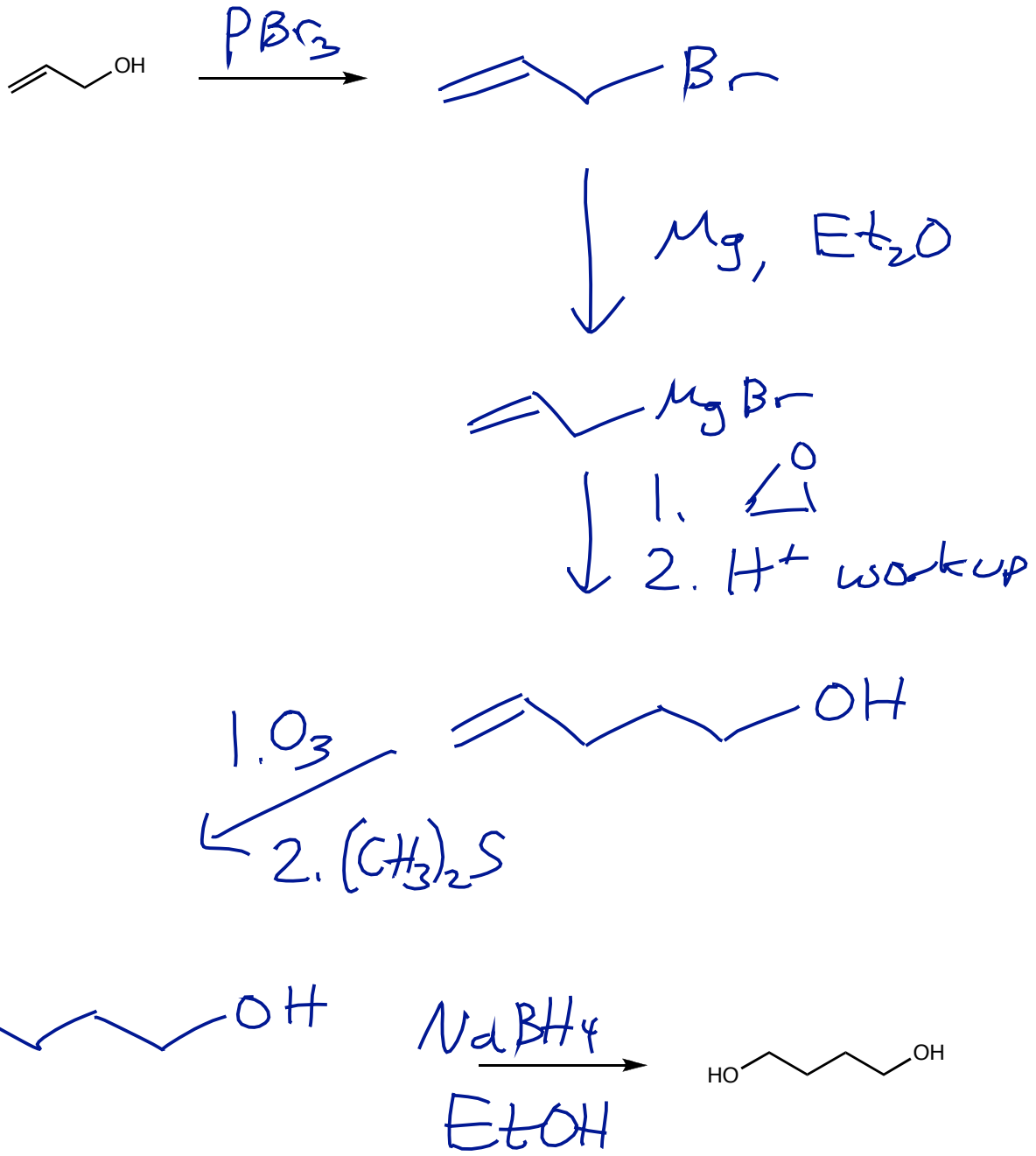
Homework!

Test Yourself Now!

synthesis.

Check your answer...

Provide a complete synthesis of the desired product from the indicated starting material. You may use any organic or inorganic reagents in your synthesis.



Tomorrow:

Last day of the

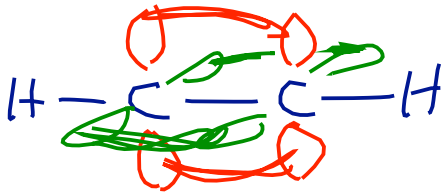
"fall semester"

Mon
Tues } Spectroscopy
↳ (Alcohol)

Yesterday: epoxide day

Today: Alkyne day.

Friday: Conjugation day.



Nomenclature of Alkynes

- Draw skeletal structures for:

acetylene

(C_2H_2) "ethyne"

$H-C\equiv C-H$ (sp hybrid)

linear (4 atoms linear)

dimethylacetylene

$H_3C-C\equiv C-CH_3$

1-butyne

carbon here!

$HC\equiv C-$ or $HC\equiv$

2-butyne

$H_3C-C\equiv C-CH_3$ or

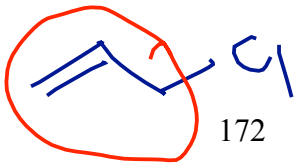
carbons!

propargyl chloride

alkyne version of allyl,

$HC\equiv C-Cl$

propargyl

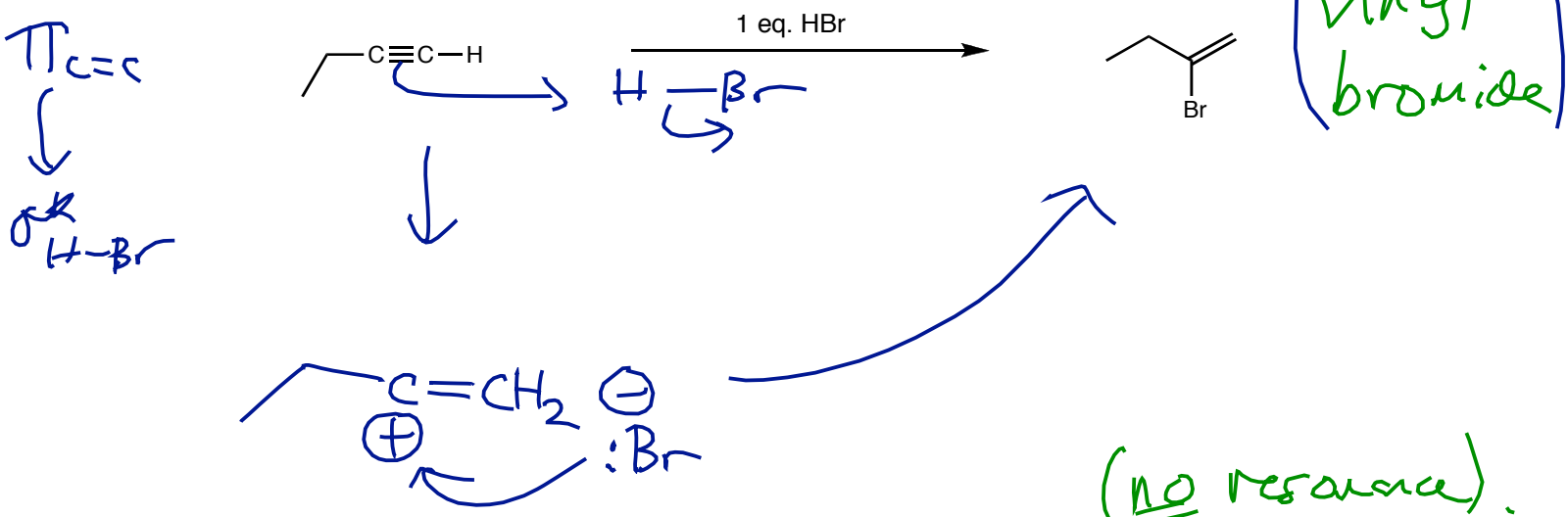
Allyl chloride 

Reading: Section 14.1

Alkynes are like 2 alkenes .... except...

