Learning Guide for Chapter 13 - Alkynes

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I. Introduction to Alkynes

Classifying Alkynes

Which of these is an alkyne? What is the other one called?



alkyne hydrocarbon w/ a C---C

unsaturated ketone not a hydrocarbon, so not an alkyne

Which of these is a terminal alkyne? Which is an internal alkyne?





internal injuries internal combustion engine

internal alkyne C---C between 2 C's terminal alkyne C---C on the end

a terminal disease an airport terminal

Alkenes could also be labeled this way, but they usually aren't. Why not?

alkenes - no change in properties or behavior alkynes - different IR, acid//base properties, reactivity

Hybridization and bond formation

What hybridization do each of the carbons in acetylene have?



Geometry

What geometry do carbons in triple bonds have? linear

Draw a 6 carbon alkyne with the triple bond on the end. Then draw a 6 carbon alkyne with the alkyne in the middle.



How big does a ring have to before it can contain a triple bond (and be stable)?

at least 9 carbons one more than trans C=C in a ring unstable! stable cyclooctyne has been isolated by polymerizes at room temp

Stereochemistry

Can the carbon in a triple bond be a stereocenter? no :)





Can alkynes be chiral? yes

other C's in the molecule can be stereocenters

Molecular formula

How many units of unsaturation does a triple bond have? 2

What is the molecular formula for a simple alkyne? C_nH_{2n-2}

What would be the formula of an alkyne with 10 carbons?

 $C_{10}H_{18}$

What would be the formula of a cyclic alkyne with 10 carbons?

 $C_{10}H_{16}$



Stabilization

Which is more stable, an internal alkyne or a terminal alkyne? Why?



terminal less stable internal more stable like C=C : more stable = more conjugated

pi bonds overlap neighboring w/ C-H bonds (hyperconjugation)

we'll look at delta H's on p 15

Reactivity

Where are the two places that alkynes can react?



How can a terminal alkyne react with a base?



How can an alkyne react with an acid? With an electrophile?





– 226 kJ/mol to break pi bond

How is the product of an alkyne reaction different from the product of an alkene reaction?



II. Natural Occurrences and Uses of Alkynes

Alkynes are rarely found in nature. What is one exception?

diacetylene \blacksquare C₄H₂

found in carbon-rich atmospheres of Uranus, Neptune, Pluto, Titan, Triton

Unsaturated compounds with carbon-carbon triple bonds have been found. How many are known? What do they often have in common?

about 1000 known often toxic

Here are some examples:



an oil found in chrysanthenums, exhibits fungicidal activity



fatty acid found in the seed of a plant native to Guatemala



a neurotoxin found in hemlock



highly toxin compound isolated from "poison arrow" frogs in the lower Amazon basin

Unsaturated compounds with carbon-carbon triple bonds have also been isolated or synthesized for use as drugs. Here are some examples:



birth control agent Ortho-Novum, Loestrol, Ovral, etc parsalmide



perscription analgesic Parsal, Sinovial

pargyline



antihypertensive drug Eudatin, Supirdyl



anticancer drug - derivatives have been made
which are more potent, more selective, easier
to synthesize

What is the most useful alkyne in industry?

acetylene HC≡CH used in cutting and welding torches

How is it made?

1) heat limestone and carbon to 2000°C, then add water

$$CaO + 3C \longrightarrow Ca^{+2} :=: + CO \xrightarrow{H_2O} HC \equiv CH + Ca(OH)_2$$

2) heat methane to 1500°C for 0.01 sec

 $CH_4 + O_2 \longrightarrow HC \equiv CH$

How is it stored?

can't be stored as a liquid under pressure - heat or shock cause it to decompose to carbon and hydrogen and explode

stored dissolved in acetone under moderate pressure, absorbed onto firebrick

What happens when it burns?

