH_2NH_2 + CHCI_3 + 3KOH \longrightarrow A + B + 3H_2O$$

the compounds A and B respectively are

- (a) C₂H₅CN and 3KCI
- (b) CH₃CH₂CONH₂and 3KCl
- (c) C₂H₅NC and K₂CO₂
- (d) C₂H₅NC and 3KCl
- 28 Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.

$$\bigoplus_{(l)}^{+} \bigoplus_{(l)}^{NH_3} \bigoplus_{(ll)}^{+} \bigoplus_{(ll)}^{NH_3}$$

- (a) II is not an acceptable canonical structure because carbonium ions are less stable than ammonium ions
- (b) II is not an acceptable canonical structure because it is non-aromatic
- (c) II is not an acceptable canonical structure because the nitrogen has 10 valence electrons
- (d) II is an acceptable canonical structure
- **29** The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is



30 The structure of the compound formed, when nitrobenzene is reduced by lithium aluminium hydride (LiAlH₄) is

(a)
$$\langle D \rangle$$
 NH—NH— $\langle D \rangle$ (b) $\langle D \rangle$ NH₂ (c) $\langle D \rangle$ N — N— $\langle D \rangle$ (d) $\langle D \rangle$

31 Final major product obtained in the following transformation is

Br
$$\xrightarrow{\text{CH}_{3}}$$
 Base/CH₃I $\xrightarrow{\text{Ag}_2\text{O}}$ $\xrightarrow{\text{Ag}_$

32 Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic compound *A*. The organometallic compound reacts with ethanal to give an alcohol *B* after mild acidification. Prolonged treatment of alcohol *B* with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane *C*. Identify the alcohol *B*.

(a)
$$CH_3$$
 (b) OH CH_3 (c) CH_3 (d) CH_3

$$A \leftarrow \begin{array}{c} CH_3 \\ CH_3$$

A and B respectively are

OH
18
 (a) $(CH_3)_2C$ — CH_2OH , $(CH_3)_2$ C — CH_2OCH_3 OH OCH $_3$ (b) $(CH_3)_2C$ — CH_2OH , $(CH_3)_2C$ — CH_2OH

$$(c) (CH_3)_2 C - CH_2OH, (CH_3)_2 C - CH_2OCH_3$$

$$(d) (CH_3)_2 C - CH_2OH, (CH_3)_2 C - CH_2OCH_3$$

$$(d) (CH_3)_2 C - CH_2OCH_3, (CH_3)_2 C - CH_2OH$$

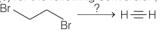
- 34 (CH₃)₃ CMgCl on reaction with D₂O produces
 - (a) (CH₃)₃COD

(b) (CD₃)₃CH

(c) (CH₃)₃CD

(d) (CD₃)₃CD

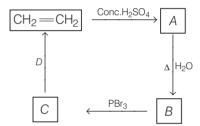
35 The reagent(s) for the following conversion, is/are



(a) alcoholic KOH

→ [IIT JEE]

- (b) alcoholic KOH followed by NaNH₂
- (c) aqueous KOH followed by NaNH₂
- (d) Zn / CH₃OH
- **36** Identify *B* and *D* in the following sequence of reactions.



- (a) Methanol and bromoethane
- (b) Ethyl hydrogen sulphate and alcoholic KOH
- (c) Ethyl hydrogen sulphate and aqueous KOH
- (d) Ethanol and alcoholic KOH
- **37** Which compound does not give precipitate with ammoniacal silver nitrate solution?

