

Our country, our future

Chapter 3: Alkynes

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Alkynes

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General formula CnH2n-2 where n≥2

Т

hey contain a triple bond

Examples

HC Ethyne

CH₃C CH Propyne

 CH_3CH_2C Eut-1-yne

 $CH_3C \equiv CCH_3$ But-2-yne

Preparation

1. From vicinal dihalides.

Vicinal dihalides are halides with two halogen atoms on adjacent carbon atoms

The reaction is carried out by refluxing vicinal dihalides with a mixture of an alcohol with its sodium or potassium salt.

Example
$$CH_{3}CHCHCH_{3} \xrightarrow{Et\bar{O} / EtOH} CH_{3}C \xrightarrow{ECCH_{3}}$$
Rr Br

Mechanism

2. Preparation of alkyne from carbon

$$Ca (s) + 2C(s) \xrightarrow{\text{heat}} CaC_2 (s)$$
or
$$CaO (s) + 3C (s) \xrightarrow{\text{heat}} CaC_2 (s) + CO (g)$$

$$CaC_2 (s) + 2H_2O \xrightarrow{\text{HC}} CH + Ca(OH)_2$$

3. Preparation of long chain alkyne from ethyne

Exercise

4. Synthesize

Questions involving synthesis requires a student to write a series of reactions leading the formation of products from the reactant(s). Most time more than one equation is required because reactions of organic compounds are specific that we may need to convert the reactants into intermediate compounds before a product can be obtained.

For instance, before baking bread, wheat flour is first convert to dough. Usually think of the intermediates to enable you complete a synthesis equation.

Solution

(a)
$$CH_3CH_2OH$$
 $\xrightarrow{conc. H_2SO_4}$ H_2C $\xrightarrow{CH_2}$ H_2C $\xrightarrow{CH_2}$ $\xrightarrow{CH_2}$ $\xrightarrow{Et\bar{O} / EtOH}$ HC \xrightarrow{CH} $\xrightarrow{Et\bar{O} / EtOH}$ HC

(b)
$$CH_3CH_2CI$$
 $Et\bar{O} / EtOH$ H_2C CH_2 H_2C CH_3 H_2C CH_4 H_2C CH_5 H_6 H_7 H_8 H_8

Physical properties

- 1. They range from gases to liquids to solids
- 2. They are insoluble in water but soluble in organic solvents

Chemical properties.

1. They burn in oxygen to give carbon dioxide, water and heat.

Example

$$2C_2H_4 + 5O_2 \longrightarrow 4CO_2 + 2H_2O_{+ heat}$$

They are used as fuel because they produce heat

2. Reduction

Depending on conditions, alkyne may be reduced to alkenes or alkenes

Example

Note that reduction of alkyne to alkene has synthetic value because alkenes are more reactive than alkanes.

Example

Synthesize

$$CH_3C \longrightarrow CH \xrightarrow{LiAlH_4,dry \text{ ether}} CH_3CH \longrightarrow CH_2 \xrightarrow{HBr/peroxide} CH_3CH_2CH_2Br$$

Not that the first part of the synthesis involves reduction alkynes to alkene.

3. Addition reactions

Alkyne undergo addition reactions like alkenes except that the addition occurs twice.

(a) Addition of HX (X=Cl, Br, and I

Example

$$CH_3C \xrightarrow{HCl} CH_3C \xrightarrow{Cl} CH_3$$

$$CH_3C \xrightarrow{CH_3C} CH_3$$

Mechanism

$$CH_3C \longrightarrow CH_3C \longrightarrow CH_3C \longrightarrow CH_2$$

$$CH_3C \longrightarrow CH_3C \longrightarrow CH_2$$

Then

$$\begin{array}{c} \text{Cl} & \text{Cl} \\ \text{CH}_3\text{C} \longrightarrow \text{CH}_2\text{C} \longrightarrow \text{CH}_3\text{C} \longrightarrow \text{CH}_3\text{C} \\ \text{Cl} & \text{Cl} \end{array}$$

(b) Addition of halogens

The halogen is diluted with carbon tetrachloromethane (to prevent explosion) Example

$$CH_3C \longrightarrow CH_2/CCl_4 \longrightarrow CH_3C \longrightarrow CH_3C \longrightarrow CH$$

$$CH_3C \longrightarrow CH_3C \longrightarrow CH$$

$$CH_3C \longrightarrow CH$$

Mechanism

$$CH_3C \longrightarrow CH_3C \longrightarrow CH_3C \longrightarrow CH_3C \longrightarrow CH_3C$$

