Lecture 19
Organic Chemistry 1

Professor Duncan Wardrop

March 16, 2010

Chapter 9

Alkynes Sources and Nomenclature

Sections 9.1 - 9.6

Exam Two

- Monday, April 5
- 6:00-7:15 p.m.
- 250 SES
- Chapters 6-10, 13
- Makeup Exam: Monday, April 12, time t.b.a.

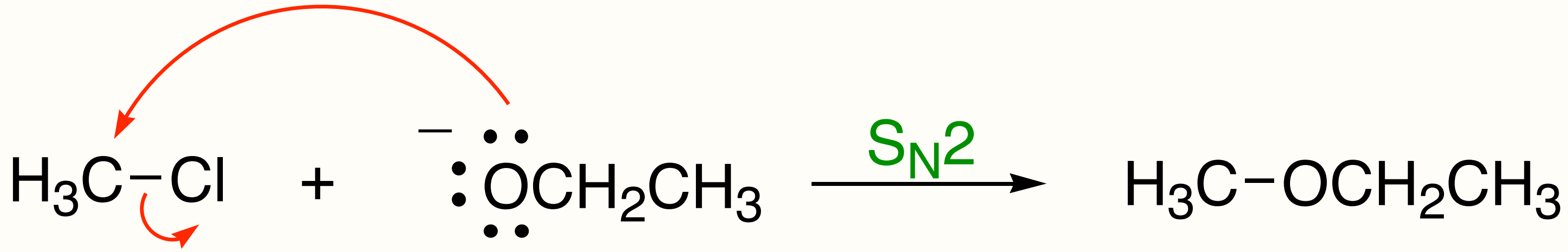
Makeup policy: There are no makeup exams without **prior** approval. Only students showing proof of a class conflict will have the option to take a makeup exam. To be added to the makeup list, you must email me no later than Friday, April. 2.

Self-Test Question

Which column lists the correct mechanistic symbol for each description?

	[✓ A]	B	C	D	E
Methyl halides react with sodium ethoxide in ethanol only by this mechanism.	S_N2	S_N1	E2	S_N2	S_N1
Unhindered primary halides react with sodium ethoxide in ethanol mainly by this mechanism.	S_N2	S_N2	S_N2	S_N2	S_N1
Cyclohexyl bromide reacts with sodium ethoxide in ethanol, mainly by this mechanism.	E2	S_N1	E2	S_N2	S_N1
The product obtained by solvolysis of *tert*-butyl bromide in ethanol arises by this mechanism.	S_N1	S_N2	S_N2	S_N2	E2
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.	E2	E2	S_N1	S_N1	E2

Substitution/Elimination Review



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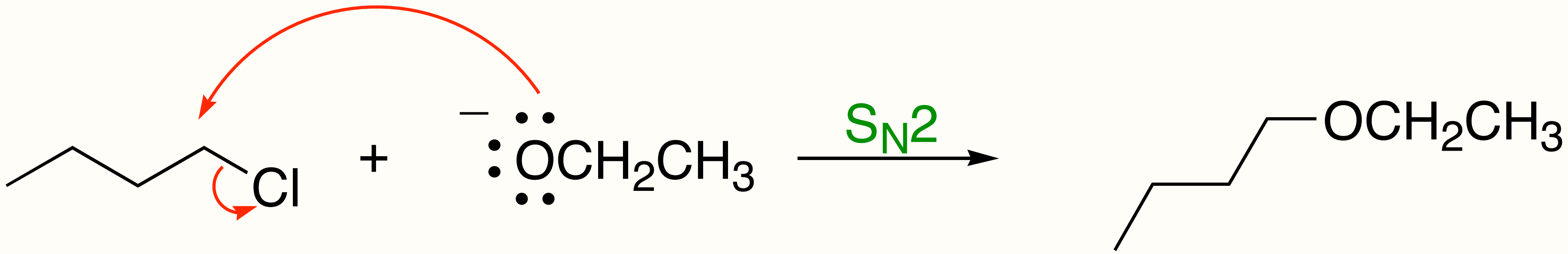
The product obtained by solvolysis of *tert*-butyl bromide in ethanol arises by this mechanism.
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.

- methyl halide =
- no carbocation intermediate =
- 2nd order mechanism
- only one carbon =
- must be substitution

Substitution/Elimination Review



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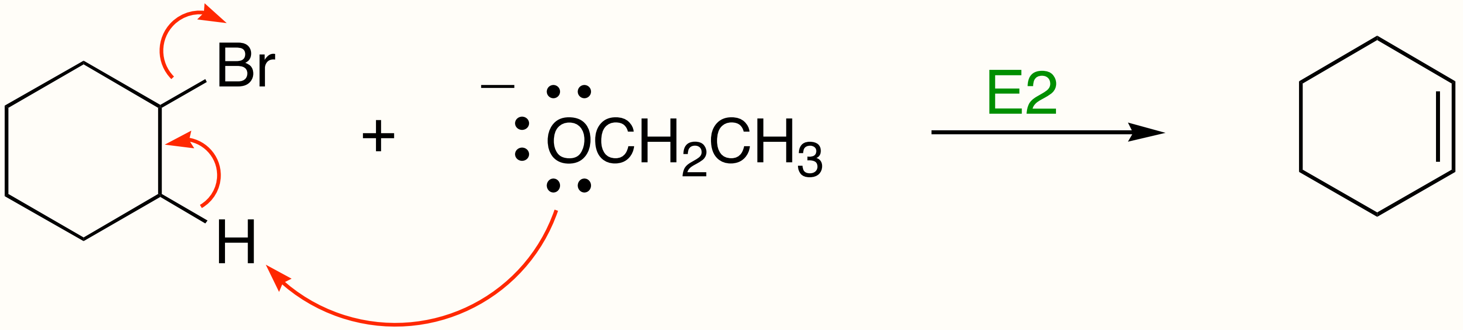
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.

- primary halide =
- no carbocation intermediate =
- 2nd order mechanism
- primary halide and small nucleophile = low steric hinderance =
- substitution is favored

Substitution/Elimination Review



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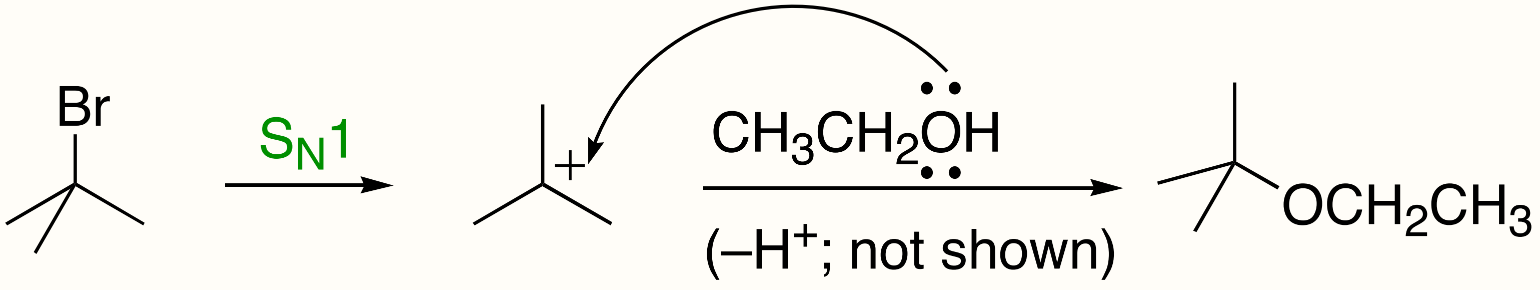
The product obtained by solvolysis of *tert*-butyl bromide in ethanol arises by this mechanism.
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.