Addition of HX to Alkynes

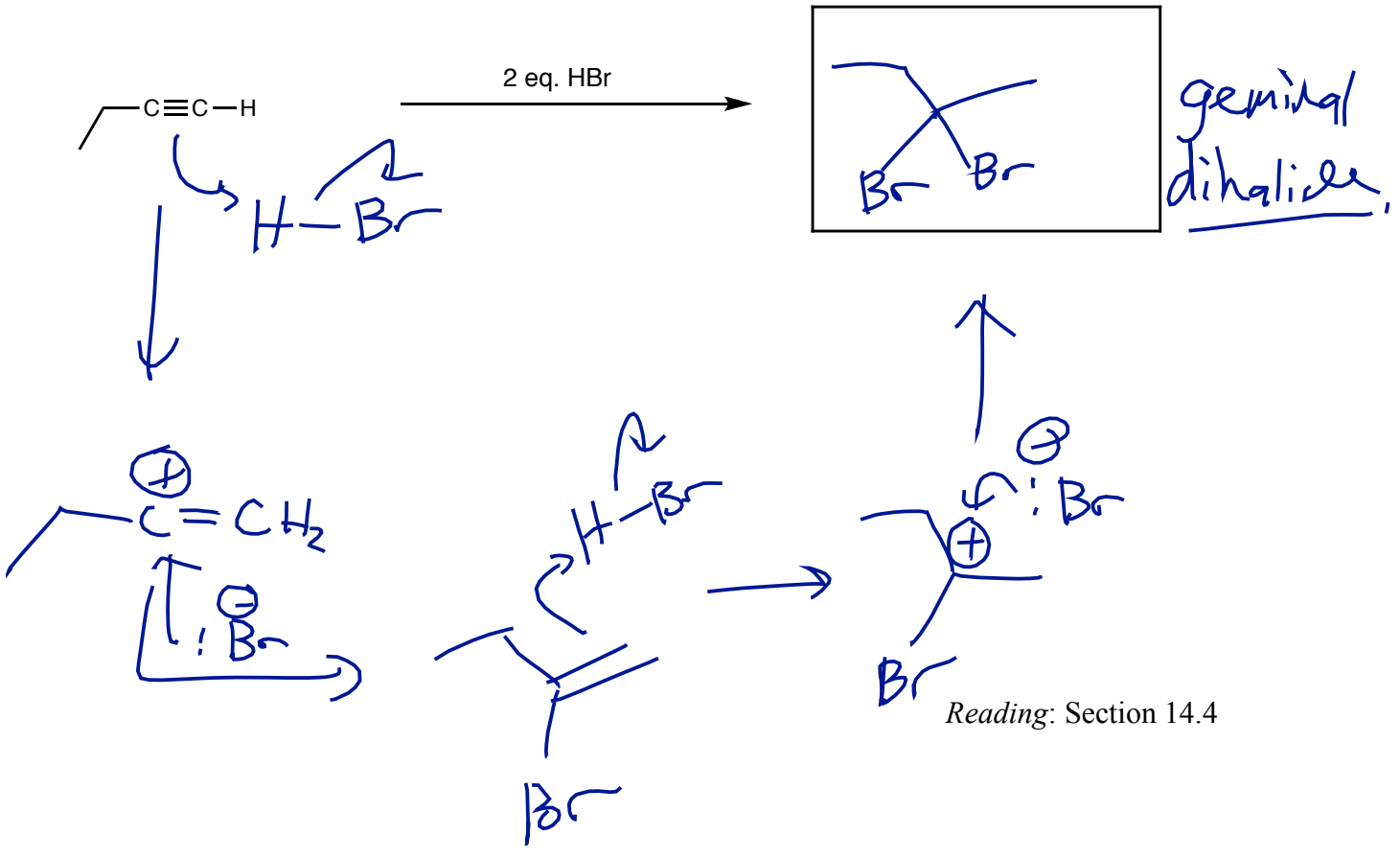
- Draw a complete curved-arrow mechanism for the following reaction:



a vinyl bromide

vinylic carbocation (sp hybrid) → very unstable (no resonance).

- Predict the product and draw a complete curved-arrow mechanism for the following reaction:

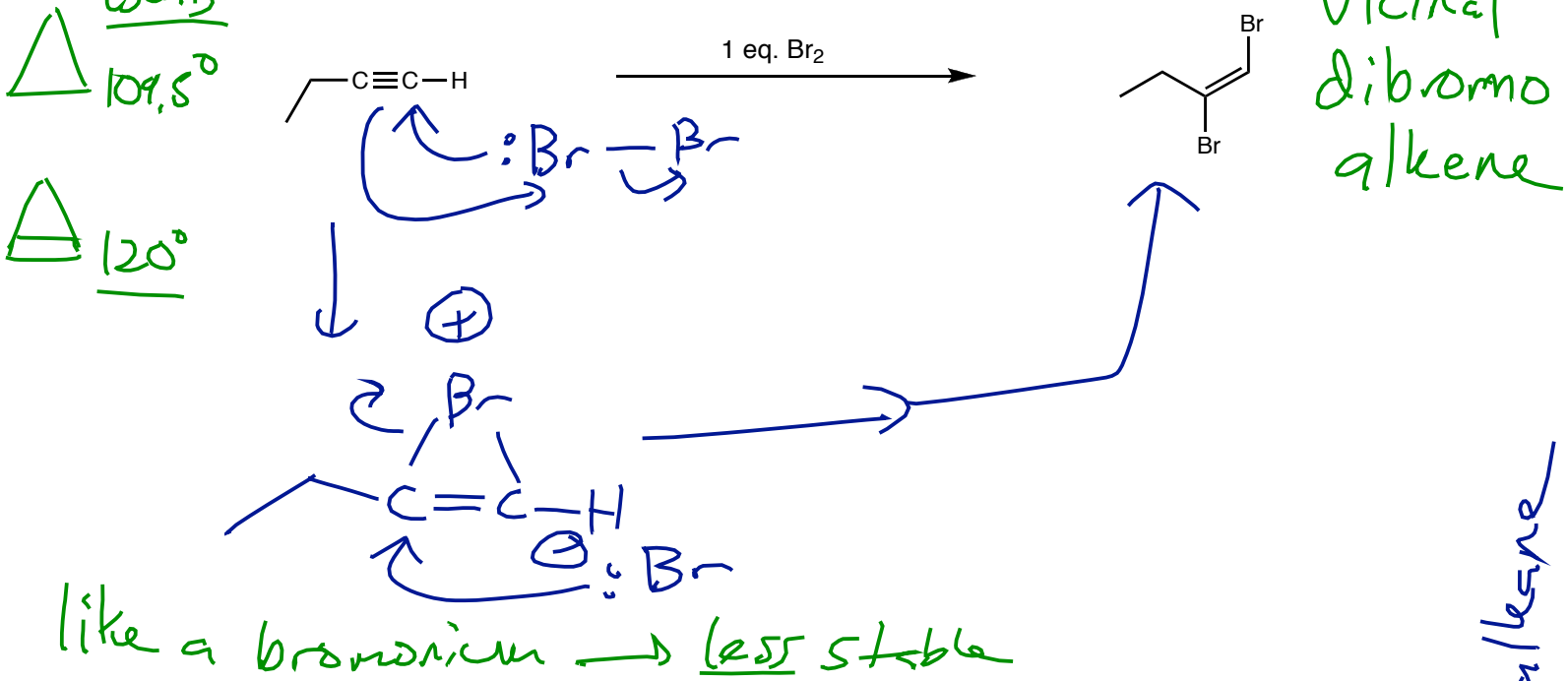


geminal dihalide.