Then
$$Cl$$
 Cl Cl_3C — $CHCl_2$ — $CHCl_2$ — $CHCl_2$ — $CHCl_2$ — Cl Cl Cl

Exercise

Complete and write a mechanism

$$CH_3CH_2C$$
 \longrightarrow CH_3CH_2C

Solution

$$CH_3CH_2C = CH \xrightarrow{Br_2/CCl_4} CH_3CH_2C \xrightarrow{Br} Br$$

$$CH_3CH_2C = CH_3CH_2C \xrightarrow{CH_3CH_2C} CH_3CH_2C$$

Mechanism

Then
$$CH_{3}CH_{2}C \longrightarrow CH_{3}CH_{2}C \longrightarrow CH_{3}C$$

(c) Addition of water.

The reaction is catalyzed by mercury (II) sulphate and dilute sulphuric acid. Carbonyl compounds are formed.

Example

$$HC = CH \xrightarrow{Hg^{2+}. H^+ (aq)} CH_3CHO$$

Mechanism

HC
$$\longrightarrow$$
 CH \longrightarrow HC \longrightarrow CH $_2$ \longrightarrow CH $_3$ \longrightarrow CH $_4$ \longrightarrow CH $_4$ CH $_4$ CH $_4$ \longrightarrow CH $_4$ CH $_4$ CH $_4$ CH $_4$ CH $_4$ CH $_4$ CH $_$

Exercise

Complete and write a mechanism

$$CH_3CH_2C$$
 \longrightarrow CH $HgSO_4$, $dil H_2SO_4$

Solution

$$CH_3CH_2C = CH \xrightarrow{HgSO_4, \text{ dil } H_2SO_4} CH_3CH_2C - CH_3$$

Mechanism

$$CH_3CH_2C \longrightarrow CH_3CH_2C \longrightarrow CH_2C \longrightarrow$$

Then
$$CH_3CH_2C \longrightarrow CH_2 \longrightarrow CH_3CH_2C \longrightarrow CH_2 \longrightarrow CH_3CH_2C \longrightarrow CH_3$$

$$H_2O+ \longrightarrow CH_3CH_2C \longrightarrow CH_2 \longrightarrow CH_3$$

$$H_2O+ \longrightarrow CH_3CH_2C \longrightarrow CH_3$$

(d) Reaction of terminal alkyne

Alkynes with a triple bond at the end of the chain react with ammoniacal silver nitrate or ammoniacal copper I chloride to form white precipitate or red precipitate respectively.

Example

$$CH_3CH_2C$$
 \longrightarrow CH_3CH_2C \longrightarrow CH_3CH_2C \longrightarrow CH_3CH_2C \longrightarrow CH_3CH_2C \longrightarrow CH_3CH_2C

This reaction is used to distinguish alkynes with a triple bond at the end from those with a triple bond in the middle of the chain.

Exercise

Name one reagent that can be used to distinguish between the following pairs compounds. In each case state what will be observed when the reagent is treated with each of the compound of the pair.

(b)
$$C = CCH_3$$
 and $CH_2C = CH$

Reagent: ammoniacal silver nitrate

Observation

(a) CH_3CH_2C \longrightarrow CH white precipitate

CH₃C CCH₃ no observable change

(b)
$$C = CCH_3$$
 no observable change $CH_2C = CH$ white precipitate

Revision questions

- 1. 10cm³ of a hydrocarbon X was exploded with 70 cm³ of Oxygen and cooled, the final volume was 55cm³. The volume of the mixture reduced to 15cm³ when shaken with concentrated potassium hydroxide solution.
 - (a) Determine the molecular formula of X.
 - (b) Write and name all isomers of X.
 - (c) X formed a red precipitate with ammonial copper 1 chloride,
 - (i) Identify X.
 - (ii) Write equations and suggest mechanism for the reaction between X and acidified water, hydrogen in presence of palladium catalyst and hydrogen peroxide.
 - (d) Write equations and conditions to show how X can be prepared from a named
 - (i) Alcohol
 - (ii) Alkyl halide.