(a)
$$C_2H_5$$
— $C \Longrightarrow CH$

(b)
$$CH_3 - C \equiv C - CH_3$$

(d)
$$Ph$$
— CH_2 — $C \equiv CH$

38 Thermal decomposition of

$$(a) \qquad \begin{array}{c} \bigoplus & \bigoplus \\ \text{CH}_2\text{NMe}_3\text{OH gives} \end{array}$$

$$(a) \qquad \begin{array}{c} \bigoplus \\ \text{CH}_2 \end{array} \qquad (b) \qquad \begin{array}{c} \bigoplus \\ \text{NMe}_2 \end{array}$$

$$(c) \qquad \begin{array}{c} \bigoplus \\ \text{CH}_2\text{OH} \end{array} \qquad (d) \qquad \begin{array}{c} \bigoplus \\ \text{CH}_3 \end{array}$$

- **39** The dihalogen derivative *X* of a hydrocarbon with three carbon atoms reacts with alcoholic KOH and produces another hydrocarbon which forms a red precipitate with ammoniacal Cu₂Cl₂. *X* gives an aldehyde on reaction with aqueous KOH. The compound *X* is
 - (a) 1, 3-dichloropropane
- (b) 1, 2-dichloropropane
- (c) 2, 2-dichloropropane
- (d) 1, 1-dichloropropane

Direction (Q. Nos. 40-44) In the following questions, Assertion (A) followed by a Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) A is correct but R is incorrect
- (d) Both A and R are incorrect
- **40** Assertion (A) Phenol forms 2,4,6-tribromophenol on treatment with Br_2 in carbon disulphide at 273 K.

Reason (R) Bromine polarises in carbon disulphide.

→ [NCERT Exemplar]

[INCERT Exemplai]

41 Assertion (A) Pent-1-ene and pent-2-ene are position isomers.

Reason (R) Position isomers differ in the position of functional group or a substituent. →[NCERT Exemplar]

42 Assertion (A) The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.

Reason (R) The intermediate carbanion is stabilised due to presence of nitro group.

43 Assertion (A) *trans*-2-butene on reaction with Br₂ gives *meso*-2,3-dibromobutane.

Reason (R) The reaction involves *syn*-addition of bromine.

44 Assertion (A) Anilinium chloride is more acidic than ammonium chloride.

Reason (R) Anilinium ion is resonance stabilised.

45 Given,

$$A = \bigcirc OMe \qquad B = \bigcirc OH \qquad C = \bigcirc OH$$

The decreasing order of the acidic character is

- (a) A > B > C
- (b) B > A > C
- (c) B > C > A
- (d) C > B > A
- 46 2,3-dimethylpentane on treatment with Cl₂/hv produces how many monochloro isomers (only constitutional isomers)?
 - (a) 4

- (b) 5 (d) 8
- (c) 6
- **47** Which one of the following is an example of Hell-Volhard-Zelinsky reaction?

(a)
$$RCOOH \xrightarrow{\text{(i) B}_2H_6} RCH_2OH$$

(b)
$$R_2$$
CHCOOH $\xrightarrow{\text{(i)}} Br_2 \xrightarrow{\text{(Red P)}} R_2$ CCOOH R_2

(c)
$$COOH \xrightarrow{NH_3} \Delta$$

(d)
$$RCOOH \xrightarrow{PCl_5} RCOC$$

- 48 Zeisel's method is used to estimate
 - (a) alcoholic group
 - (b) amino group
 - (c) methoxy group
 - (d) halo group
- 49 Identify C, in the following reaction.

$$\begin{array}{c}
NO_2 \\
\hline
Sn/HCI \\
A \\
\end{array}$$

$$A \xrightarrow{NaNO_2} B \xrightarrow{NaNH_2} O$$

- (a) Benzamide
- (b) Benzoic acid
- (c) Chlorobenzene
- (d) Aniline

50 Match the reactions given in Column I with the names given in Column II.

Column I		Column II
A. $X + RX \xrightarrow{Na} R$	1.	Fittig reaction
B. 2 +2Na Ether +2Na X	2.	Wurtz Fittig reaction
C. $N_2^{+} \overline{N}_2^{-} \times N_2^{-} \times $	3.	Finkelstein reaction
D. $C_2H_5CI + NaI \xrightarrow{Dry acetone} C_2H_5I + NaCI$	4.	Sandmeyer reaction
Codes A B C D A B C	D	