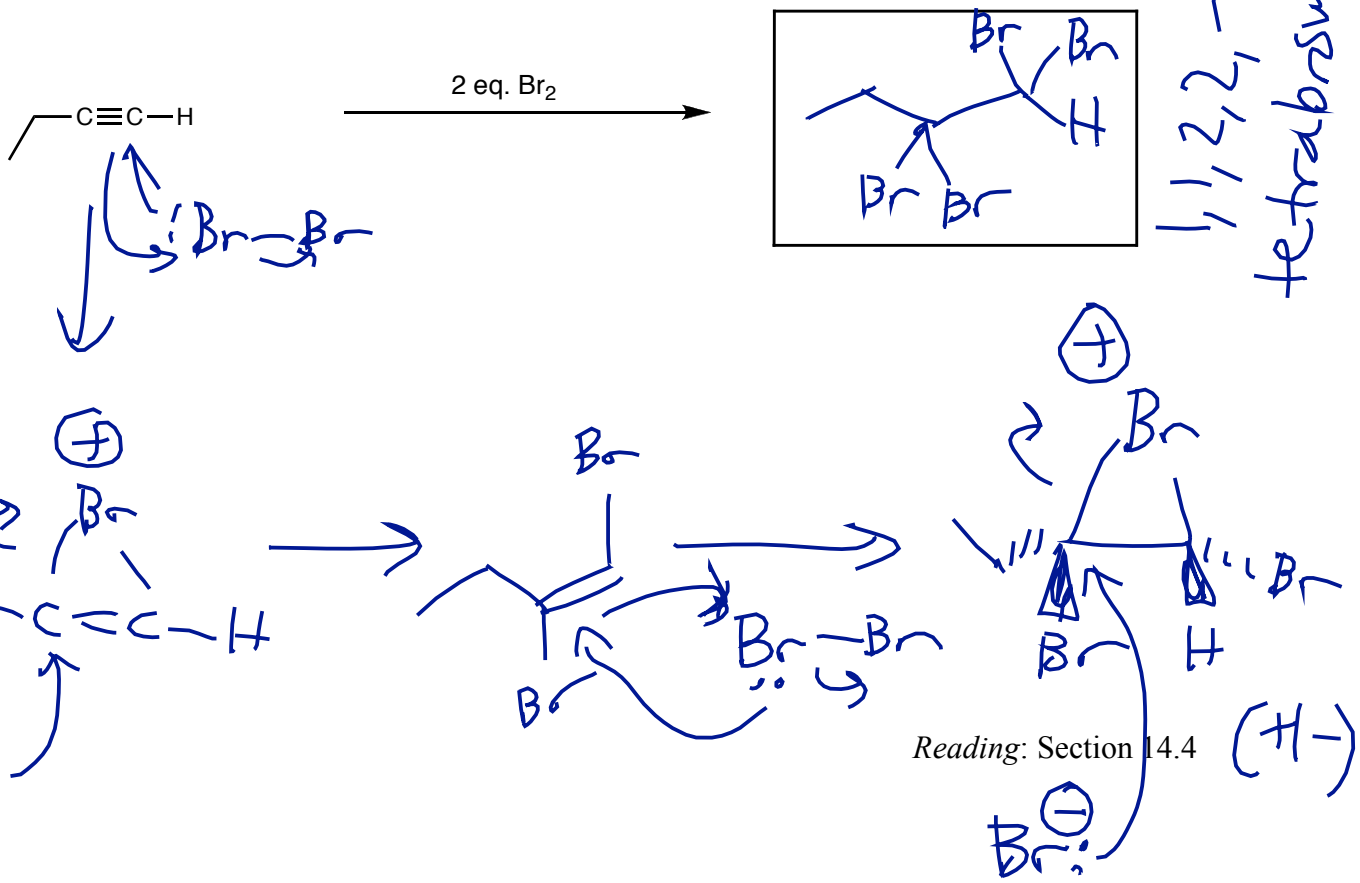
Reading: Section 14.4

Addition of Halogens (X_2) to Alkynes

- Draw a complete curved-arrow mechanism for the following reaction:



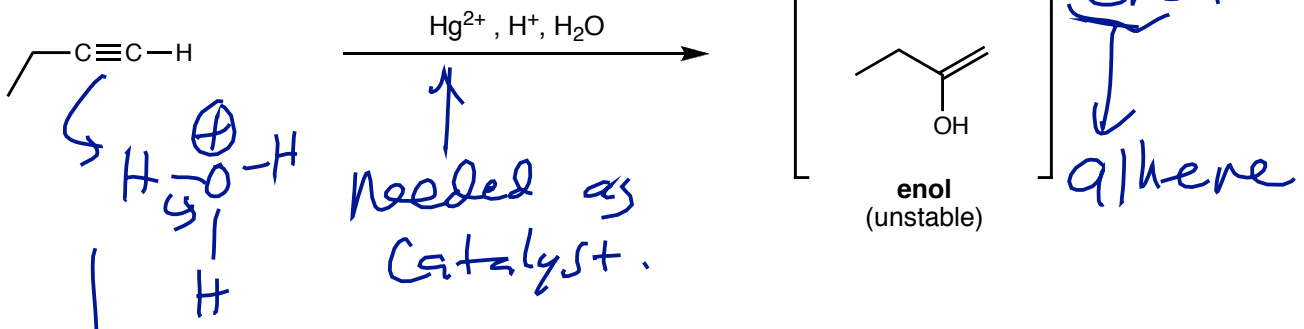
- Predict the product and draw a complete curved-arrow mechanism for the following reaction. Be sure to show the **stereochemistry** of the product!