- secondary halide =
- carbocations usually <u>favored</u> only when tertiary =
- mostly a 2nd order mechanism
- secondary halide = significant steric hinderance
- elimination is favored

Substitution/Elimination Review



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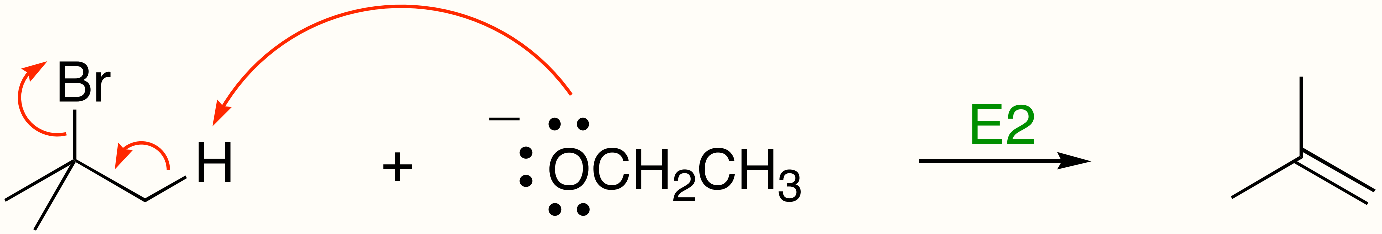
The product obtained by solvolysis of *tert*-butyl bromide in ethanol arises by this mechanism.
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.

- tertiary halide =
- carbocation intermediate =
- 1st order mechanism
- tertiary halide = significant steric hinderance
- pKa ($CH_3CH_2OH_2^+$) = -1.7 (solvolysis = very weak base)
- substitution favored; only bases whose conjugate acids have pKa ≥ 15.7 do elimination

Substitution/Elimination Review



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The product obtained by solvolysis of *tert*-butyl bromide in ethanol arises by this mechanism.
In ethanol that contains sodium ethoxide, *tert*-butyl bromide in ethanol reacts mainly by this mechanism.

- tertiary halide = larger steric hinderance=
- elimination favored when base is strong (conjugate acid pKa ≥ 15.7)

- Although carbocation intermediate is possible, E2 is generally faster than E1, even for 3° alkyl halides

Next Quiz (after Spring Break). . .

Three synthesis questions from the synthesis handout.

pdf available at http://www.chem.uic.edu/chem232/

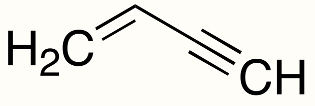
Nomenclature

acetylene and **ethyne** are both acceptable IUPAC names for the molecule below

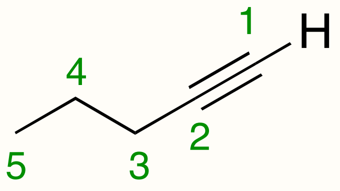
$$H-C\equiv C-H$$

Nomenclature

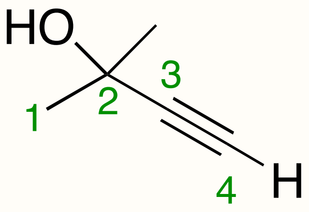
All nomenclature rules remain the same as for alkenes except **-yne** is used as the parent suffix; Alkenes have higher priority than alkynes.



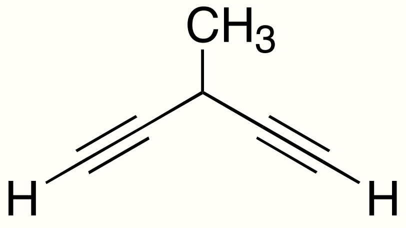
1-buten-3-yne



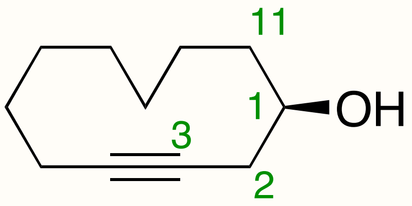
1-pentyne



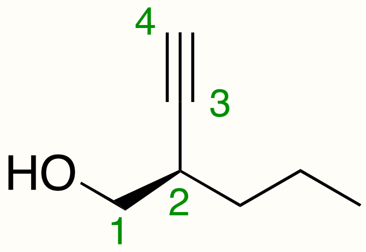
2-methyl-3-butyn-2-ol



2-methyl-1,4-pentadiyne



(R)-cycloundec-3-ynol

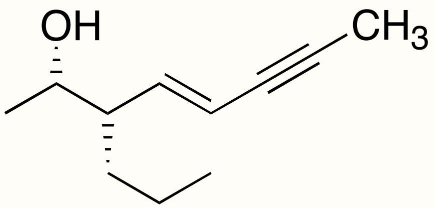


(R)-2-propyl-3-butyn-1-ol

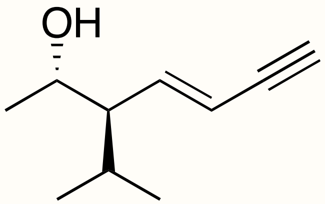
Self-Test Question

Which structural formula is
(2*S*,3*S*)-(*E*)-3-propylhept-4-en-6-yn-2-ol?

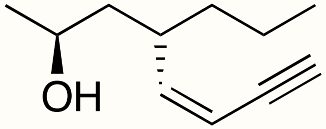
A



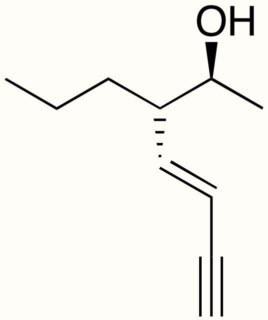
B



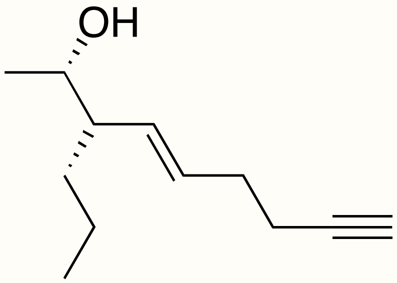
C



[✓ D]