- ABCD
- ABCL
- (a) 1 2 4 3
- (b) 2 1 4 3
- (c) 1 2 3 4
- (d) 2 3 1 4

ANSWERS

1 (b)	2 (a)	3 (a)	4 (d)	5 (c)	6 (d)	7 (c)	8 (b)	9 (a)	10 (c)
11 (c)	12 (b)	13 (b)	14 (c)	15 (c)	16 (d)	17 (c)	18 (c)	19 (c)	20 (c)
21 (d)	22 (c)	23 (c)	24 (b)	25 (b)	26 (a)	27 (d)	28 (c)	29 (c)	30 (c)
31 (d)	32 (a)	33 (c)	34 (c)	35 (b)	36 (d)	37 (b)	38 (a)	39 (d)	40 (d)
41 (a)	42 (a)	43 (c)	44 (c)	45 (c)	46 (c)	47 (b)	48 (c)	49 (d)	50 (b)

Hints and Explanations

1.	Species	Valence electrons	Magnetic behaviour
	Carbonium ion	6	Diamagnetic
	Free radical	7	Paramagnetic
	Carbene	6	Diamagnetic
	Nitrene	6	Diamagnetic

- **2.** O₃ is responsible for greenhouse effect. Its contribution is about 8%.
- **3.** Greater the +/-effect, greater the nucleophilic power. The +/-effect of ethyl is greater than +/-effect of methyl group.

$$\begin{array}{c} & & & \\ \text{C}_2\text{H}_5 & \longrightarrow & \text{S} - \text{H}, \text{CH}_3 & \longrightarrow & \text{C} - \text{O}^-, \\ & & & \\ \text{CH}_3 & \longrightarrow & \text{NH}_2, \text{NC} & \longleftarrow & \bar{\text{C}} \text{H}_2 \end{array}$$

4. $CH_4 + CI_2 \xrightarrow{hv} CH_3CI$ (Free radical substitution)

The steps involved in the process are as follows:

$$CI \longrightarrow CI \xrightarrow{hv} CI^{\bullet} + CI^{\bullet}$$
 $CH_4 + CI^{\bullet} \longrightarrow CH_3 + HCI$

$$\label{eq:continuous_continuous$$

5.
$$CH_3 - C = NH_2 - NH_2 - NH_3 = N + H_2O$$

6. When acetaldehyde is treated with aqueous sodium hydroxide solution, it undergoes aldol condensation because of the presence of α -H-atom.

$$\begin{array}{c} \text{2CH}_3\text{CHO} & \xrightarrow{\text{dil.NaOH}\,(aq\;)} & \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} \\ & \text{Aldol shows optical isomerism} \\ & \xrightarrow{\Delta} & \text{CH}_3\text{CH} = \text{CHCHO} \\ & \text{(Shows geometrical isomerism)} \end{array}$$

Due to resonance stabilisation option (c) forms more stable free radical.

$$\begin{array}{c} \textbf{8.} \overset{\text{CH}_2}{\mid \mid} \xrightarrow{\text{HBr}} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{Hydrolysis}} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{Na}_2\text{CO}_3} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{I}_2(\text{excess})} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{I}_2(\text{excess})} \xrightarrow{\text{Iodoform}} \overset{\text{Indeform}}{\text{(Yellow ppt. Collisions)}} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3}{\mid} \xrightarrow{\text{CH}_3} \overset{\text{CH}_3} \overset{\text$$

9. Compound (a) is an enantiomer of compound (A) because in them, the configuration of two groups, i.e. CH₃ and C₂H₅ are reversed at the chiral carbon.