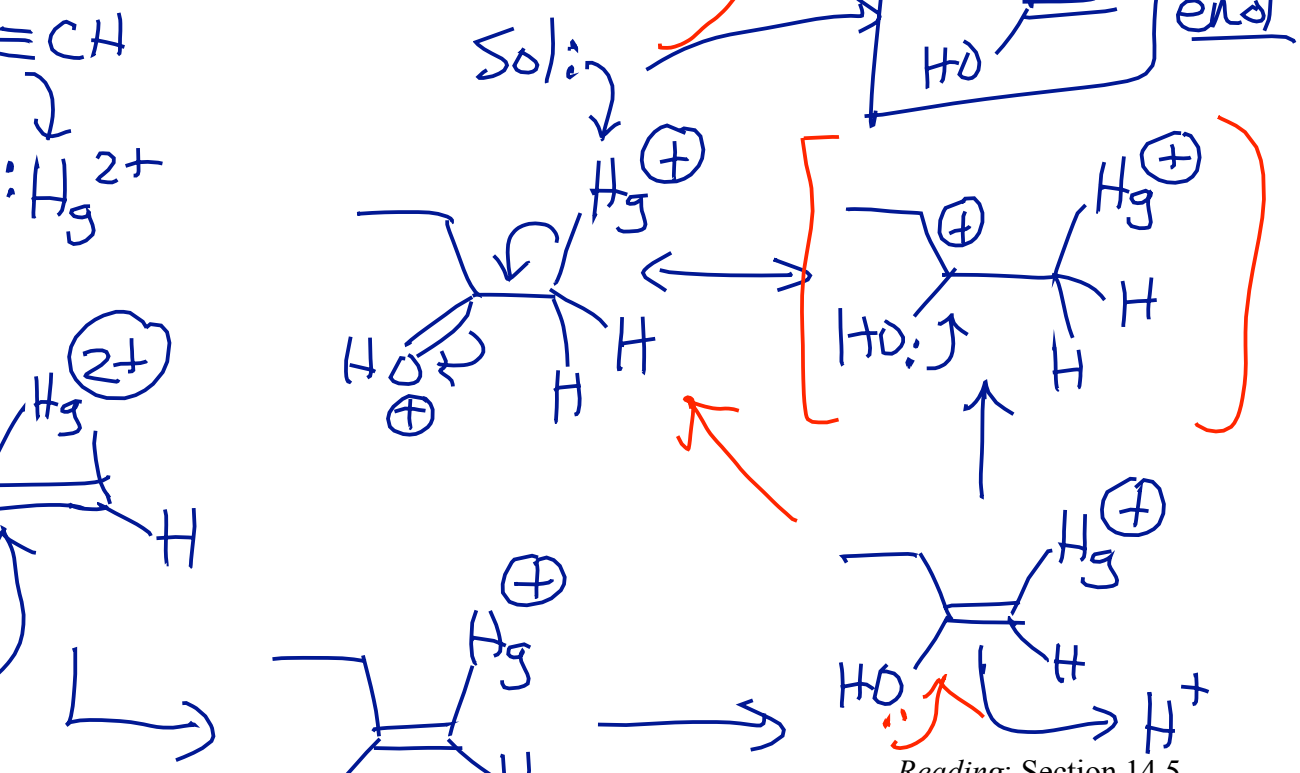


Reading: Section 14.4

Addition of Water to Alkynes: Enol Formation

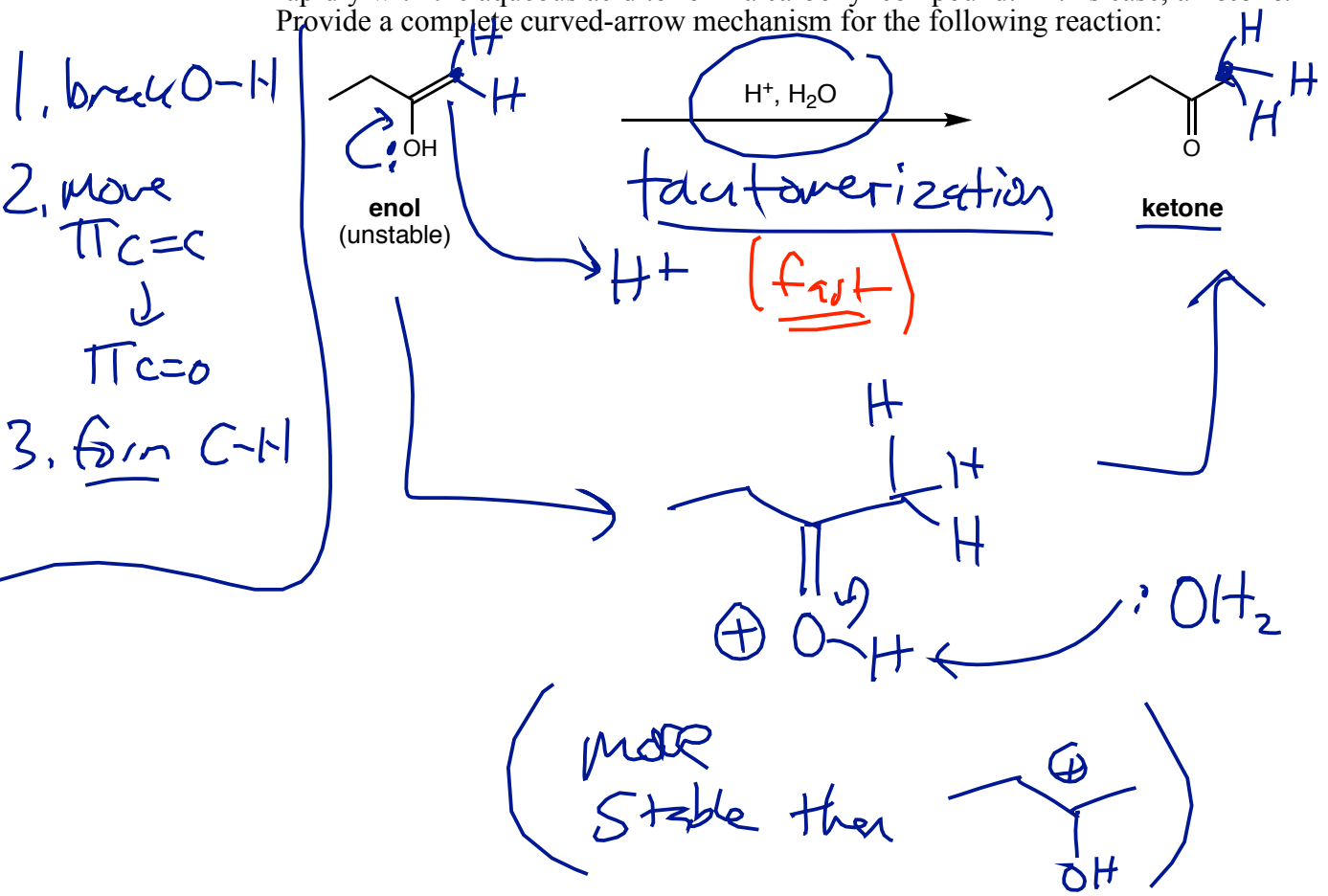
The following reaction produces an **unstable** intermediate known as an **enol** (alk**ene** + alco**hol** = **enol**). Draw a complete curved-arrow mechanism for this reaction up to the formation of the enol.