E

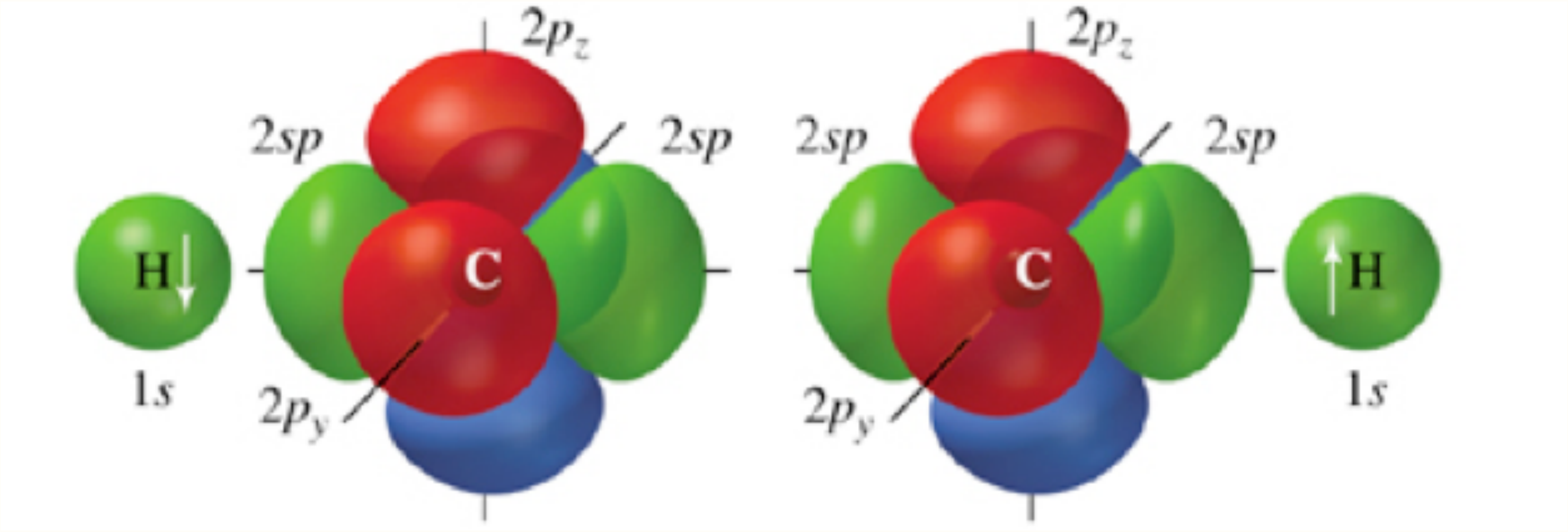


Chapter 9
Properties of Alkynes

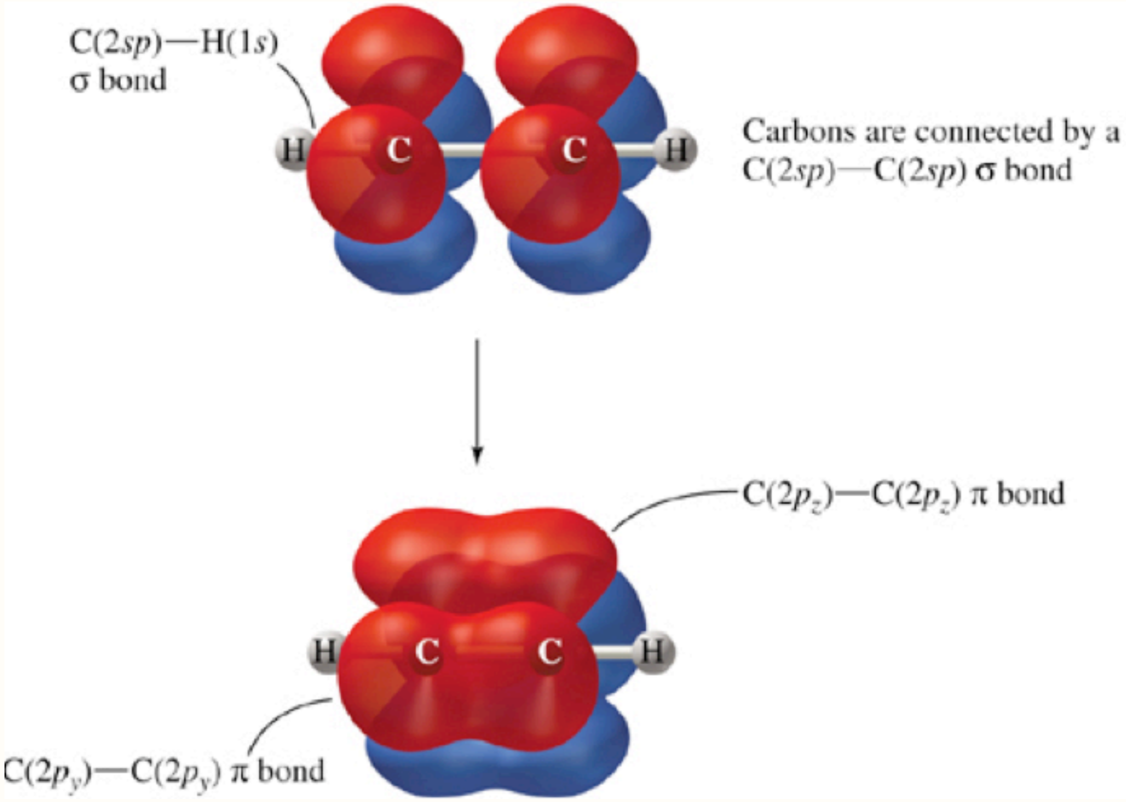
Sections: 9.3-9.5

Structure of Alkynes

Orbitals on sp-Hybridized Carbons



Triple Bond: 2 pi-bonds & 1 sigma-bond



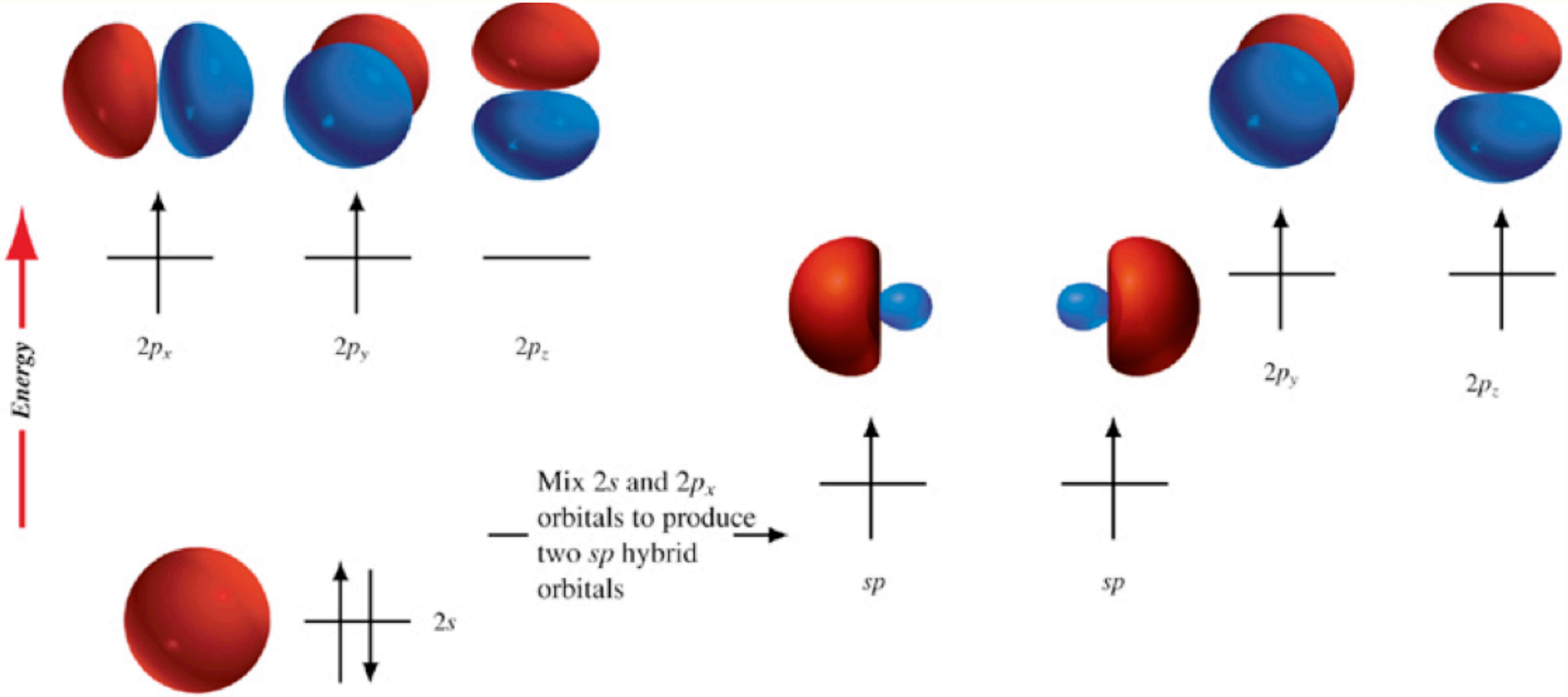
A triple bond is formed by three orbital overlaps