Maleic anhydride

12.
$$CH_3C = CH \xrightarrow{NaNH_2} CH_3 - C = CNa \xrightarrow{CH_3CH_2Br} -NaBr$$

$$CH_3C = C \cdot CH_2CH_3 \xrightarrow{Lindlar's catalyst} \xrightarrow{H_3C} C = C \xrightarrow{CH_2CH_3} C \xrightarrow{CS alkene} C \xrightarrow{CS a$$

13. When alkane is passed over ${\rm AlCl}_3$ in presence of HCl, isomerisation takes place.

$$\begin{array}{c} \operatorname{CH_3CH_2CH_3} \xrightarrow{A \mid \text{Cl}_3 \mid \text{HCl}} \operatorname{CH_3} \longrightarrow \operatorname{CH_3}$$

14. Methyl ketones are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound.

-CF $_3$ group withdraws electrons from the ring, shows -M effect, makes ring electron deficient, thus deactivates ring for electrophilic substitution.

16.
$$CH_2 = CH - O - CH_3 \xrightarrow{HBr} CH_3 - CH - OCH_3$$

First protonation occurs, two possible intermediates are

$$^+ \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{OCH}_3$$
 and $\text{CH}_3 - ^+ \text{CH} - \text{OCH}_3$
 $^+ \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{OCH}_3$ and $\text{CH}_3 - ^+ \text{CH} - \text{OCH}_3$
 $^+ \text{CH}_2 \rightarrow \text{CH}_3$ and $\text{CH}_3 - ^+ \text{CH} - \text{OCH}_3$
 $^+ \text{CH}_3 - ^+ \text{CH}_3$
 $^+ \text{CH}_3$

II is more favourable, hence Br attacks and product is

$$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{OCH}_3 \\ \text{H} \quad \text{H} \quad \text{H} \\ \text{I} \quad \text{Br} \quad \text{S}^{\circ} \text{ (C - H) bond has minimum bond energy, hence easily gives} \\ \text{2-bromo-2-methylbutane.} \\ \text{H} \quad \text{CH}_3 \\ \text{Br} \quad \text{Br} \\ \text{Br}_2 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \\ \end{array}$$

Stability of I > II, hence I is predominant.

19.
$$CH_2$$
= $CHCH$ = CH_2 + HBr — CH_3 CHCH= CH_2 + CH_3 CH= $CHCH_2$ Br
Br
1,4-addition product
1,2-addition product

Addition is through the formation of allylic carbocation.

$$\begin{array}{c} \operatorname{CH_2} = \operatorname{CH} \overset{\oplus}{\operatorname{CHCH_3}} \longleftrightarrow \operatorname{CH_3CH} = \operatorname{CH} \overset{\oplus}{\operatorname{CHCH_2}} \\ \operatorname{2^o allylic (more stable)} & \operatorname{1^o allylic (less stable)} \end{array}$$

Under mild conditions (–80°C), kinetic product is the 1,2-addition product and under vigorous conditions (40°C), thermodynamic product is 1,4-addition product. Hence, 1-bromo-2-butene is the major product under given conditions.

- **20.** Any aliphatic carbon with hydrogen attached to it on combination with benzene ring will be oxidised to benzoic acid by ${\rm KMnO_4}/{\rm H^+}$.
- **21.** For positive iodoform test, alcohol molecule must have CH₃—CH— group.

22. Addition of HCN is nucleophilic reaction. Greater the electron deficiency of carbonyl group, higher the rate of reaction.

23.
$$CH_2 = CH_2 \xrightarrow{H_2O/H^+} CH_3CH_2OH$$

$$CH_3 - CH - CH = CH_2 \xrightarrow{H_2O/H^+} CH_3 - CH_3 -$$

Suitable reagent is chromic acid in aqueous acetone solution while others will also affect (C=C) bond.

25. $A + \text{NaOH} \longrightarrow \text{alcohol} + \text{acid}$ (Cannizaro reaction) $A \text{ must be aldehyde without H at } \alpha\text{-carbon}$.

