CHAPTER FOUR: ALKYNES

- Alkynes are hydrocarbons that contain carbon carbon triple bond.
- They have a general formula of C_nH_{2n-2}

Nomenclature

- The IUPAC nomenclature for alkynes is similar to that for alkenes.
- Find the longest continuous chain of carbon atoms that includes the triple bond and change the -ane ending of the parent alkane to -yne.
- The chain is numbered from the end closest to the triple bond, and the position of the triple bond is designated by its lower numbered carbon atom.
- Substituents are given numbers to indicate their locations.

$$H - C \equiv C - H$$
 $H - C \equiv C - CH_3$ Ethyne /Acetylene Propyne

HC
$$\equiv$$
CCH2CH3CH3C \equiv CCH31-Butyne
But-1-yne2-Butyne
But-2-yneCH3CH2CH2C \equiv CHCH3CH2C \equiv CCH31-Pentyne
Pent-1-yne2-Pentyne
Pent-2-yneCH3CHC \equiv CH
CH3(CH3)3CC \equiv CCH3
4,4-Dimethyl-2-pentyne

3-Methyl-1-butyne 3-Methylbut-1-yne

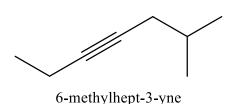
4,5-dimethylhex-2-yne

$$CH_{3}CH_{2}CH_{2}CH_{2}\overset{4}{C}H\overset{5}{C}H\overset{6}{C}H_{2}\overset{7}{C}H_{2}\overset{8}{C}H_{2}\overset{9}{C}H_{3}$$

$$C\overset{1}{\Longrightarrow}\overset{2}{C}\overset{1}{C}H_{3}$$

4-Butylnon-2-yne





Preparation of Alkynes

1. Addition of water to calcium carbide

$$CaC_2$$
 + $2H_2O$ \longrightarrow $Ca(OH)_2$ + $H-C \equiv C-H$

2. Dehydrogenation of ethene

$$CH_2 = CH_2$$
 Δ $H - C = C - H + H_2$

3. Alkylation of acetylene (ethyne) and terminal alkynes

 An acetylide ion is a strong base and powerful nucleophile. It can displace a halide ion from a suitable substrate, giving a substituted acetylene.

$$R-C \equiv C : - + R'-X \longrightarrow R-C \equiv C-R' + X^-$$
(R-X must be a primary alkyl halide)

HC≡CH + NaNH₂ → HC≡CNa + NH₃ Sodium amide

HC≡CNa + R-X → HC≡CR + NaX

e.g

HC≡CNa + CH₃CH₂CH₂CH₂-Br → HC≡C-CH₂CH₂CH₃ + NaBr

(CH₃)₂CHCH₂C≡CH
$$\frac{1) \text{ NaNH}_2, \text{ NH}_3}{2) \text{ CH}_3\text{Br}}$$
 → (CH₃)₂CHCH₂C ≡CCH₃

$$C≡C-H \frac{1) \text{ NaNH}_2}{2) \text{ Ethylbromide}}$$
 → $C≡C-CH_2\text{CH}_3$

4. Elimination Reactions

- In some cases, we can generate a carbon carbon triple bond by eliminating two molecules of HX from a dihalide.
- Dehydrohalogenation of a geminal or vicinal dihalides gives a vinyl halide. Under strongly basic conditions, a second dehydrohalogenation may occur to form an alkyne.

$$CH_{3}CH_{2}CHCHCH_{3} \xrightarrow{1) NaNH_{2}, NH_{3}} \longrightarrow CH_{3}CH_{2}C \Longrightarrow CCH_{3}$$

REACTION OF ALKYNES

1. Addition reactions

i) Hydrogenation

a) Using H₂ and an active metal (Pt, Rh, Pd, Ni)

RC
$$\equiv$$
CR' + 2H₂ $\xrightarrow{\text{Pd, Pt, Ni}}$ RCH₂CH₂R'
Alkane

HC \equiv C-CH₂CH₃ + 2H₂ $\xrightarrow{\text{Pt}}$ CH₃CH₂CH₂CH₂CH₃

CH₃CH₂CHCH₂C \equiv CH + 2H₂ $\xrightarrow{\text{Ni}}$ CH₃CH₂CHCH₂CH₂CH₃

b) Using Lindlar Catalyst

- Hydrogenation of an alkyne can be stopped at the alkene stage by using a "poisoned" (partially deactivated) catalyst made by treating a good catalyst with a compound that makes the catalyst less effective.
- Lindlar's catalyst poisoned palladium catalyst, composed of powdered BaSO₄ coated with palladium, poisoned with quinoline.
- In an internal alkyne, syn addition gives a cis product (Z).

$$R - C \equiv C - R'$$

$$H_2, Pd/BaSO_4$$

$$Quinoline$$

$$(Lindlar's catalyst)$$

$$CH_3C \equiv CCH_2CH_2CH_3 + H_2$$

$$Lindlar's catalyst$$

$$H_3C$$

$$CH_2CH_2CH_3$$

$$H$$

$$Cis-hex-2-ene$$

$$CH_{3}(CH_{2})_{3}C = C(CH_{2})_{3}CH_{3} \xrightarrow{H_{2}} H_{3}C(H_{2}C)_{3}$$

$$Lindlar Pd$$

c) Metal – ammonia reduction to trans alkenes.

