JEE Advanced Archive DTS-4

46.(A) Oxymercuration-demercuration brings about Markovnikov's addition of water as:

$$CH_{3} - CH_{2} - C \equiv C - H + H_{2}O \xrightarrow{\text{HgSO}_{4}} \begin{bmatrix} CH_{3} - CH_{2} - C = CH_{2} \end{bmatrix} \xrightarrow{\text{CH}_{3} - CH_{2} - C - CH_{3}} CH_{3} - CH_{2} - C - CH_{3}$$

47.(D) According to the IUPAC conventions, compound can be numbered as:

$$H_2^1 = {\overset{2}{C}} + {\overset{3}{C}} + {\overset{4}{C}} + {\overset{5}{C}} = {\overset{6}{C}} - H$$

Here, C-2 is sp² and C-3 is sp³-hybridised.

48. (a)
$$+ O_3 \xrightarrow{Zn-H_2O} \xrightarrow{DOH} \xrightarrow{CH_3} \xrightarrow{CH_3C} \xrightarrow{CH_3} \xrightarrow{CH_3} \xrightarrow{CH_3D} \xrightarrow{CH_3D}$$

49.(D) Terminal alkynes forms silver salt with Tollen's reagent while alkene does not react with Tollen's reagent.

$$CH_3 - C \equiv C - H + AgNO_3 \xrightarrow{NH_3(aq)} CH_3 - C \equiv C Ag \downarrow$$
white ppt

Therefore, Tollen's reagent can be used to distinguish a terminal alkyne like propyne from alkene as well as from internal alkynes.

Ease of catalytic hydrogenation depends upon the size of groups present at the doubly bonded carbon. Larger the size of groups, difficult the hydrogenation. Therefore, in the given situation, disubstituted alkene reacts at faster rate than tri and tetra substituted alkenes. Among disubstituted, the stability order is: cis < trans < geminal

51.(A)
$$CH_3 - CH_2 - CH = CH_2 \xrightarrow{HBr} CH_3 - CH_2 - CH - CH$$

Secondary radical formed before formation of product that is $\,{\rm CH_3-CH_2-c^{\!\!\!\bullet}H^-\,CH_2Br}$

Secondary free radical is intermediate in this reaction.

52.(C) In addition of HBr to an alkene, in the presence of peroxide, both the propagation steps are exothermic: $HBr + RO^{\bullet} \longrightarrow ROH + Br^{\bullet}$

Propagation

$$\begin{cases} \operatorname{CH}_3 - \operatorname{CH} = \operatorname{CH}_2 + \operatorname{Br}^{\bullet} & \longrightarrow \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 \operatorname{Br} \\ \\ \operatorname{CH}_3 - \operatorname{CH} - \operatorname{CH}_2 \operatorname{Br} + \operatorname{HBr} & \longrightarrow \operatorname{CH}_3 - \operatorname{CH}_2 - \operatorname{CH}_2 \operatorname{Br} + \operatorname{Br}^{\bullet} \end{cases} \quad \Delta H < 0$$

In case of addition of HCl and HI one of the propagation step is endothermic, hence reaction fail to occur.

53.(B)
$$HOCl \longrightarrow HO^- + Cl^+$$

$$CH_3 - CH = CH_2 + Cl^+ \longrightarrow CH_3 - CH \xrightarrow{Cl^+} CH_2 \xrightarrow{HO^-} CH_3 - CH - CH_2$$

i.e. reaction is initiated by Cl⁺ (chloronium ion electrophile)

54.(B) Hydrogenation with poisoned palladium brings about syn hydrogenation of alkyne and does not affect double bonds:

55.(B)
$$\begin{array}{c} CH_3 \\ C = C \\ CH_3 \\ CH_3 \\ \end{array} + Br_2 \longrightarrow \begin{array}{c} CH_3 \\ H - C - Br \\ H - C - Br \\ CH_3 \\ \end{array}$$

Meso product (Plane of symmetry present)

Product formed through electrophilic addition of alkene. Addition of bromine to trans-2-butene yield meso product because anti addition to trans alkene yield meso product.

56.(A) $Me - S - Me + ozonide \longrightarrow product + (CH₃)₂SO, Dimethyl sulphoxide is water soluble.$

When $(CH_3)_2S$ is used with O_3 , reductive ozonolysis of alkene occur $(CH_3)_2S$ changes into $(CH_3)_2SO$ & remaining part of $(CH_3)_2S$ evaporates.

57.
$$CH_3 \xrightarrow{\text{Lindlar's}} CH_3 \xrightarrow{\text{catalyst}} H \xrightarrow{\text{Cis-isomer}} (\text{syn addition of } H_2 \text{ across } C \equiv C)$$

58.(B) Bromination is highly selective, occurs at the carbon, where the most stable free radical is formed

$$\begin{array}{c} \operatorname{CH_3}-\operatorname{CHD}-\operatorname{CH}-\operatorname{CH_3}+\operatorname{Br}^\bullet & \longrightarrow \operatorname{CH_3}-\operatorname{CHD}-\overset{\bullet}{\operatorname{C}}-\operatorname{CH_3}+\operatorname{HBr} \\ & \downarrow \\ \operatorname{CH_3} & \operatorname{CH_3} \\ & \text{(a tertiary free radical)} \end{array}$$

59.(D) Ammoniacal Cu_2Cl_2 forms red precipitate with terminal alkynes. It can be used to distinguish terminal alkynes from non-terminal alkynes:

$$CH_{3}-CH_{2}-C\equiv C-H+Cu_{2}Cl_{2}\xrightarrow{\quad NH_{3}(aq)\quad }CH_{3}-CH_{2}-C\equiv C-Cu\downarrow CH_{3}$$

60.
$$CH_3CH_2 - C \equiv C - H \xrightarrow{\text{(i) NaNH}_2} CH_3 - CH_2 - C \equiv C - CH_2 - CH_3 (X)$$

$$CH_{3}CH_{2} - C \equiv C - CH_{2}CH_{3} \xrightarrow{Pd/BaSO_{4}} H_{2} \xrightarrow{H_{2}} C_{2}H_{5}$$

$$C_{2}H_{5} \xrightarrow{Alk.KMnO_{4}} H \xrightarrow{C_{2}H_{5}} C_{2}H_{5}$$

$$C_{2}H_{5} \xrightarrow{(meso\ diol)} C_{2}H_{5}$$

$$C_{2}H_{5} \xrightarrow{(meso\ diol)} C_{2}H_{5}$$