2 + NaOH
$$\longrightarrow$$
 C₆H₅CH₂OH + C₆H₅COONa

Benzaldehyde

26.
$$C_2H_5NC + H_2O \xrightarrow{H^+} HCOOH + C_2H_5NH_2$$

 $C_2H_5NH_2 + H^+ \longrightarrow C_2H_5NH_3^+$
Salt

Salt

Salt

Salt

27.
$$CHCl_3 + KOH \longrightarrow : CCl_2 + KCl + H_2O$$
 $CH_3CH_2NH_2 + : CCl_2 \longrightarrow CH_3CH_2NC + 2HCl$

Carbylamine

or $CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2NC$
 $+3 KCl + 3H_2O$

- **28.** In the given resonating structures, structure II is not an acceptable canonical structure because the nitrogen has ten valence electrons.
- **29.** In structure (c), N-atom forms five bonds and contains positive charge, so the structure is not possible.
- **30.** Nitrobenzene on reduction with LiAIH₄ gives azobenzene.

$$NO_2$$
 $Nitrobenzene$
 NO_2
 $Nitrobenzene$

Azobenzene

Aromatic nitro compounds on reduction with ${\rm LiAlH_4}$ gives azo compounds and not primary amines. Aliphatic nitro compounds are reduced to primary amines with ${\rm LiAlH_4}$.

31. Br
$$\xrightarrow{\text{CH}_3/_2\text{NH}}$$
 excess $\text{(H}_3\text{C)}_2\text{N}$ $\xrightarrow{\text{CH}_3\text{I}}$ (excess),base $\xrightarrow{\text{Benzene}}$ $\xrightarrow{\text{Ag}_2\text{O}}$ $\text{(H}_3\text{C)}_3\text{N}$ $\xrightarrow{\text{H}}$ $\xrightarrow{\text{H}}$ $\text{(CH}_3)_3$

33.
$$(CH_3)_2C \xrightarrow{CH_2} \xrightarrow{CH_3O^-} (H_3C)_2C \xrightarrow{CH_2OCH_3} \xrightarrow{CH_3OH} (H_3C)_2C \xrightarrow{CH_2OCH_3} \xrightarrow{CH_3OH} (B)$$

$$(H_{3}C)_{2}C \xrightarrow{C} CH_{2} \xrightarrow{H^{+}} (H_{3}C)_{2}C \xrightarrow{C} CH_{2} \xrightarrow{H^{+}} CH_{2} \xrightarrow{O} 18$$

$$H \xrightarrow{18OH} H \xrightarrow{18O} H \xrightarrow{18O} H \xrightarrow{18O} H \xrightarrow{H^{+}} (H_{3}C)_{2}C \xrightarrow{C} CH_{2} \xrightarrow{H^{+}} OH OH$$

34.
$$(CH_3)_3C - MgCI + D_2O \longrightarrow (CH_3)_3C \cdot D + MgCI(OD)$$
Grignard reagent

[Grignard reagent when reacts with a protic solvent, gives alkane.]

35. Br
$$\xrightarrow{Alc. KOH}$$
 \xrightarrow{Br} $C = C$ \xrightarrow{H} $\xrightarrow{NaNH_2}$ $H = H$

Vinylic bromide is more stable and stronger base $(-NH_2^-)$ is required for elimination.

- **37.** Only terminal alkynes give precipitate with ammoniacal silver nitrate solution. Among the given, $CH_3 C \equiv C CH_3$ is not a terminal alkyne. Thus, it does not give precipitate with ammoniacal AgNO $_3$.
- **38.** The formation of the alkene in an elimination reaction is called Hofmann elimination (thermal decomposition). Elimination of hydrogen occurs from the β-carbon. So,

39. *X* is a three carbon compound with two halogen atom, so its molecular formula is $C_3H_6Cl_2$. Only terminal alkynes give red ppt. with ammoniacal Cu_2Cl_2 , so the hydrocarbon produced by the reaction of *X* with alcoholic KOH, must be a terminal alkyne i.e. $CH_3C \equiv CH$.