2 pi (π) bonds: side-to-side overlap of two sets of p-orbitals; 4 π-electrons

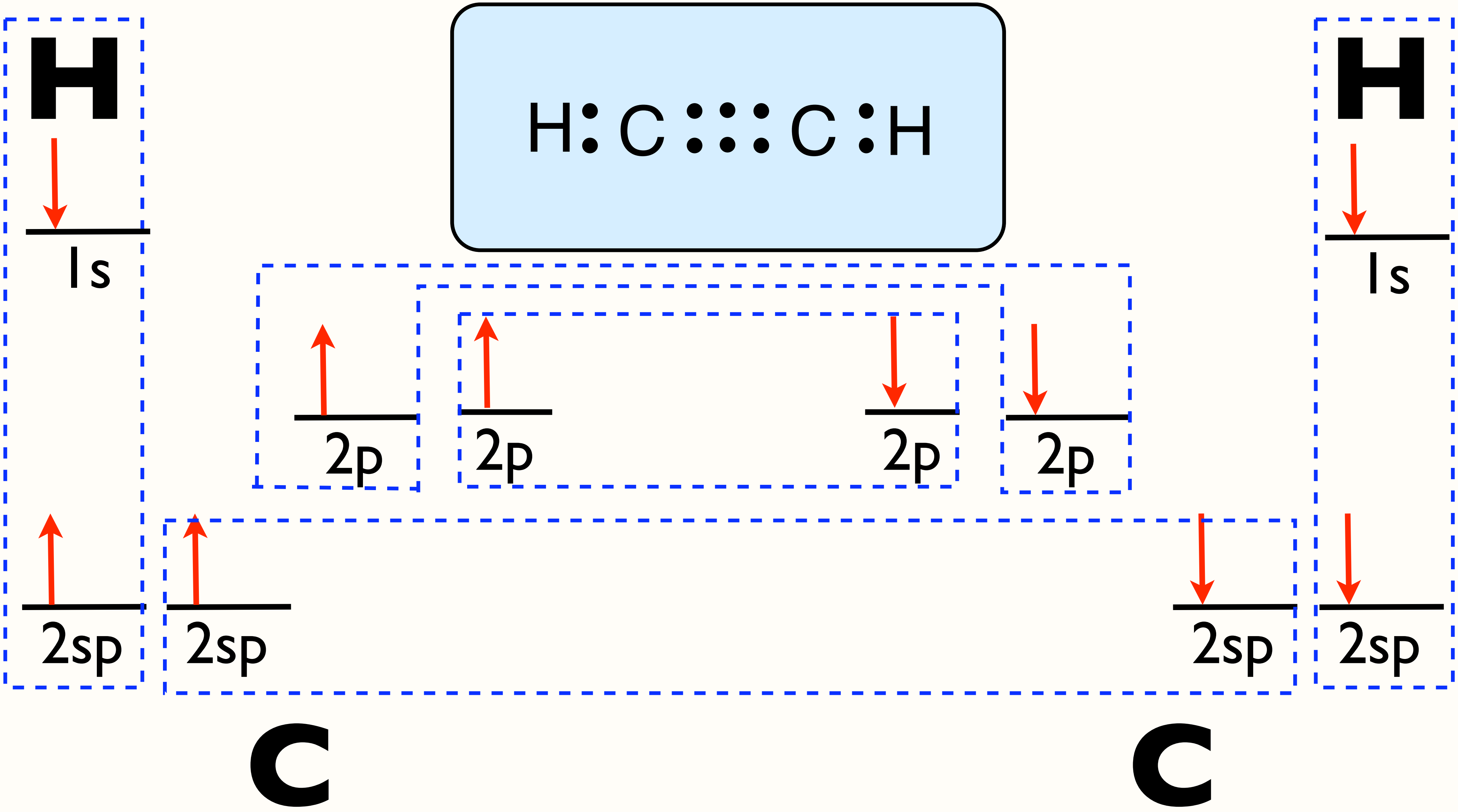
1 sigma (σ) bond: head-to-head overlap of two sp^2-orbitals

Hybridization

Two p-orbitals are Reserved–Not Hybridized

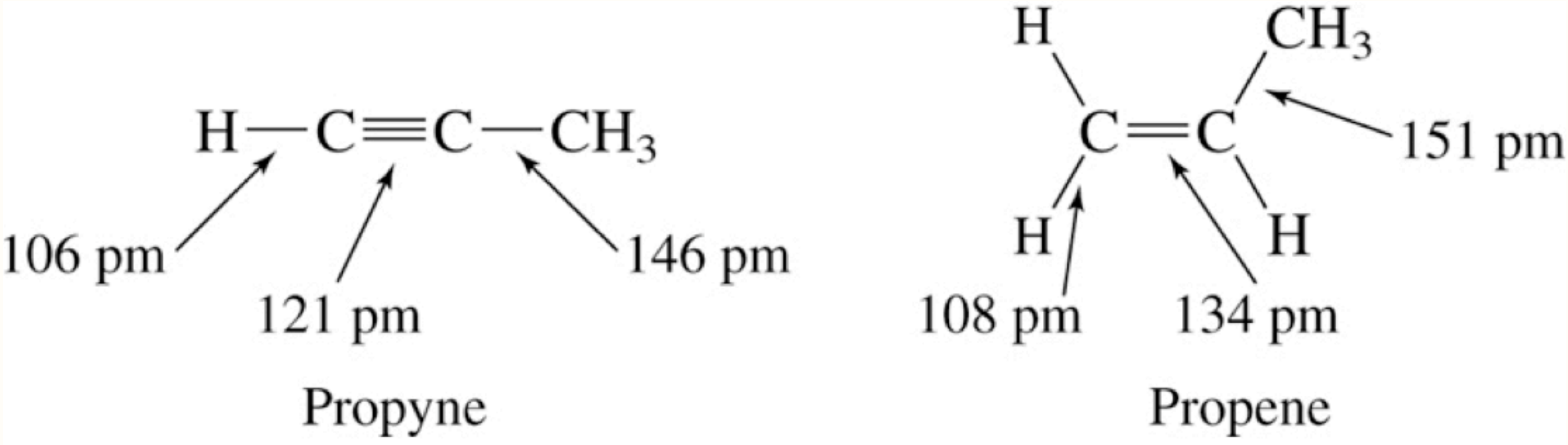


Valence Model of Bonding in Acetylene (with Hybridization)



