SUBJECTIVE SOLVED EXAMPLES

Example - 1 Give the structure of A, B and C (explanation are not required):

- (i) $A(C_4H_8)$ which adds on HBr in the presence and in the absence of peroxide to give same product, C_4H_9Br
- (ii) $B(C_4H_8)$ which when treated with H_2O/H_2SO_4 gives $C_4H_{10}O$ which cannot be resolved into optical isomers.
- (iii) $C(C_6H_{12})$, an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound C_6H_{14} .

SOLUTION:

(i) A: CH₃CH=CHCH₃ symmetric alkenes give same product.

(ii) B:
$$CH_3 - C = CH_2 \xrightarrow{H_2O} CH_3 - C - CH_3$$
; optically inactive (No chiral centre) $CH_3 \xrightarrow{CH_3} CH_3$

Example - 2 An organic compound $E(C_5H_8)$ on hydrogenation gives compound $E(C_5H_{12})$. Compound $E(C_5H_{12})$ on hydrogenation gives formaldehyde and 2-ketopropanal. Deduce the structure of compound $E(C_5H_{12})$.

SOLUTION: In such questions, by working backwards we join:

$$>$$
 C = O + O = C $<$ \longrightarrow $>$ C = C $<$

Note: Since 2-ketopropanal has two keto groups, hence there must be 2 moles of HCHO.

(E)
$$\frac{O_3}{Zn-H_2O}$$
 2HCHO + CH₃ -C-CHO \Rightarrow E is: $CH_2 = C - CH = CH_2$ (Isoprene)

Example - 3 The hydrocarbon, A adds one mole of hydrogen in the presence of a platinum catalyst to form neo-hexane. When A is oxidised vigorously with $KMnO_4$, a single carboxylic acid, B is isolated. Give the structures of A and B.

SOLUTION:

Example - 4 What are product A, B and C in the following rection?

$$CH_3$$
 H_2 A OO $B+C$

SOLUTION: Visualise the structure of given compound as follows:

Example - 5 Identify the products A, B and C and the reagent R in the following reactions:

(i)
$$(CH_3)_2 C - CH_2 CH_3 \xrightarrow{alc. KOH} A$$
 (ii) $HC \equiv CH \xrightarrow{H_2O} B$

(iii)
$$A \xrightarrow{R} B + C$$

SOLUTION:

(i)
$$CH_3$$
 CH_3 CH_3 CH_3 $CH_3 - C - CHCH_3$ $CH_3 - C = CHCH_3$ (Saytzeff's product)
$$CH_3 - C - CHCH_3 \xrightarrow{RO^-} CH_3 - C = CHCH_3$$
 (Saytzeff's product)

(ii)
$$HC \equiv CH \xrightarrow{H_2O} CH_2 = CHOH \xrightarrow{Tautomerises} CH_3CHO$$
(B)

(iii)
$$CH_3$$
 $CH_3 - C = CHCH_3 \xrightarrow{R} CH_3CHO + (C)$

R is clearly $O_3/Zn-H_2O$ and (C) is acetone (CH_3COCH_3)

$$CH_3 \xrightarrow{\mid} CH_3 - C = CHCH_3 \xrightarrow{Q_3} CH_3CHO + (CH_3)_2C = O$$
(A)
(B)
(CH_3)

Example - 6 De-hydro-bromination of two compounds A and B gives the same compound C. C regenerates A and B when reacts with HBr in the presence and absence of peroxide respectively. The hydrolysis of A and B gives isomeric products D and E respectively. C when reacts with benzene in presence of H⁺ ions gives 1, 1-Diphenylethane. Identify the compounds A to E.

SOLUTION: Visualizing the flow chart of the question as follows.

A
$$\xrightarrow{-HBr}$$
 C $\xrightarrow{Peroxide}$ A $\xrightarrow{aq. KOH}$ D \xrightarrow{HBr} B $\xrightarrow{aq. KOH}$ E $\xrightarrow{C_6H_6}$ 1, 1-Diphenyl ethane $\xrightarrow{CH-CH_3}$

Recall Friedal Craft alkylation

 \Rightarrow C is an alkene containing a – C = C – bond, hence C is vinyl benzene. C: C:

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

As per given reactions in question:

A:
$$\longrightarrow$$
 CH₂CH₂Br B: \longrightarrow CH-CH₃ D: \longrightarrow CH₂CH₂OH E: \longrightarrow CH-CH

Example - 7 An organic compound A, C_5H_9Br de-colourises bromine water and alk. $KMnO_4$. It gives B, $C_5H_{11}Br$ when treated with H_2 , Pd-carbon in methanol. The reaction of A with $NaNH_2$ gives C with the evolution of NH_3 . C does not react with sodium but reacts with Lindlar catalyst to give D. It also reacts with $Na/liquid\ NH_3$ to give E. Both D and E are isomers. Identify the compounds A to E with proper reasoning.

SOLUTION:

Visualizing the flow chart of the question as follows:

Since D and E are isomers obtained by partial hydrogenation of 'C' (C: an alkyne) from two different reagents, D and E must be geometric isomers with molecular formula C_5H_{10} . "Check this as follows"

(A)
$$C_5H_9Br \xrightarrow{NaNH_2} C_5H_8 + NH_3 + Br^-$$

$$C(C_5H_8) \xrightarrow{H_2} C_5H_{10} (D \text{ and } E)$$

The alkene with molecular formula, C_5H_{10} showing geometric isomerism is only 2-Pentene [CH₃CH = CHC₂H₅]

$$CH_3$$
 $C = C$ H $C = C$ H $C = C$ H $C = C$ C_2H_5 $C = C$ C_2H_5 $C = C$

Hence the compound (C) is 2-Pentyne (Non-terminal alkynes do not react with Na).

$$CH_{3} - C \equiv C - C_{2}H_{5}$$

$$CH_{3} - C \equiv C$$

$$CH_{3} - C$$

$$CH_{3} - C \equiv C$$

$$CH_{3} - C$$

$$CH$$

A can be:

$$CH_3C = CH - C_2H_5$$
 or $CH_3CH = C - C_2H_5$
 Br Br

Both will give 2-Pentyne with NaNH₂.

Accordingly B can be:

$$\begin{array}{cccc} \operatorname{CH_3CH-CH_2-C_2H_5} & \text{ or } & \operatorname{CH_3CH_2-CHC_2H_5} \\ & \operatorname{Br} & & \operatorname{Br} \end{array}$$