 $2 \text{ HC} \equiv \text{CH} + 5 \text{ O}_2 \longrightarrow 4 \text{ CO}_2 + 2 \text{ H}_2\text{O}$

6000° F - hottest flame from a commonly available organic gas

yellow, smoky flame in air, clear blue flame in pure oxygen

What is polyacetylene? What is it used for?

long chain of single, double bonds / made from acetylene

used for foil packaging for computer parts (dissipates static charge), light-weight batteries

when treated with iodine, first polymer to conduct electricity - nearly as good as silver - 2000 Nobel Prize

III. Physical Properties of Alkynes

Give the following properties of alkynes:

polarity nonpolar

water solubility not soluble

density less dense than water - will float

melting and boiling points similar to alkenes and alkanes of the same MW

flammability highly flammable

storage issues polymerizes easily, sometimes explosively

odor strong, pungent odor

state of matter 2-4 C's - gas; 5-10 C's - liquid; 10+ C's - solid

IV. Spectroscopy of Alkynes

IR Spectroscopy

What two bonds do alkynes have that alkanes do not?

 $C \equiv C$ 2200-2100 cm⁻¹

C-H on $C\equiv C$ around 3300 cm⁻¹



How do the IR spectra of terminal alkynes differ from those of internal alkynes?



How does the carbon-carbon triple bond band compare to a double bond band?

C---C 2200-2100 C=C 1680-1620 higher frequency - stronger bond

How does the triple bond in an alkyne compare to the triple bond in a nitrile?

C---C vs C---N C---N is much deeper, absorbs more light (more polar)

How does the C-H on an alkyne compare to the C-H on an alkene?

C-H on C---C 3100-3000 higher frequency, separate from C-H deeper

C-H on C=C ~3300 lower frequency, left side of C-H small

¹<u>H NMR Spectroscopy</u>

Where do H's on terminal alkynes appear?

1.7 - 3.1 ppm (not very useful, too many other things show up there)

Is the H on a terminal alkyne always a singlet?

no - can be split by H's farther away than one C because of the pi bonds (long range coupling), but the coupling constants are very small (two peaks of doublet very close together)

¹³C NMR Spectroscopy

Where do C's in the triple bond of an alkyne appear? 65-85 ppm (not very useful either)

V. Nomenclature of Alkynes

Common names

Give common names of the following compounds.



methylacetylene



phenylacetylene



cyclopentylacetylene



cyclopropylmethylacetylene





diisopropylacetylene

IUPAC names

What steps should you follow when naming an alkyne?

- 1. determine stereochemistry, if any
- 2. choose the principle chain and name it
- 3. number the principle chain
- 4. name and order the substituents

What are the priorities for choosing the principle chain?

1. must contain the C---C, any C=C (all, if possible)

2. longest

3. most substituents



1,4-pentadiyne



4-hexen-1-yne

How are the names formed?

one C---C: change "ane" to "yne", put # in front

two or more C---C: change "ane" to "yne", add "adi" or "atri" before it, put # in front

C---C and C=C: change "ane" to "en" then add "yne", put C=C # in front, C---C inside

What are the priorities for numbering the principle chain?

1. C---C or C=C, whichever comes first

- 2. if numbers are the same, C=C
- 3. first substituent
- 4. alphabet

LG Ch I3 p I0 LG Ch I3 p I0 C ---C over substituent C ---C over substituent



lowest # to first in alphabet if #'s are the same

How do you name a substituent containing a carbon-carbon triple bond?

add "yn" before "yl"

(no common names like vinyl and allyl as there are in alkenes)

ethyl



ethynyl

Where do you number a substituent from?

where it is connected to the ring



Name the following compounds.



1-pentyne



1,5-hexadiyne



3-propyl-1-hexyne



<u>trans</u>-3-penten-1-yne or (\underline{E})-



 (\underline{S}) -3-chloro-1-cyclooctyne



4-methyl-2-pentyne

1-penten-3-yne



4-(2-propynyl)-1-cyclopentene



 (\underline{Z}) -3-<u>sec</u>-butyl-3-penten-1-yne

or (\underline{Z}) -3-(1-methylpropyl)-3-penten-1-yne



1-cyclopentyl-1,4-pentadiyne

Draw the following compounds, using the correct geometry!

5-methyl-3-octyne

"yne is a line"



3-ethynyl-1-cyclohexene





(notice what a big difference that C=C makes)

VI. Acid-base Properties of Alkynes

How does the electronegativity of an atom affect the acidity of a H attached to it?

more EN - more acidic

How acidic would you expect a H attached to a C to be?

not very acidic at all - C has low EN

Why are alkynes more acidic than alkenes or alkanes?

hybridization: $sp > sp^2 > sp^3$ alkanes ~50, alkenes ~44, alkynes 26

remember this number!

What is the conjugate base of an alkyne called?



