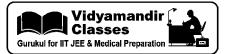
81



SOLUTIONS

Module - 3 / JEE-2022

| IN-CHAPTER EXERCISES | Chemistry | Hydrocarbons |
|----------------------|-----------|--------------|
|----------------------|-----------|--------------|

EXERCISE-A

1.
$$(CH_3)_3 - C - MgI + CH_3NH - H^{\delta+} \longrightarrow (CH_3)_3 - C - H_{(alkane)}$$

(i) Grignard reagent as base.

(iii)
$$(CII_3)_2 - CII - MgBr + OH \longrightarrow (CH_3)_2 - CH_2$$

(iv)
$$CH_3$$
 CH - CH_2 C1 HI $Red P$ CH_3 CH - CH_2

2. (A) CH₄: % H =
$$\frac{4}{16} \times 100 = 25$$
 (check similarly for others)

- **3. (A)** Alkylhalide on reduction with Zn-Cu couple in ethanol form alkane.
- **4. (A)** Excess of C_2H_6 when reacts with Cl_2 in presence of UV light gives maximum yield of C_2H_5Cl . Excess of Cl_2 form polyhalides.
- 5. (B) MeMgBr + DOD \longrightarrow CH₃D
- **6.** (ACD) Reduction of ketones by HI/Red P will not produce ethane.

1. (i)
$$CH_3 = CH_2 \xrightarrow{\delta + \delta - CH_3} C-CH_2-I \quad (Markovnikov's product)$$

$$CH_3 = CH_3 + CH_3$$

(ii)
$$CH_3CH_2 - C = CH_2 \xrightarrow{\begin{array}{c} \delta_+ & \delta_- \\ I - CI \end{array}} CH_3 - CH_2 - C - CH_2 - I$$

$$CH_3 \qquad CH_3$$

2. (i)
$$CH_3CH_2CH_2CH = CH_2 \xrightarrow{1. Hg(OAc)_2/THF/H_2O} CH_3CH_2CH_2CH - CH_3$$

$$CH_3CH_2CH_2CH = CH_2 \xrightarrow{1. Hg(OAc)_2/THF/H_2O} CH_3CH_2CH_2CH - CH_3$$

$$OH$$

[JEE-2022/Module - 3] Chemistry

IN-CHAPTER EXERCISES



(ii)
$$\begin{array}{c} CH_3 & CH_3 \\ | & | \\ CH_3 - C - CH = CH_2 \xrightarrow{\quad "} CH_3 - C - CH - CH_3 \text{ (Markovnikov's product)} \\ | & | & | \\ CH_3 & CH_3 \text{ OH} \end{array}$$

Hydroboration oxidation follows Anti - Markovnikov's addition (HBO) 3.

(ii)
$$CH_3$$
 CH_3 CH

4. (i)
$$CH_3 = CH_3 + OH + CH_3 + CH_$$

(iv)
$$H_2C = O + O = C = O + O = CH_2$$
 \leftarrow $H_2C = C = CH_2$

(iv)
$$H_2C = O + O + C = O + O + C + C = CH_2$$

(v) $H_2C = O + OHC - C = O + H_2C = O \leftarrow H_2C = C - C = CH_2$
 CH_3

α-keto propionaldehyde

5. (i)
$$CH_3CH = CHCH_3 + Cl_2 \xrightarrow{400^{\circ}C} CH_3CH = CHCH_2$$
 (allylic substitution)

(ii)
$$Et \longrightarrow C = CH_2 \xrightarrow{1. BH_3/THF} Et \longrightarrow CH - CH_2$$
OH

(iv)
$$CII_3CII + CII - COOH$$

Symmetric alkenes give same product with reference to Markovnikov's and Anti-Markovnikov's addition. 6. (C)

IN-CHAPTER EXERCISES



8. (C)
$$\begin{array}{c} \text{CH}_2\text{COOK} \\ \text{CH}_2\text{COOK} \end{array} \xrightarrow{\begin{array}{c} \text{H}_2\text{O} \\ \text{Electrolysis} \end{array}} \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array}$$
9. (A) $\begin{array}{c} \text{CH}_2 = \text{CH}_2 \xrightarrow{\text{HOCl}} \text{CH}_2 - \text{CH}_2 \\ \text{Cl} \end{array}$

10. (B) CH₃CH CHCHO
$$\frac{\text{(O)}}{\text{KMnO}_4/\text{H}^+/\Delta}$$
 CH₃COOH + $\frac{\text{COOH}}{\text{COOH}}$

Reagent (R) = ? is clearly $\xrightarrow{\text{B}_2\text{H}_6 \text{ or BH}_3}$ Anti-Markovnikov's addn.