Bond Strength

triple bonds = stronger and shorter



Comparison of Ethane, Ethylene and Ethyne

	Ethane	Ethylene	Ethyne
C-C distance	153 pm	134 pm	120 pm
C-H distance	111 pm	110 pm	106 pm
H-C-C angles	111.0°	121.4°	180°
C-C BDE	368 kJ/mol	611 kJ/mol	820 kJ/mol
C-H BDE	410 kJ/mol	452 kJ/mol	536 kJ/mol
hybridization of C	sp^3	sp^2	sp
% *s*-character	25%	33%	50%
pK_a	62	45	26

Acidity

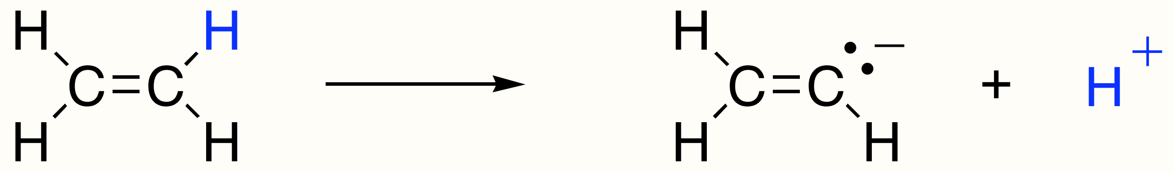
increased s-character =
increased electronegativity of carbon =
electrons closer to the nucleus =
stronger acid

pK_a = 26 sp

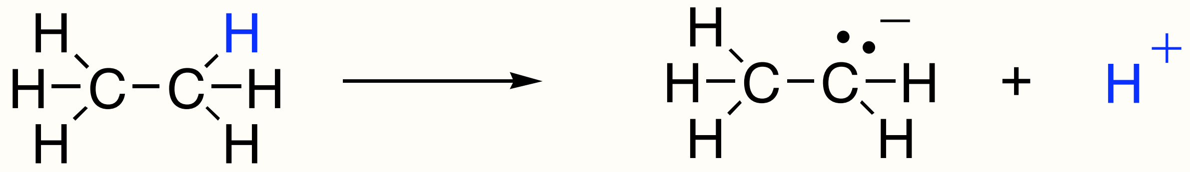
$H-C\equiv C-H \longrightarrow H-C\equiv C:^{-} + H^{+}$

carbanion,
acetylide

pK_a = 45 sp^2

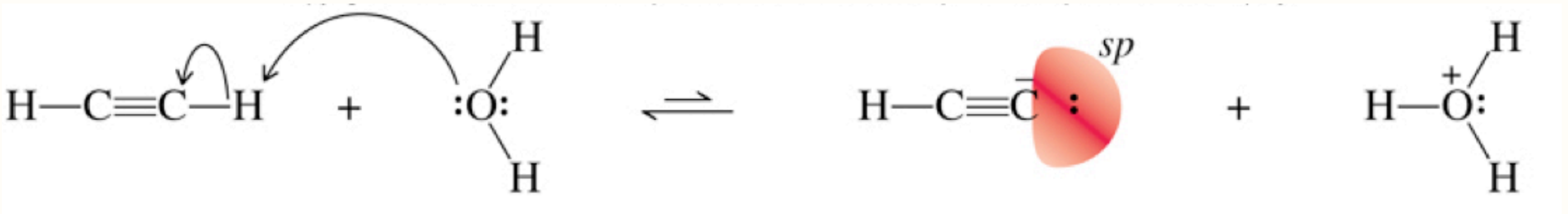


pK_a = 62 sp^3



Aqueous Acid-Base Equilibria

Water is not a strong enough base to significantly deprotonate terminal alkynes.



Acetylene
($pK_a = 26$)

Water
($pK_a = 15.7$)

Acetylide ion

Hydronium ion
($pK_a = -1.7$)

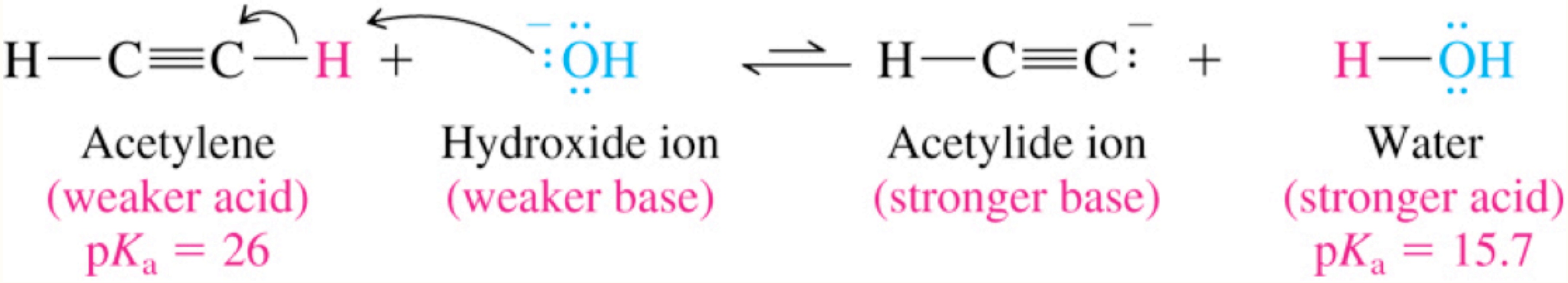
$$K_{eq} = 10^{-[\text{pKa (acid left) - pKa (acid right)}]}$$

$$K_{eq} = 10^{-(26 - -1.7)}$$

$$K_{eq} = 10^{-27.7}$$

Aqueous Acid-Base Equilibria

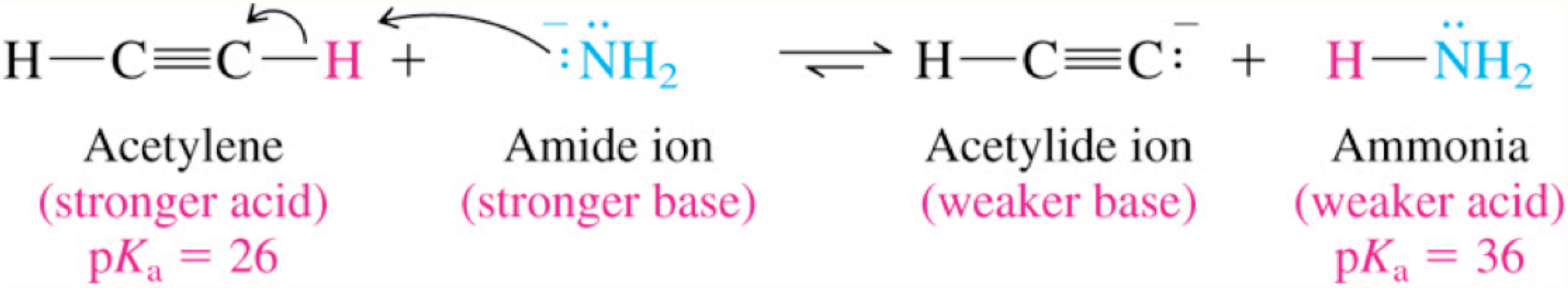
Even hydroxide (the strongest base that can exist in water) is not a strong enough base to significantly deprotonate terminal alkynes.