What kind of base would be required to successfully react with an alkyne?

to favor the products, pKa must be larger than 26 look on chart

NaH Na⁺ H:⁻ \longrightarrow H₂ pKa 35

 $NaNH_2 \qquad Na_{H}^{+} \stackrel{N}{\longrightarrow}_{H} \longrightarrow NH_3 \quad pKa 36$

What would happen if an acetylide ion came in contact with an acid with a pKa less than 26?



How do alkyne anions react? Nu or base



Which is more useful? S_N^2 - most common way of making alkynes E2 is a waste of acetylide ion - better to use t-butoxide



LG Ch 13 p 14

VII. Synthesis of Alkynes by Elimination

When alkynes can't be formed by a substitution reaction, what other method is available?





VIII. Reduction of Alkynes to Form Alkenes and Alkanes

What kinds of compounds can be formed when alkynes undergo an addition reaction with hydrogen?



When an alkyne is reacted with H₂ and a metal catalyst, what kind of product results?



Why can't we isolate the product of the first stage of this reaction?

it reacts with the H_2 , Pd/C to form an alkane

Why does the alkene intermediate have cis stereochemistry? syn addition

How can this reaction be used to determine the relative stability of terminal and internal alkynes?



How could you use this reaction to synthesize an alkane chain?



What can you do to stop the reaction at the alkene?

use a less reactive catalyst - often called a "poisoned" catalyst

Lindlar catalyst = Pd/CaCO₃, PbOAc, quinoline



What advantage does this have over E2 reactions to make alkenes?

no constitutional isomers, no stereoisomers

What this can you tell about the reactivity of alkenes and alkynes from this reaction?

alkynes are more reactive - they will react, alkenes won't

How can a trans alkene be formed?

can't use addition of H₂ - always syn addition

totally different reaction needed



How is the Na here different from NaH?

no charge - Na metal = Na \cdot still has valence e-

Why can this be called a dissolving metal reaction?

sodium metal dissolves in ammonia - deep blue color

Where do the H's come from?

from the ammonia

What is the mechanism of this reaction?





Na : NH₂

Synthesize the following compounds from an alkyne.



IX. Addition of HX and X₂ to Alkynes

Addition of HX

If HCl, HBr, or HI is added to an alkyne, what product will result?



Which of these reactions demonstrates regioselectivity, and which side gets the halide?

terminal alkynes - halide goes to the more substituted side

What will happen if an internal alkyne is not symmetrical?

two products

What will happen if a second equivalent of HX is added?

geminal dihalide results

What happens if there is peroxide present in an HBr addition?



Addition of X₂

What products are formed when one or two equivalents of Br₂ are added to an alkyne?



X. Hydration of Alkynes

Acid- and mercury-catalyzed hydration

What reagents are required to add water across a carbon-carbon triple bond?



What kind of product results? What happens to it?

tautomerization - H and == change places

Which side is favored on a terminal alkyne? more substituted side



What will happen if an internal alkyne is not symmetrical? 2 products



Hydroboration-oxidation of alkynes

What product results when an alkyne is treated with a borane reagent?



What complication could occur? How do we prevent this?

C=C in the enol could react with the borane again internal alkynes - steric hindrance of alkyne is enough terminal alkynes - use sterically hindered borane reagent



disiamylborane

dicyclohexylborane

What regioselectivity is observed when an alkyne is treated with a borane reagent?



How could the following compounds be synthesized from an alkyne?



XI. Oxidation of Alkynes

What happens when an alkyne reacts with KMnO₄?



Match the following reactions and products:



Summary of alkyne reactions

Synthesis of alkynes

acetylene> terminal alkyne	HC≣CH NaNH ₂ =
terminal alkyne 🔶 internal alkyne	$= \frac{\text{NaNH}_2}{\text{CH}_3\text{Br}} = $
vicinal dihalide 🔶 alkyne	$X \xrightarrow{X} \frac{\text{NaNH}_2 \text{ or}}{\text{KOH}, 200^{\circ}\text{C}} \text{ HCECH}$
geminal dihalide 🛛 → alkyne	$\begin{array}{ c c c c c } X & & \underbrace{\text{NaNH}_2 \text{ or}}_{X} & & \underbrace{\text{HC}ECH}_{KOH, 200^{\circ}C} & \text{HCECH} \end{array}$

Reactions of alkynes