Addition of Water to Alkynes: Enol Hydrolysis

- The enol is **not** the final product of the reaction of an alkyne with water. The enol reacts rapidly with the aqueous acid to form a carbonyl compound: in this case, a **ketone**. Provide a complete curved-arrow mechanism for the following reaction:



- Show the complete synthetic transformation from an **alkyne** to a **ketone**:

Other ways: — Ozonolysis

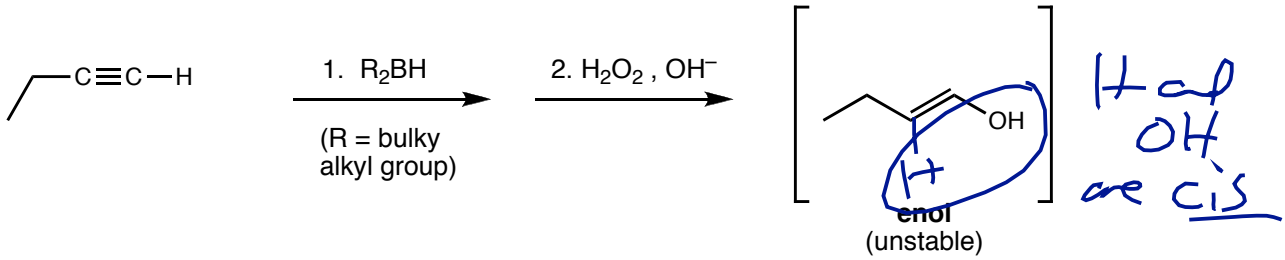
— HIO_4 cleavage of OH OH

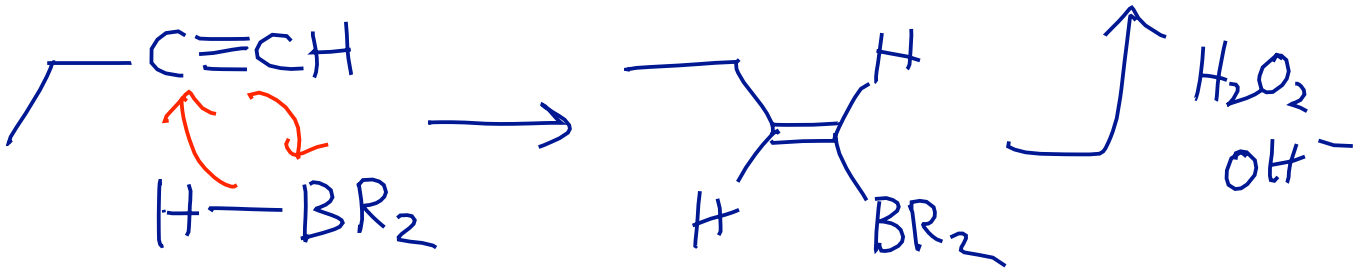
Reading: Section 14.5

— Oxidation of 2° alcohols with CrO_3

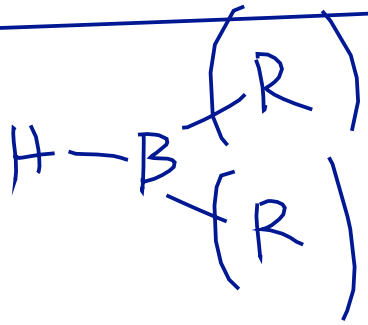
Hydroboration/Oxidation of Alkynes: Enol Formation

- The following reaction produces an **unstable** intermediate known as an **enol** (alk**ene** + alcoh**ol** = **enol)**. Draw a complete curved-arrow mechanism for this reaction up to the formation of the enol. You should also explain why the alkene geometry is *trans* (that is, you should explain the **stereochemistry**!)

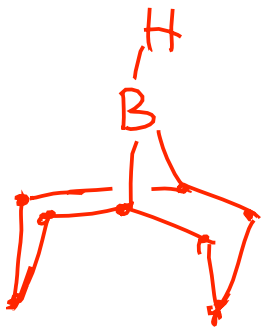




still has $\pi_{C=C}$ could react with another H—BR_2

not BH_3. Use 

bulky R's prevent second hydroboration

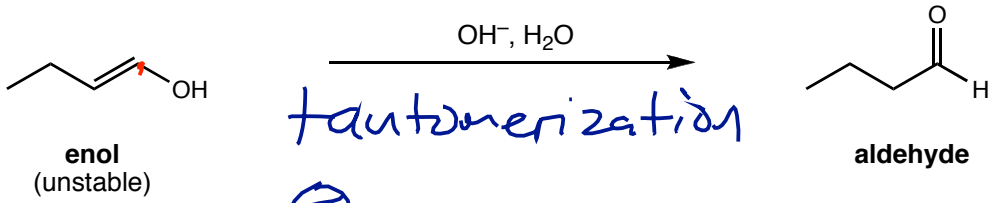
Example: 9-BBN 

9-borabicyclononane

Reading: Section 14.5

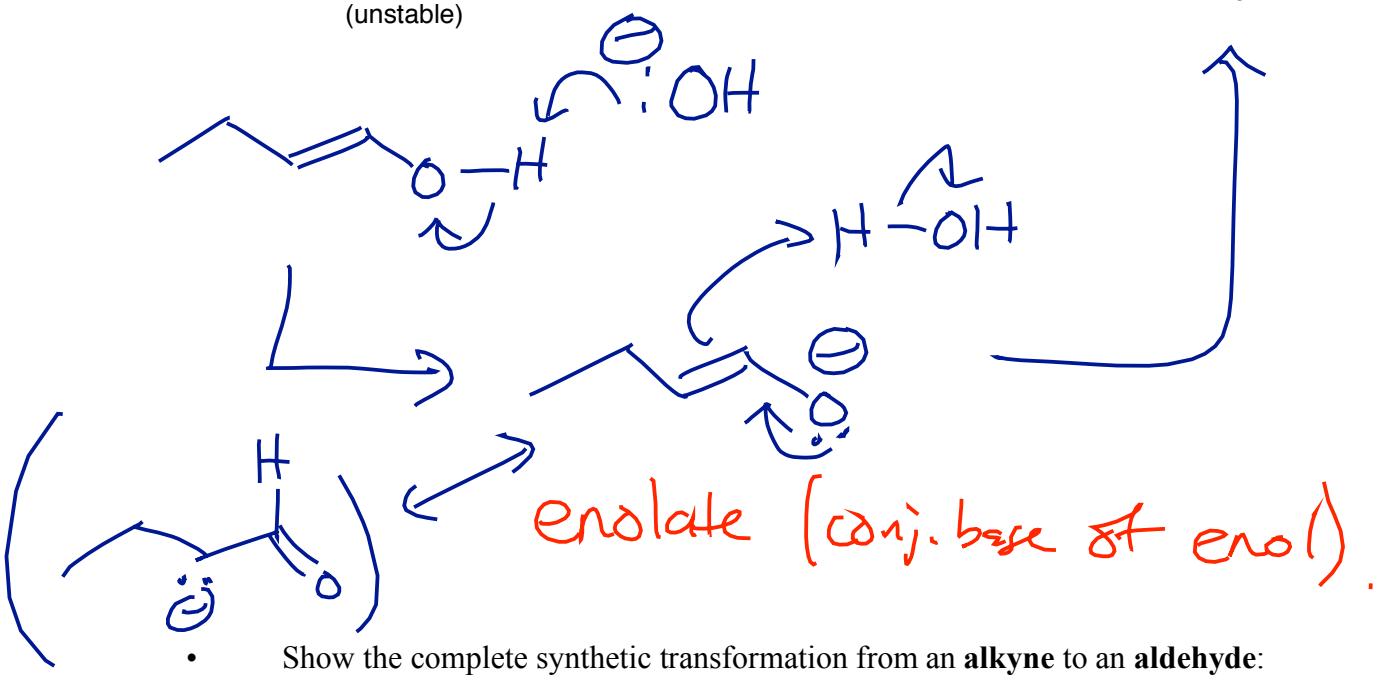
Hydroboration/Oxidation of Alkynes: Enol Hydrolysis