$$\begin{array}{c} \text{C}_{3}\text{H}_{6}\text{Cl}_{2} \xrightarrow{\text{Alc: KOH}} \text{CH}_{3}\text{C} \!\equiv\! \text{CH} \xrightarrow{\text{Ammoniacal Cu}_{2}\text{Cl}_{2}} \\ \text{CH}_{3}\!\text{C} \!\equiv\! \text{CCu} \downarrow \\ \text{Red ppt.} \end{array}$$

Compound (X) gives an aldehyde when reacts with aqueous KOH. This suggests that both the halogens are present on same terminal carbon atom. Thus, the formula of compound X is

and the reactions are as follows:

$$CH_3CH_2CH \xrightarrow{CI} \xrightarrow{Alc. KOH}$$

$$X$$
Appropriated Cu Cl

$$CH_3C \equiv CH \xrightarrow{Ammoniacai Cu_2Cl_2} CH_3C \equiv CCu \downarrow$$
Red ppt.

$$CH_3CH_2CH \xrightarrow{CI}_{Aq. KOH}$$

$$\begin{array}{c} \text{OH} \\ \text{CH}_3\text{CH}_2\text{CH} \\ \text{Unstable} \end{array} \\ \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$$

40. Correct Assertion Phenol forms 2,4,6-tribromophenol on treatment with Br₂ in water.

Correct Reason In H₂O, phenoxide ion is formed which highly activates it towards electrophilic substitution reaction.

41.
$$\overset{5}{\text{C}}\text{H}_3 - \overset{4}{\text{C}}\text{H}_2 - \overset{3}{\text{C}}\text{H}_2 - \overset{2}{\text{H}}\overset{2}{\text{C}} = \overset{1}{\text{C}}\text{H}_2$$

$$\overset{5}{\text{C}} \text{H}_3 - \overset{4}{\text{C}} \text{H}_2 - \overset{3}{\text{H}} \overset{1}{\text{C}} = \overset{1}{\text{C}} \text{H} - \overset{1}{\text{C}} \overset{1}{\text{H}}_3$$

When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton then it shows position isomerism. Double bond is a functional group whose position varies.

42. Both Assertion and Reason are correct as presence of nitro group (electron withdrawing group) with respect to halogen activates the aryl halides towards nucleophilic substitution reaction because the carbanions formed in the reaction are stabilised by the NO₂ group.

43. *trans*-2-butene reacts with Br₂ to produce *meso-2*,3- dibromobutane but it does not involve *syn* addition of Br₂.

44. Anilinium chloride is more acidic than NH₄Cl because it forms salt with water and liberate amine when treated with strong base.

$$C_6H_5NH_3CI^- + NaOH \longrightarrow C_6H_5NH_2 + H_2O + NaCI$$

Anilinium ion does not show resonance because charge dispersion at ring may involve pentavalent nitrogen structure.

45. According to Lewis, electron acceptor compounds are called acids. Therefore, compounds having tendency to accept electrons will be more acidic. The correct order of acidic character is as follows:

$$\begin{array}{c|cccc}
OMe & NO_2 \\
\hline
OH & OH & OH \\
(A) & (B) & (C)
\end{array}$$

46. Six isomers (only constitutional)

47. When aliphatic carboxylic acids react with bromine in the presence of red phosphorus, they give α -halogenated acids. This reaction is known as Hell-Volhard-Zelinsky reaction.

48. Zeisel's method is used to estimate the methoxy group in an organic compound. In this method, organic compound having methoxy group is treated with HI and the alkyl halide thus formed as further treated with AgNO₃ to precipitate AgI.

49.
$$NO_2$$
 NH_2
 $NANO_2$
 N

50. $A \rightarrow 2$; $B \rightarrow 1$; $C \rightarrow 4$; $D \rightarrow 3$