$$K_{eq} = 10^{-[\text{pKa (acid left) - pKa (acid right)}]}$$
$$K_{eq} = 10^{-(26\ -\ 15.7)}$$
$$K_{eq} = 10^{-10.3}$$

Amide Deprotonates Terminal Alkynes

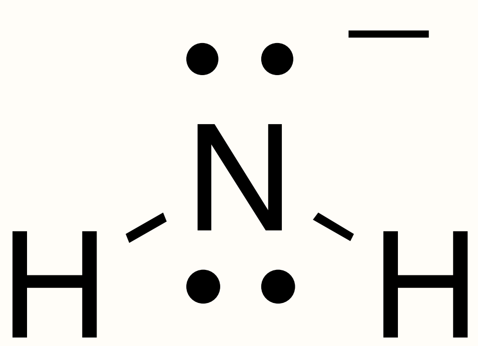
Sodium amide ($NaNH_2$) is the most common base for completely deprotonating terminal alkynes.



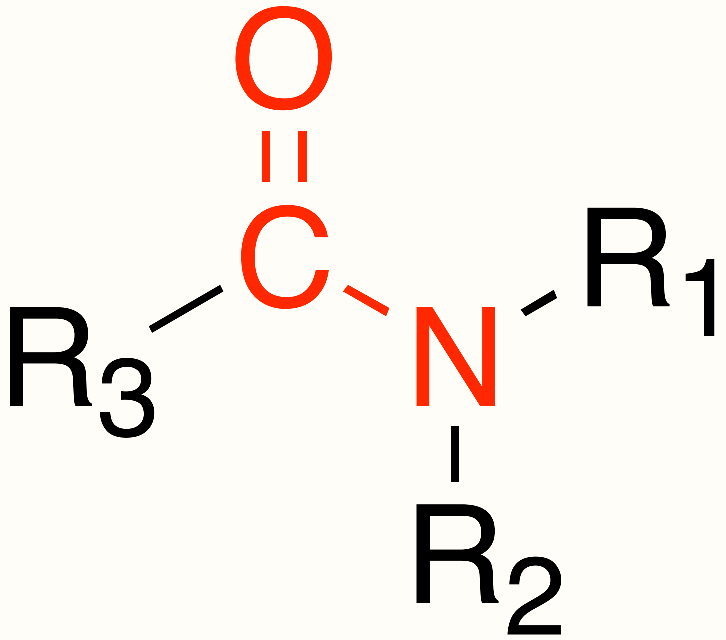
$$K_{eq} = 10^{-[\mathrm{pKa\ (acid\ left)\ -\ pKa\ (acid\ right)}]}$$
$$K_{eq} = 10^{-(26\ -\ 36)}$$
$$K_{eq} = 10^{10}$$

Diambiguation of Amide

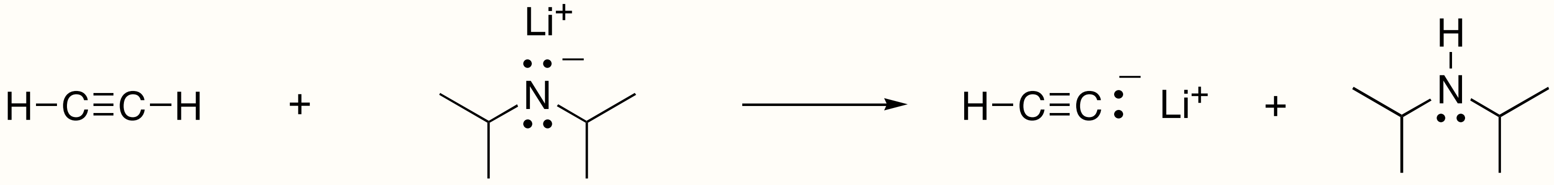
1. Conjugate base of an amine



2. Carbonyl with a C-N bond



Other Commonly Encountered Bases



lithium diisopropyl amide
(LDA)

$pK_a = 36$

$$H-C\equiv C-H \;+\; CH_3CH_2CH_2\ddot{\underset{\cdot\cdot}{C}}H_2^{-}\;Li^+ \longrightarrow H-C\equiv C\!:^{-}\;Li^+ \;+\; CH_3CH_2CH_2CH_3$$

n-butyl lithium
(*n*-BuLi)

$pK_a = 62$

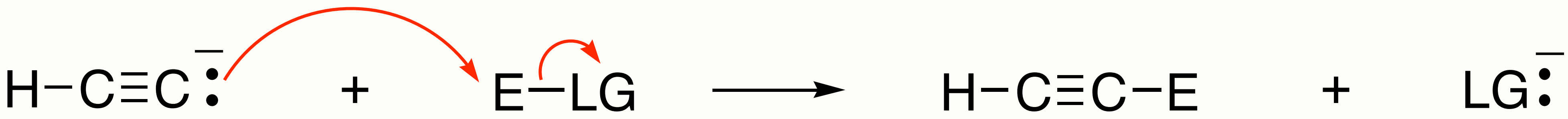
$$H-C\equiv C-H \;+\; Na^+H\!:^{-} \longrightarrow H-C\equiv C\!:^{-}\;Na^+ \;+\; H_2$$

sodium hydride
(NaH)

pK_a = very large

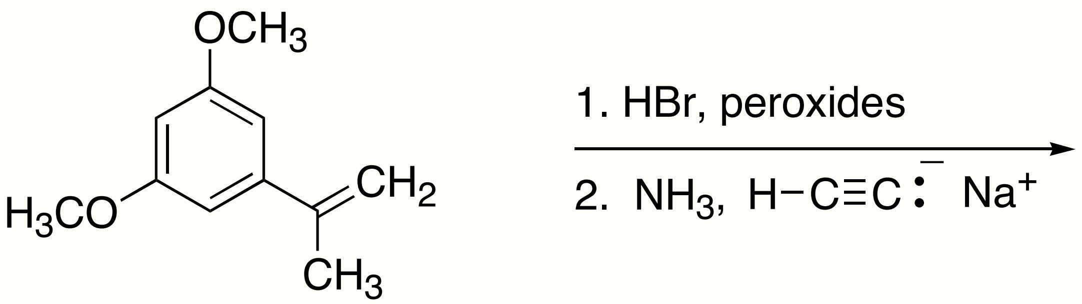
Acetylides are Nucleophiles!