12. (A)
$$CH_3$$
 $C = CH_2$ CH_3 CH_3 CH_4 CH_3 CH_5 CH_5 CH_5 CH_5 CH_5 CH_6 CH_6 CH_7 CH_8 CH_8 CH_8 CH_8 CH_9 CH

13. (C) $CH_2 = CH_2$ is least stable alkene (Saytzeff's rule)

14. (A)
$$(CH_3)_3 - C - CH = CH_2 \xrightarrow{1. Hg(OAc)_2/THF/H_2O} (CH_3)_3 - C - CH - CH_3$$
OH

(Markovnikov's product)

- **15. (D)** A: Test of unsaturation B: Test of unsaturation All being unsaturated will respond positively
 - C: Test for Terminal alkynes $(R C \equiv CH)$

16. (D)
$$R - CH = CH - R' + HBr \longrightarrow R - CH_2 - CH - R'$$

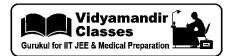
- For 3-bromohexane, alkene can be 2-Hexene or 3-Hexene.
- **17. (B)** Compare stabilities of given alkenes. The one which is least stable will show hydrogenation most easily. Observe RCH = CHR is least stable among all.
- 18.(B) 2-Butanol on acid catalyzed dehydration produces a mixture of 1-Butene, cis-2-Butene and Trans-2-Butene.

Meso isomer

$$CH_3 \longrightarrow C = C \longrightarrow CH_3 \longrightarrow H \longrightarrow Br \longrightarrow Br \longrightarrow CH_3$$

Total five isomeric product.

[JEE-2022/Module - 3] Chemistry



- 19.(D) Addition of HCl on alkene takes place according to Markovnikov's rule by electrophilic addition reaction mechanism.
- **20.(A)** Due to presence of chiral carbon atom.

EXERCISE-C

1. (i)
$$CH_3CH_2C \equiv C - CH_2CH_3 \xrightarrow{\text{quino line} \\ \text{(Syn addn)}} \xrightarrow{\text{Et}} C = C \xleftarrow{\text{Et}} H$$

(ii)
$$C = CH$$
 $\frac{HOH}{Hg^{2+}/H^{+}}$ $C = CH_2$ $C - CH_3$ (Tautomerisation) Acetophenone

2. (A)
$$Ag - \overset{-\delta}{C} = \overset{-\delta}{C} - Ag + \overset{+\delta}{2}H - \overset{-\delta}{C}I \longrightarrow HC = CH + 2AgCl_{(s)}$$

- **3. (A)** Terminal alkyne on oxymercuration form methyl ketone.
- **4. (D)** $CH_3CH_2C \equiv CH$ is a Terminal alkyne.

1-Butyne
$$\begin{array}{c} Amm \\ \hline AgNO_3 \\ \hline \\ CH_2CH_2-C \equiv C-Ag \downarrow (White) \\ \hline \\ Amm \\ \hline \\ Cu_2Cl_2 \\ \end{array}$$
 $CH_3CH_2-C \equiv C-Cu \downarrow (Red)$

Non-terminal alkynes do not respond to above tests.

1. (i) $\frac{\operatorname{Br}_2}{\operatorname{CCl}_4}$ Br Me Br Me Br Me Br Me Br (trans form) (anti addn.)

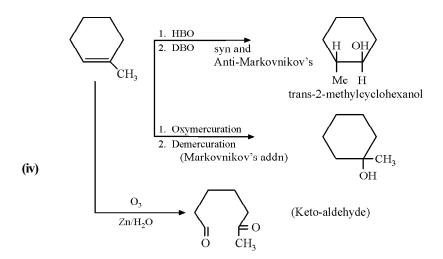
(ii)
$$\begin{array}{c} & & & \\ & &$$



(iii)
$$D_2$$

$$Cis-1.2-Dideutrocyclol$$

cis-1,2-Dideutrocyclohexane [syn addn] (same as hydrogenation)



2. (A) Reactivity of cycloalkanes is inversely proportional to stability.

Stability follows :
$$\begin{array}{c} \\ \\ \\ \\ \\ \end{array}$$

(cyclo propane has the least bond angle hence more strained therefore it is most reactive.)

3. (C)
$$\frac{\text{alk.}}{\text{KMnO}_4}$$
(syn: hydroxylation)
$$\frac{\text{H}}{\text{OH}} = \frac{\text{H}}{\text{OH}}$$

$$\begin{array}{c} O & O \\ \hline \textbf{L} & \begin{array}{c} CH_3-C-CH_2-CH_2-C-CH_3 \\ \hline \\ CH_2 \end{array} \end{array} \xrightarrow{\hspace*{0.5cm}} \begin{array}{c} 2HCHO+CH_3-C-CH_2CH_2-C-CH_3 \\ \hline \\ O \end{array}$$

II.
$$CH_3 = \frac{1}{2} + \frac{1$$

[JEE-2022/Module - 3] Chemistry



Observe that IV does not give the desired product.