 A useful alternative to catalytic partial hydrogenation for converting alkynes to alkenes is reduction by a group 1 metal (Lithium, Sodium or Potassium) in liquid ammonia.

$$R-C \equiv C-R + Na/NH_3 \longrightarrow R$$

$$C = C + Na/NH_3 \longrightarrow R$$

$$CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow{Na} \longrightarrow R$$

$$CH_3C \equiv CCH_3CH_3 \xrightarrow{Na} \longrightarrow R$$

$$CH_3C \equiv CCH_3CH_3$$

ii) Addition of hydrogen halides

- Follows markonikov's orientation.

$$R-C \equiv C-H + H-X \longrightarrow R \longrightarrow R \longrightarrow R \longrightarrow R \longrightarrow R \longrightarrow H$$

$$H-X = HCl, HBr \text{ or } HI$$

$$RC \equiv CH + H \longrightarrow X: \longrightarrow RC = CH_2 + :X: \longrightarrow RC = CH_2$$

$$:X:$$

- The reaction of pent-1-yne with HBr gives the Markonikov product.

H-C
$$\equiv$$
 CCH₂CH₂CH₃ + HBr \rightarrow H \rightarrow CH₂CH₂CH₃ \rightarrow Br \rightarrow 2-Bromopent-1-ene

 In an internal alkyne such as pent-2-yne, the carbons of triple bond are equally substituted, and a mixture of product results.

$$CH_3C = CCH_2CH_3 + HBr$$

$$H_3C - C = C - CH_2CH_3 + H_3C - C = C - CH_2CH_3$$
2-bromopent-2-ene
(E and Z isomers)
$$(E \text{ and Z isomers})$$

 Peroxides catalyze a free radical chain reaction that adds HBr across the triple bond in the anti-markonikov orientation.

iii) Hydration of alkynes to ketones and aldehydes.

 $HC \equiv CH + H_2O \xrightarrow{HgSO_4} CH_3CH$

- a) Acid-catalyzed addition of water
- Alkynes undergo acid-catalyzed addition of water across the triple bond in the presence of mercuric ion as a catalyst.
- A mixture of mercuric sulphate in aqueous sulfuric acid is commonly used as a reagent.
- Markonikov orientation.

$$R-C \equiv C-R' + H_2O \xrightarrow{slow} RCH = CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$Enol-not isolated keto-enol tautomerism$$

$$RCH = CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$Enol-not isolated keto-enol tautomerism$$

$$RCH = CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$RCH_2CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$RCH_2CR' \xrightarrow{RCH_2CR'} RCH_2CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$RCH_2CR' \xrightarrow{RCH_2CR'} RCH_2CR'$$

$$HC = CCH_{3} + H_{2}O \xrightarrow{HgSO_{4}} CH_{3}CCH_{3}$$

$$H-C = CCH_{2}CH_{3} + H_{2}O \xrightarrow{HgSO_{4}} H_{2}SO_{4}$$

$$H = CCH_{2}CH_{3} + H_{2}O \xrightarrow{HgSO_{4}} H_{2}CH_{3}$$

b) Hydroboration – Oxidation

- Hydroboration- oxidation is a two-step reaction sequence that converts an alkyne to a carbonyl compound.
- Anti markonikov addition.

$$R-C = C-R \xrightarrow{BH_3} R \xrightarrow{R} C = C \xrightarrow{R} H_2O_2, HO^- R \xrightarrow{H} C = C \xrightarrow{R} H \xrightarrow{R} C = C \xrightarrow{$$

$$CH_3-C = CH \xrightarrow{1) BH_3} CH_3$$

$$H = CH_3$$

$$H$$

iv) Addition of Halogens

- Bromine and chlorine add to alkyne just as they add to alkenes.
- The addition may either be syn or anti, and the products are often mixture of cis and trans isomers.

$$R-C = C-R' + X_2$$

$$X_2 = Cl_2 \text{ or } Br_2$$

$$X = C = C X$$

$$X = C = C X$$

$$X = C = C X$$

$$CH_{3}(CH_{2})_{3}-C \equiv CH + Br_{2}$$
 $CH_{3}(CH_{2})_{3}$
 $C=C$
 $CH_{3}(CH$

 It is usually possible to prepare a dihaloalkene by simply adding one molar equivalent of the halogen.

e.g

OH
$$\frac{\operatorname{Br}_2(1 \operatorname{mol})}{0^{\circ}\operatorname{C}}$$
 OH

- Addition of one molar equivalent of chlorine or bromine to an alkyne generally results in anti-addition and yields a trans-dihaloalkene.
- If 2 moles of halogen add to 1 mole of an alkyne, a tetrahalide results.
 e.g

$$CH_3(CH_2)_3-C \equiv C-H + 2Cl_2$$
 $CH_3(CH_2)_3C-C-H$

Oxidative Cleavage of Alkynes

Ozonolysis

 Ozonolysis of an alkyne followed by hydrolysis cleaves the triple bond and gives two carboxylic acids.

$$R-C \equiv C-R'$$
 $\xrightarrow{1) O_3}$ \longrightarrow $RCOOH + R'-COOH$

e.g

$$CH_3C \equiv CCH_2CH_3$$
 $\xrightarrow{1)O_3}$ $CH_3COOH + CH_3CH_2COOH$

$$CH_3(CH_2)_3-C \equiv C-H$$
 $\frac{1)O_3}{2)H_2O}$ $CH_3(CH_2)_3C-OH$ + $\frac{O}{HOC-H}$