- Nucleophiles Add to Electrophiles
- First C-C bond forming reaction we’ve learned
- Acetylides are small - good nucleophiles



Self-Test Question

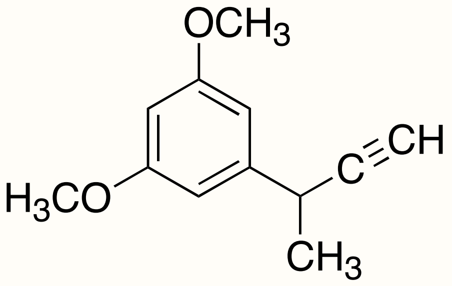
Predict the product.



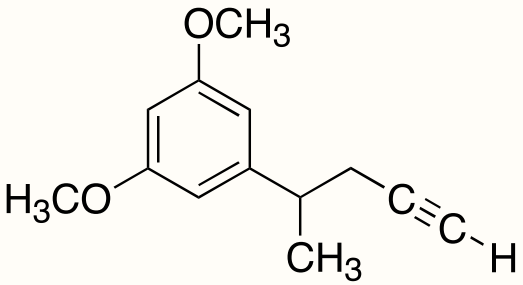
1. HBr, peroxides

2. NH_3, H−C≡C:$^-$ Na^+

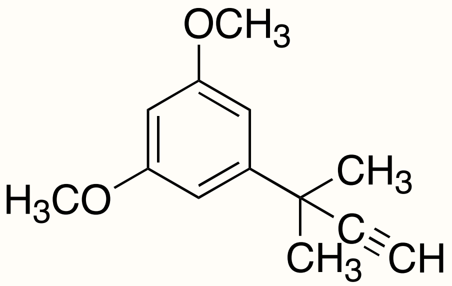
A



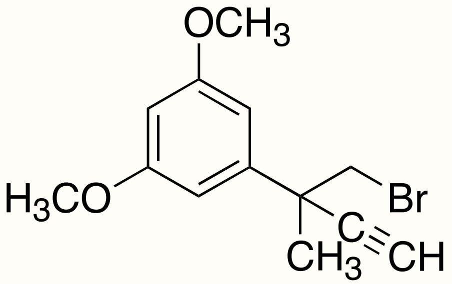
[✓ B]



C



D



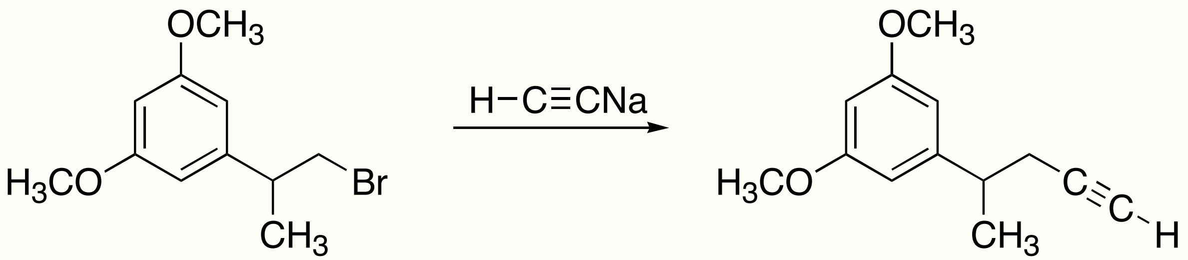
Alkylation of Terminal Alkynes and Acetylene

Chapter 9: Sections 9.6

Preparation of Alkynes

There are two main methods for the preparation of alkynes:

1. Alkylation of acetylide anions (C-C bond formation)



2. Functional group transformations (Thursday's topic)

Alkylation of Acetylene and Terminal Alkynes

alkyl group: any group derived from an alkane
alkylation: process of adding an alkyl group
alkylating reagent: electrophilic reagent causing alkylation

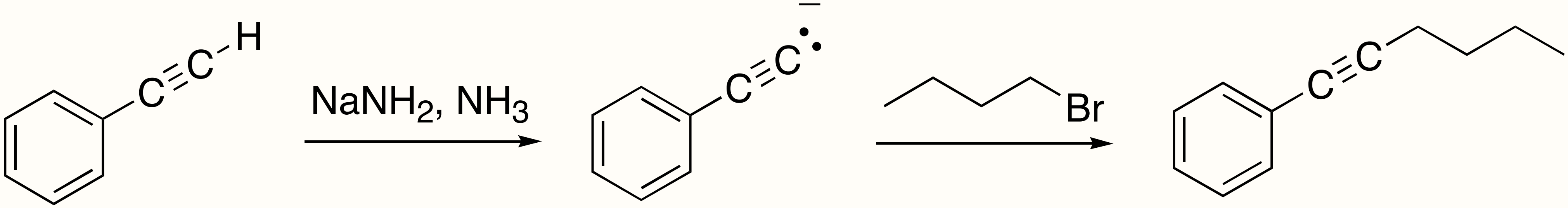
$$\mathrm{H{-}C{\equiv}C{:}^{-}\;Na^{+}} \quad + \quad \mathrm{H_3C{-}Br} \xrightarrow[\text{alkylation}]{S_N2} \mathrm{H{-}C{\equiv}C{-}CH_3}$$

acetylide
(nucleophile)

alkylating reagent
(electrophile)

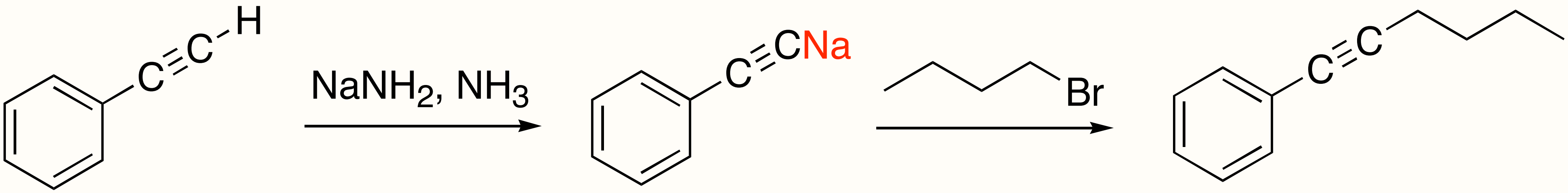
- the alkylating reagent is a primary alkyl or methyl halide
- the reaction is nucleophilic substitution
- the nucleophile is an acetylide (carbanion)

Conditions/Example



- must start with acetylene or terminal alkyne
- most common base = sodium amide ($NaNH_2$)
- solvent is typically ammonia (NH_3)
- alkylating reagent must be a 1° alkyl halide or methyl halide

Conditions/Example



positive metal counterion =
negative carbanion

- must start with acetylene or terminal alkyne
- most common base = sodium amide ($NaNH_2$)
- solvent is typically ammonia (NH_3)
- alkylating reagent must be a 1° alkyl halide or methyl halide

Dialkylation of Acetylene

$HC{\equiv}CH$

$$\Big\downarrow \begin{array}{l} \text{1. } NaNH_2,\ NH_3 \\ \text{2. } CH_3CH_2Br \end{array}$$