(ii)
$$CH_2 \stackrel{!}{=} C \stackrel{!}{=} CH - CH_3 \xrightarrow{C_3} CH_2O + CO_2 + CH_3CHO$$
(HCHO)

(iii)
$$2 \xrightarrow{3} 4 \xrightarrow{(O)} 2 \xrightarrow{\text{COOH}} \text{(Malonic acid)}$$

(iv) Lindlar's catalyst catalyze hydrogenation of only $C \equiv C$ upto C = C stage

2. As compound (E) forms formaldehyde on ozonolysis hence it is terminal alkene. Degree of unsaturation equal to two also indicate two double bonds in (E)

3. (i) (B) Allene
$$CH_2 = C = CH_2$$

$$\uparrow \qquad \uparrow \qquad \uparrow \\
sp^2 \qquad sp \qquad sp^2$$

- (ii) (C) Cummulated diene is non planar, dissymmetric compound and it is also called as allene or substituted allene.
- (iii) (A) 1,3-cyclohexadiene is conjugated diene and it is resonance stabilized. Hence its observed heat of hydrogenation is less than 240 kJ/mol.

(iv) (D)
$$H = \frac{180^{\circ}}{C} = C H = C$$
H
(v) (A) $H = \frac{180^{\circ}}{C}$



(vi) (C) It is an example of Diels - alder reaction.

4. $(CH_3)_3C - C \equiv C - CH_2 - C(CH_3)_3$; $(CH_3)_3C - CH = C = CH - C(CH_3)_3$

EXERCISE-F

ROH
$$\xrightarrow{\text{HF}}$$
 (R⁺ : Electrophile) \longrightarrow R

Hence in present case : $CH_2-CH = CH_2$ Allyl benzene

(ii)
$$+ C_2H_5OH \xrightarrow{HF} C_2H_5$$

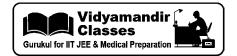
(iii)
$$CH_3 \longrightarrow COOH$$
 (phthalic acid)

2.
$$COOH$$

$$CH_3 \qquad (O) \qquad NaOH/CaO$$

$$CH_3 \qquad COOH$$

$$(Terephthalic acid) \qquad (Decarboxylation)$$



3.
$$\frac{\text{CH}_3\text{COCl}}{\text{AlCl}_3} \longrightarrow \frac{\text{O}}{\text{C}} - \text{CH}_3 \xrightarrow{\text{Zn-Hg}} \longrightarrow \text{CH}_2\text{CH}_3 \xrightarrow{\text{NBS/CCl}_4} \longrightarrow \text{Allylic Substitution}$$
Friedal-craft Acetophenone (Clemmensen's Reduction)

$$CH = CH_2 \xrightarrow{\text{EtOH}} CH - CH_2$$

$$= EtO^{-}$$

$$= EtO^{-}$$

$$| CH - CH_2 -$$

Vinyl benzene (STYRENE)

4. (i) Refer to Notes.

(ii)
$$COOH$$

NO₂
 $COOH = NO_2$

* - COOH group is a m-directing group

 $COOH = NO_2$

- 5. (C) $CH_3 \leftarrow$ is a weakly activating group, hence it show Electrophilic substitution (S_E) quite easily as compared to others.
- **6. (A)** It undergoes free radical halogenation of side chain to form benzotrichloride (C₆H₅CCl₃)
- 7. (A) Learn as a fact. OH and NH_2 : strong o/p directing NO_2 : strongly deactivating (strongly activating) (poor for substitution)
- **8.** (C) Because in alkylation, polyalkylation also takes place.
- 9. (C) n-Alkanes having six or more carbon atoms on heating to 773 K at 10 20 atm pressure in vanadium pentoxide or chromium oxide supported over alumina get hydrogenated and cyclized to benzene and its homologue.

$$CH_3 - (CH_2)_5 - CH_3 \xrightarrow{Cr_2O_3} CH_3 - (CH_3)_5 - CH_3$$

n-Heptane Toluene

10. (B) Iodination of benzene is reversible reaction therefore resulting C_6H_5I is reduced to C_6H_6 by HI.

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

11.(A) Benzene sulphonic acid on treatment with steam under pressure gives benzene.

12. (A)
$$\frac{Y}{S_E}$$
 m - isomer is major