- The enol is **not** the final product of hydroboration/oxidation of an alkyne. The enol reacts rapidly with the aqueous base (in the oxidation step) to form a carbonyl compound: in this case, an **aldehyde**. Provide a complete curved-arrow mechanism for the following reaction:

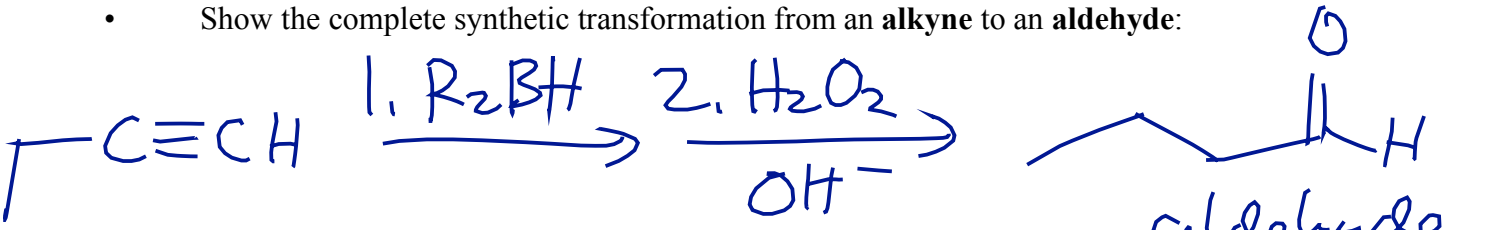


enol
(unstable)

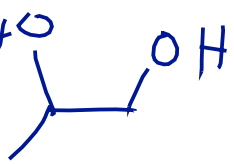
aldehyde



- Show the complete synthetic transformation from an **alkyne** to an **aldehyde**:



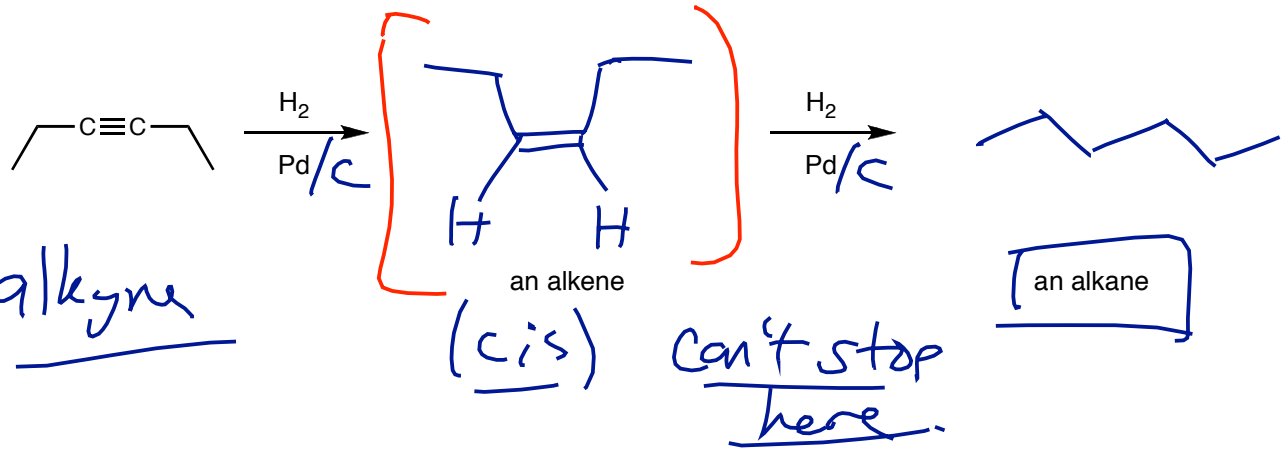
Other ways:

- ozonolysis
- HIO₄ cleavage of 
- oxidation of 1° alcohol with CrO_3 · Py ("dry")

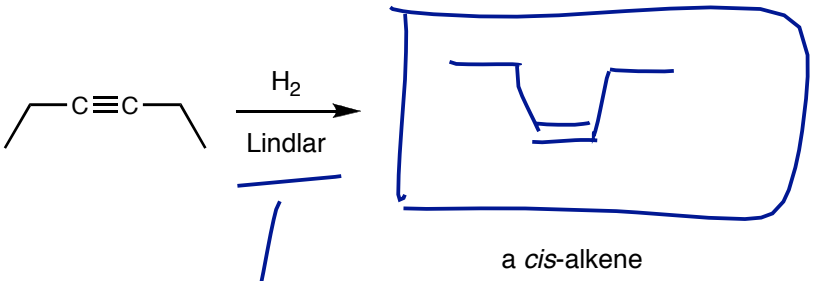
Reading: Section 14.5

Hydrogenation of Alkynes: Catalytic Hydrogenation

- Ordinarily, the reaction of an alkyne with H_2 / Pd adds *two* equivalents of hydrogen and yields an alkane. Show the intermediate and final product in the following transformation. Be sure to consider the **stereochemistry**!



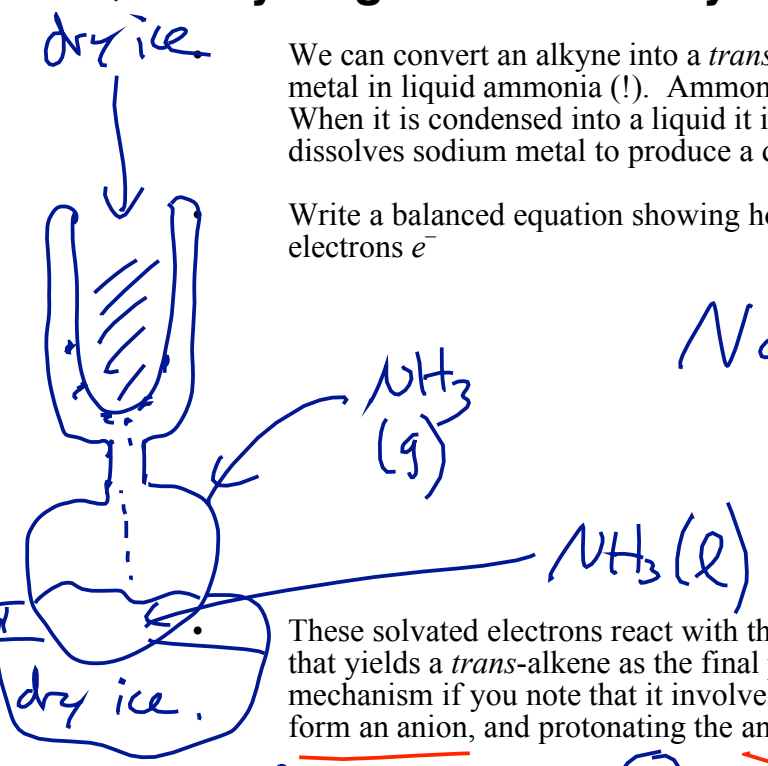
- However, we can use a **poisoned catalyst** (for example, a Lindlar catalyst) to halt the reaction at the alkene stage. This is one of the **best** ways of making a *cis*-alkene:



Hydrogenation of Alkynes: Reduction with Na in NH_3

We can convert an alkyne into a *trans*-alkene by using a unique reducing agent: sodium metal in liquid ammonia (!). Ammonia is a gas at room temperature; it boils at –33°C. When it is condensed into a liquid it is a tremendously interesting and useful solvent. It dissolves sodium metal to produce a deep blue solution that contains *solvated electrons*:

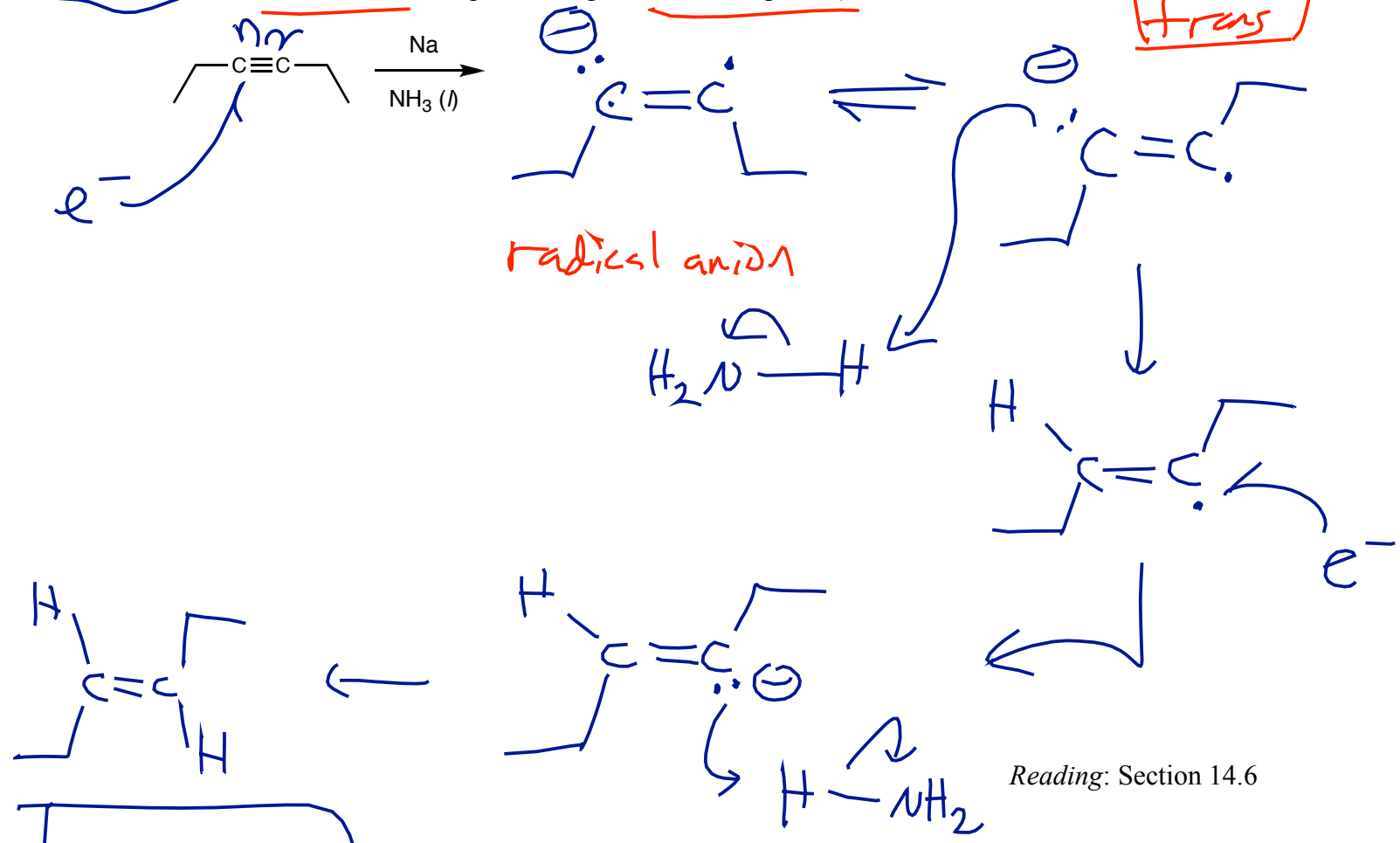
Write a balanced equation showing how Na dissolves in NH_3 to produce solvated electrons e^-



$$Na^0 \xrightarrow{liq\ NH_3} Na^+ + e^-(NH_3)$$

solvated electron

These solvated electrons react with the alkyne via an interesting free-radical mechanism that yields a *trans*-alkene as the final product. (You can remember the steps of this mechanism if you note that it involves only 2 kinds of reactions: adding an electron to form an anion, and protonating the anion using NH_3.)

