CHEM 261 Mar 28, 2017

Upcoming Topics:

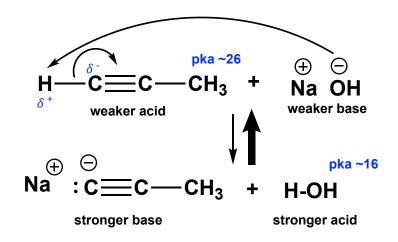
- 1. Alkyne Reactions
- 2. Radical Additions to Alkenes
- 3. Polymers
- 4. Alcohol & Sugars: Structure + Nomenclature

Review

- **:Base** picks up a proton (H⁺) very fast, may be negatively charged
- :Nucleophile attaches other atoms (like carbon)

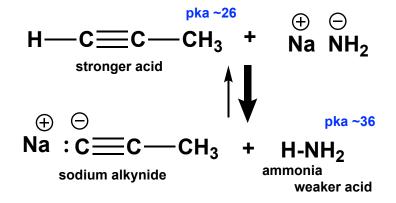
Reactions of Terminal Alkynes – Alkylation

Example 1



The stronger acid and stronger base are always on the same side. As such, the reaction is driven towards the opposite side.

Example 2



How can this terminal anion be used to form useful compounds?

Terminal alkynes/acetylenes can be deprotonated and then reacted with alkyl halides to form new carbon-carbon bonds.

General Scheme

$$R-C \equiv C-H \xrightarrow{KNH_2} R-C \equiv C: K R'H_2C \xrightarrow{X} R-C \equiv C-CH_2R'$$
terminal acetylene $PK_a \sim 26$ $PK_a \sim 36$ $PK_a \sim 36$

Example 1

HC=CH

1. NaNH₂

$$H_3$$
C=C=CH

Na I

 $C = C$

Na I

Example 2

Example 3

What about this ketone?

1)
$$H-C \equiv C-H$$

Na H_2

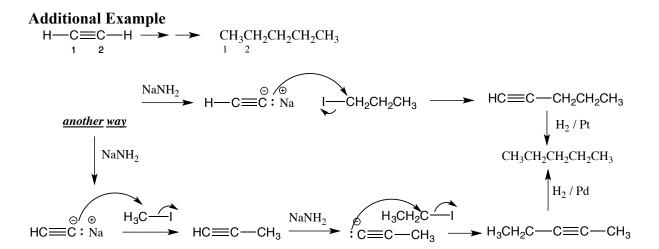
Na: $C \equiv C-H$

2) $Na: C \equiv C-H$
 $H_3C-H_2C-C \equiv C-H$
 $H_3C-H_2C-C \equiv C-H$

Step 3 mechanism:

 $H_3C-H_2C-C \equiv C-H$
 $H_3C-H_2C-C \equiv C-H$

Can you add everything together at once? No. The sodium amide will react with the alkyl halide and form a byproduct amine instead of the desired ketone.



Radical Addition to Alkenes

Recall the addition of a hydrogen halide:

By adding peroxide and heat, the following can occur via a radical mechanism.

$$\begin{array}{c} & HBr \\ \hline R-O-O-R \\ \hline R-O & O-R \\ \hline R-O & H-Br \\ \hline Br \\ \hline \end{array}$$

$$\begin{array}{c} & R-O & O-R \\ \hline R-O+Br \\ \hline \end{array}$$

$$\begin{array}{c} & Br \\ \hline \\ Br \\ \hline \end{array}$$

Now, you can combine all the different types of reactions you have learned to create your desired compound from simple starting material. For example, using propane, several compounds can be created:

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Polymers

poly – many, meros – parts

Natural Polymers:

- Nucleic acids (DNA, RNA)
- Proteins and peptides (amino acid polymers)
- Polysaccharides (cellulose)
- Fats, polyketides (polymers of acetic acid)

Human-Made Polymers

- Christian Schönbein, 1826 professor in Basel
 - o Mopped up a spill of H₂SO₄ and HNO₃ with an apron made of cotton (cellulose, a polymer of glucose),
 - He washed the apron and hung it up to dry
 - The apron exploded \rightarrow He had created gun cotton!

How did this happen?

In the presence of H₂SO₄ and HNO₂, the free hydroxyl groups form a material that spontaneously combusts.

OH OR
$$\frac{\text{HNO}_3}{\text{H}_2\text{SO}_4}$$
 OR $\frac{\text{HNO}_3}{\text{O}}$ OR $\frac{\text{H$

Another example: glycerol

Under the same conditions, glycerol will form nitroglycerine

HO OH
$$\frac{\text{HNO}_3}{\text{H}_2\text{SO}_4}$$
 O \oplus O \oplus

2 to 5 % of nitroglycerine was combined with diatomaceous earth → dynamite!

Who did this reaction? Alfred Nobel, the founder of the Nobel Prize!

- Wallace Carothers 1896-1937 DuPont
 - Nylon (polyamide)
 - o Dacron (polyester)
- Roy Plunkett 1938 DuPont
 - o Teflon (created from tetraflyoroethylene, a toxic gas)

Teflon: Polytetrafluoroethylene

Polymerization Mechanism of Teflon

repeat to form long chains