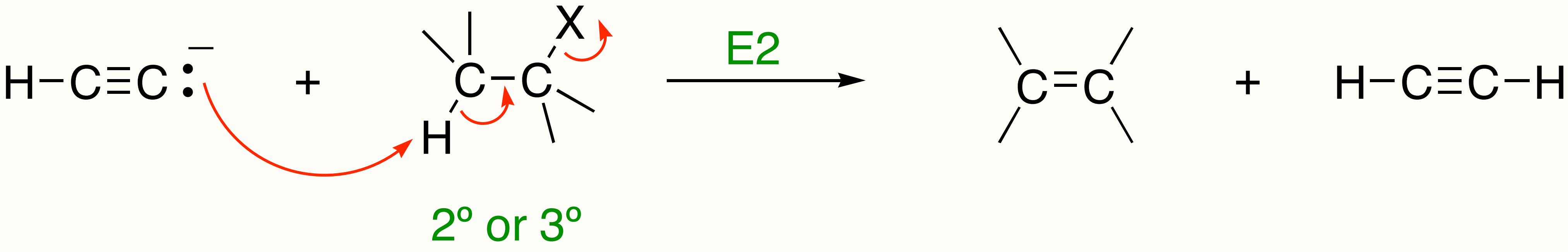
$CH_3CH_2{-}C{\equiv}CH$

$$\Big\downarrow \begin{array}{l} \text{1. } NaNH_2,\ NH_3 \\ \text{2. } CH_3Br \end{array}$$

$CH_3CH_2{-}C{\equiv}C{-}CH_3$ *internal alkyne*

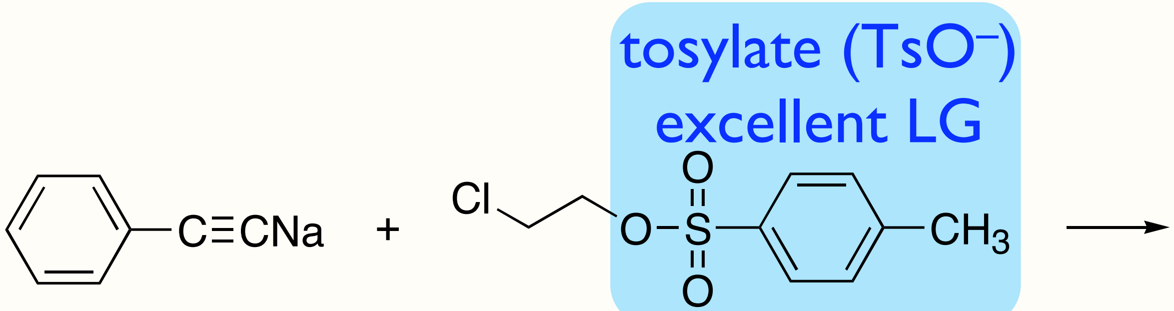
Limitation: Acetylide is a Strong Base

- acetylide is a stronger base than hydroxide =
- E2 predominates over S_N2 when alkyl halide is 2° or 3°
- acetylides can only be alkylated with 1° alkyl or methyl halides



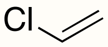
Self-Test Question

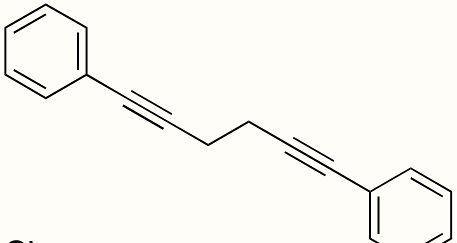
Predict the *major* organic product.

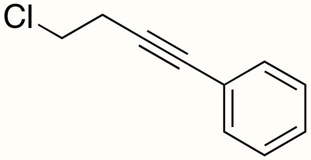


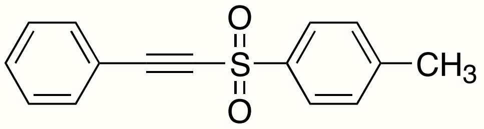
tosylate (TsO$^-$)
excellent LG

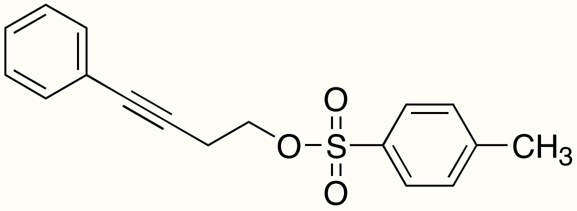
(1.0 equivalent) (1.0 equivalent)

A


B


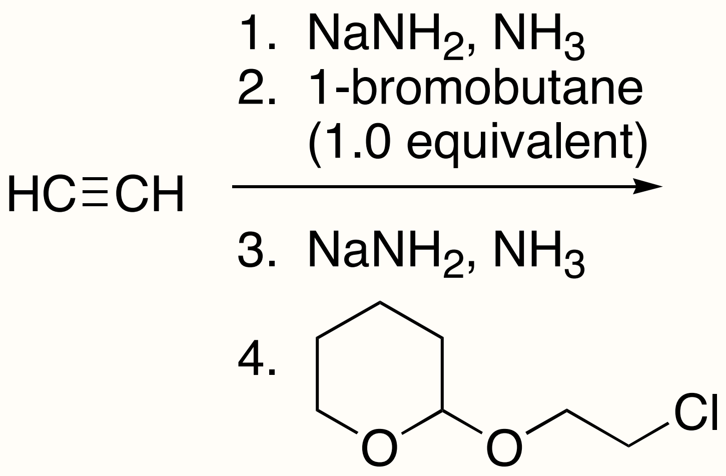
[✓ C]


D


E


Self-Test Question

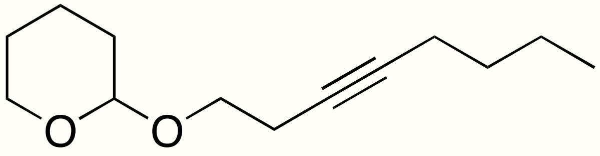
Predict the *major* organic product.



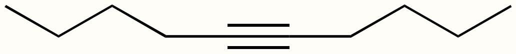
$HC{\equiv}CH$

1. $NaNH_2$, NH_3
2. 1-bromobutane (1.0 equivalent)
3. $NaNH_2$, NH_3
4.

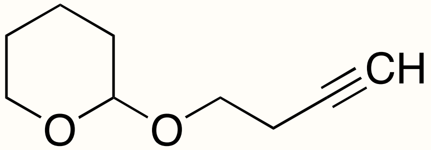
[✓ A]



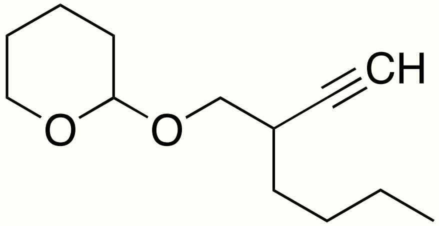
B



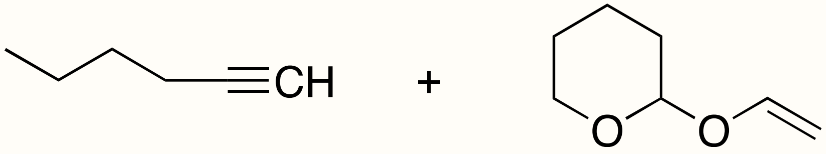
C



D



E



Next Lecture. . .

Chapter 9: Sections 9.7-9.13

Quiz This Week. . .

Chapter 8