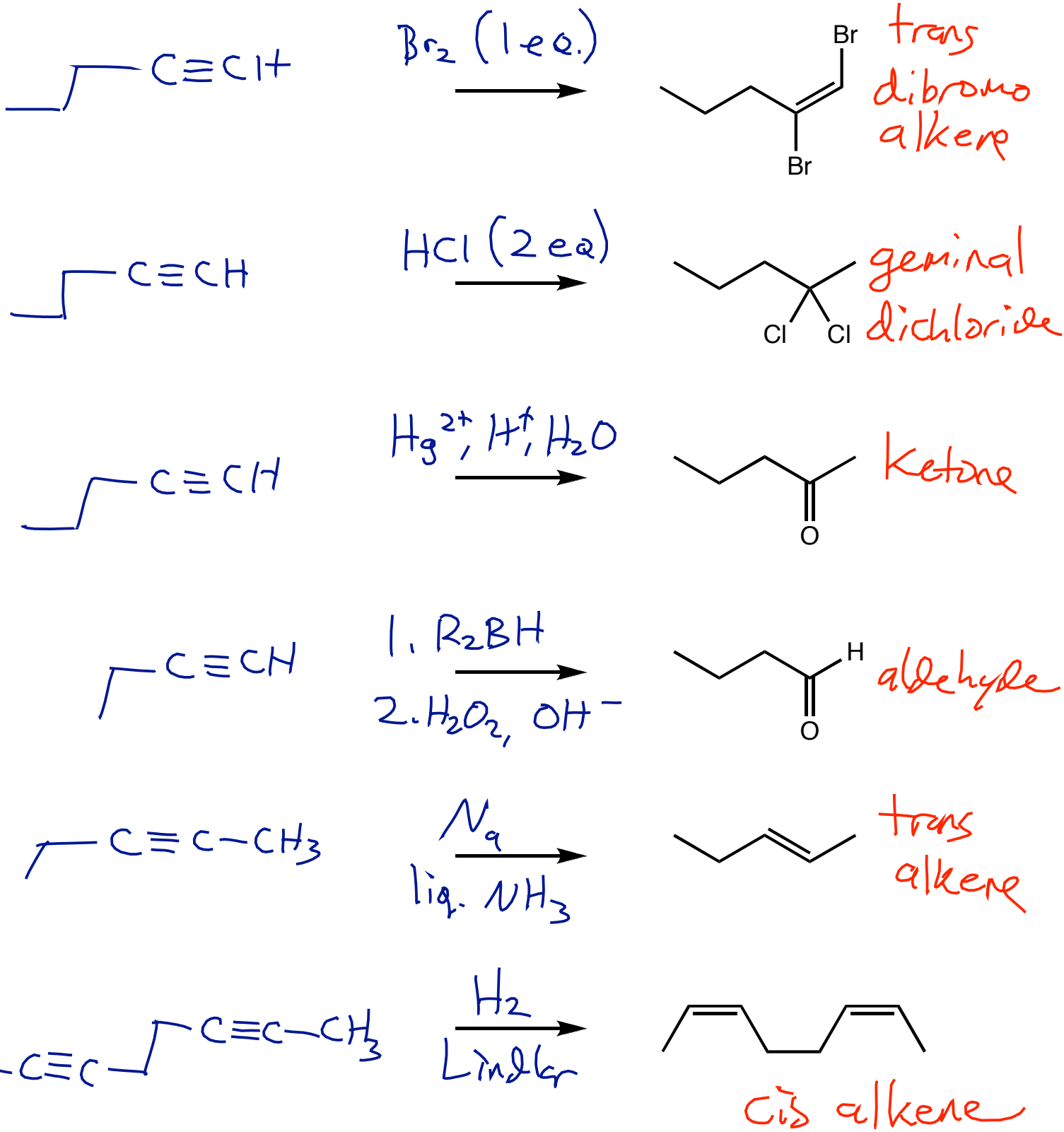


Reading: Section 14.6

you do this (homework)

Summary: Reactions of Alkynes

- Show how each of the following products could be synthesized from an alkyne:



Acidity of Terminal Alkynes

- Do you recall the pK_a's of the following species?

sp^3	sp^2	sp	
H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$	NH_3
48	45	25	35

$NH_3 \rightleftharpoons NH_2^-$ (base)

- Can you explain *why* the hydrocarbons have such different pK_a's?

sp orbitals more s-character
lower in energy
"more electronegative"

- Calculate the equilibrium constant of the following reaction:

$$HC\equiv CH + NaNH_2 \underset{\text{liq. } NH_3}{\rightleftharpoons} HC\equiv C:^{\ominus}\ Na^{\oplus} + NH_3$$

(acetylide ion) (exam 2)

pKa: 25 35

$K_{eq} = 10^{(35-25)} = 10^{10}$ go to completion

- The resulting species, often called an **acetylide anion**, is an excellent nucleophile for S_N2 reactions. (It has a Lewis structure that resembles that of what other good S_N2 nucleophile?) This might be a good way to make **carbon-carbon bonds**. . . do you recall the other ways of making carbon-carbon bonds?

$$R-C\equiv C:^{\ominus} + R'-Br \xrightarrow{SN2} R-C\equiv C-R'$$

new C–C bond

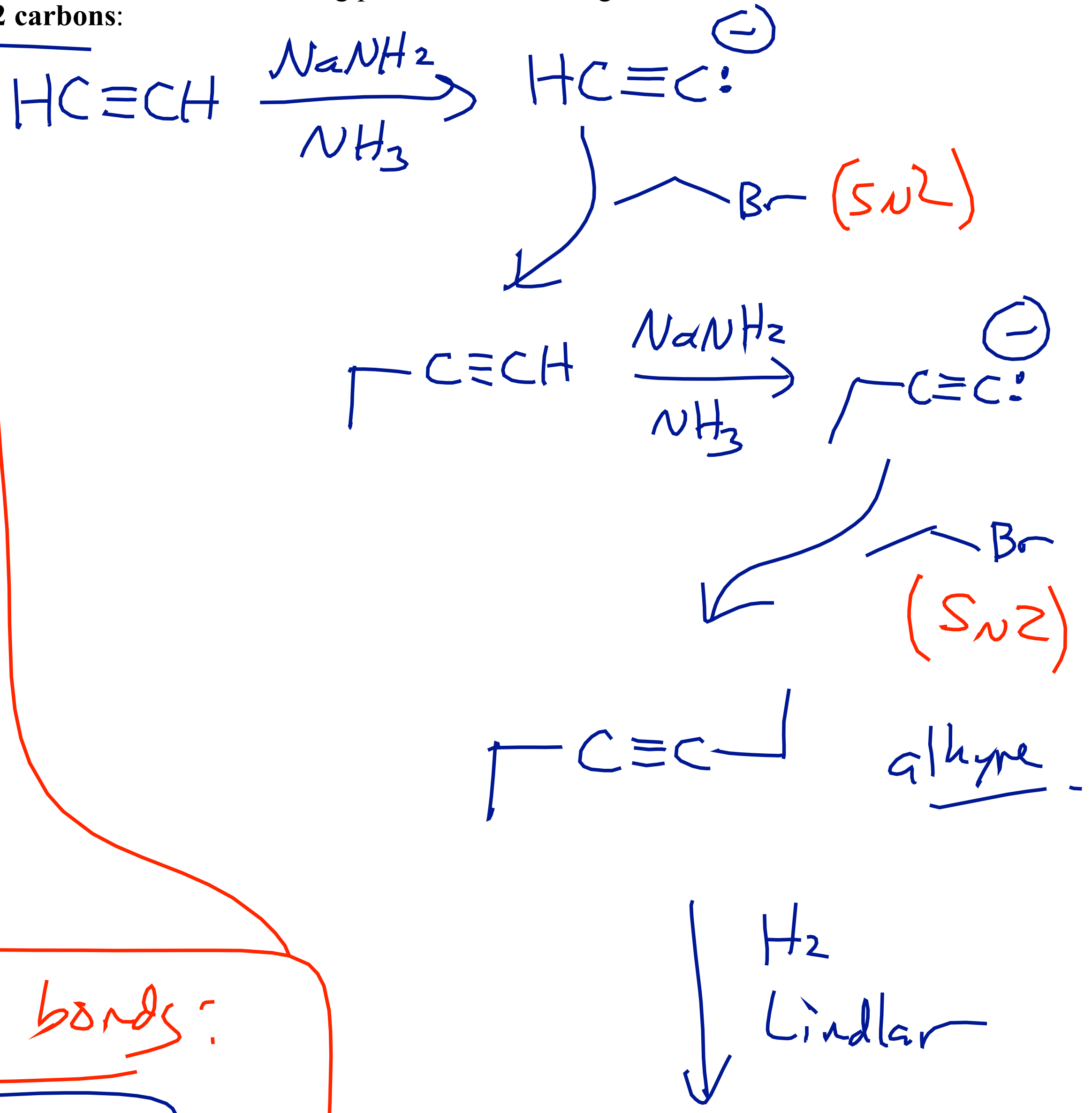
Reading: Section 14.7

Organic Synthesis Using Alkynes

- Provide a synthetic route to the following product from starting materials that contain **no more than 2 carbons**:

1. ~~Don't Panic~~!

2. Identify FG's.



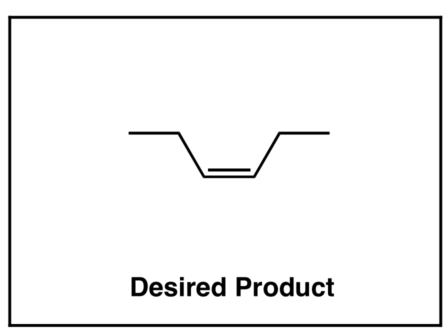
Form C–C bonds:

Epoxide + RMgX

Br + CN⁻ (SN2)

Br + RC≡C:⁻ (SN2)

cyclopropane formation!



alkene (cis)

Reading: Section 14.8