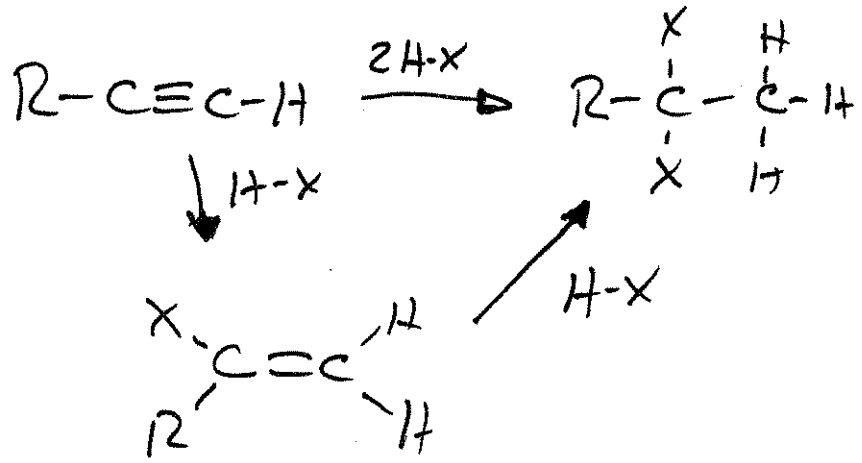
Chapter 9: Alkynes

$R-C\equiv C-R(H)$ (like H-X, Br_2 etc)

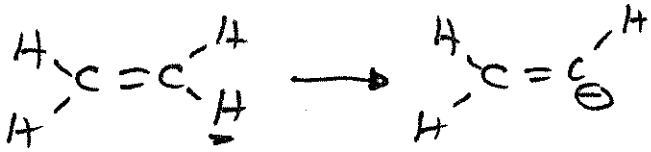
→ like alkenes can react with electrophiles at triple bond, but can add 2 equivalents (versus 1 equiv. for alkenes)

ex:



- terminal hydrogen in $R-C\equiv C-\underline{H}$ alkynes is acidic enough to be able to be removed by a strong base

$pK_a = 49$ $\quad H_3C-\underline{H} \longrightarrow H_3C^{\ominus}$

$pK_a = 39$ $\quad$ 

$pK_a = 26$ $\quad H-C\equiv C-\underline{H} \longrightarrow H-C\equiv C^{\ominus}$

- Alkynes have no cis/trans; E/Z isomerism

R-C≡C-R internal alkyne

R-C≡C-H terminal alkyne

(↑ acidic proton)

Nomenclature of Alkynes

- parent chain "ane" ending changed to "yne"
- carbon atoms that include triple bond have lowest #'s possible (C≡C takes precidence over alkyl + halogen substituents)

ex

$CH_3-C\equiv C-CH_2CH_2-Cl$

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH-C\equiv C-H$ (the CH_3 branch: $CH_2\ CH_2\ CH_3$)

Alkynes as Acids

pKa = 26

$H-C\equiv C-H$ — most acidic

(sp hybridized) ← most electronegative

pKa = 36

$H_2C=CH_2$ (sp² hybridized)

pKa = 49

H_3C-CH_3 (sp³ hybridized) ← least electronegative — least acidic

electronegativity trend

$sp > sp^2 > sp^3$

* more electronegative carbon holds e⁻s more tightly making protons easier to remove (more stable conj. base)

Preparation of Alkyne conjugate base:

→ prepared by reacting terminal alkyne w/ a strong base like $NaNH_2$
Sodium amide

$$R-C\equiv C-\underline{H} + Na^{\oplus}\overset{\ominus}{N}H_2 \xrightarrow[NH_3]{} R-C\equiv C^{\ominus}Na^{\oplus} + NH_3$$

$pKa = 26$; $pKa = 36$

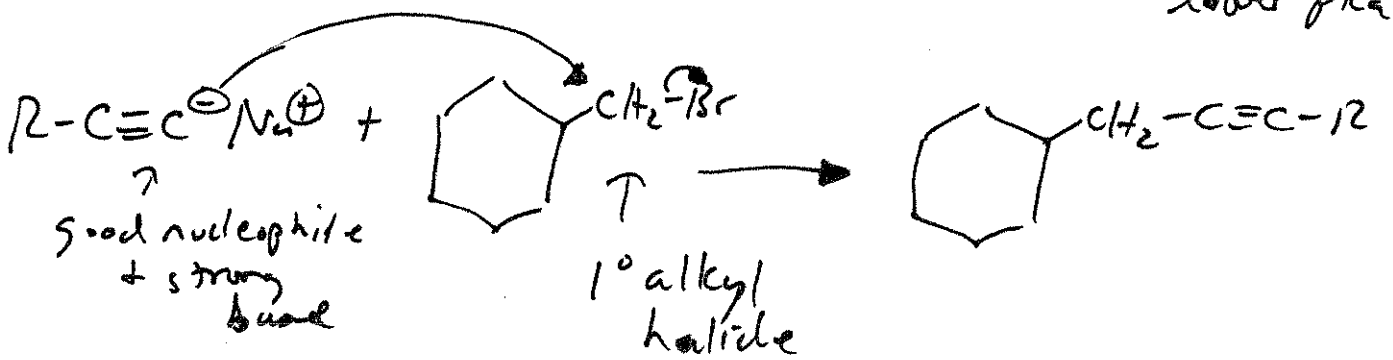
↑ a good nucleophile as well as a strong base

To make sodium amide add $Na_{(s)}$ to liquid ammonia:

$$2\,Na_{(s)} + 2\,NH_{3(l)} \longrightarrow 2\,NaNH_2 + H_{2(g)}$$

→ need to keep the terminal alkyne anion away from things that can protonate it (like H_2O, alcohols + other acids w/ lower pKa's.)

ex:



- substitution only works well for 1° alkyl halides

What do you think happens w/ 2° or 3° alkyl halides?

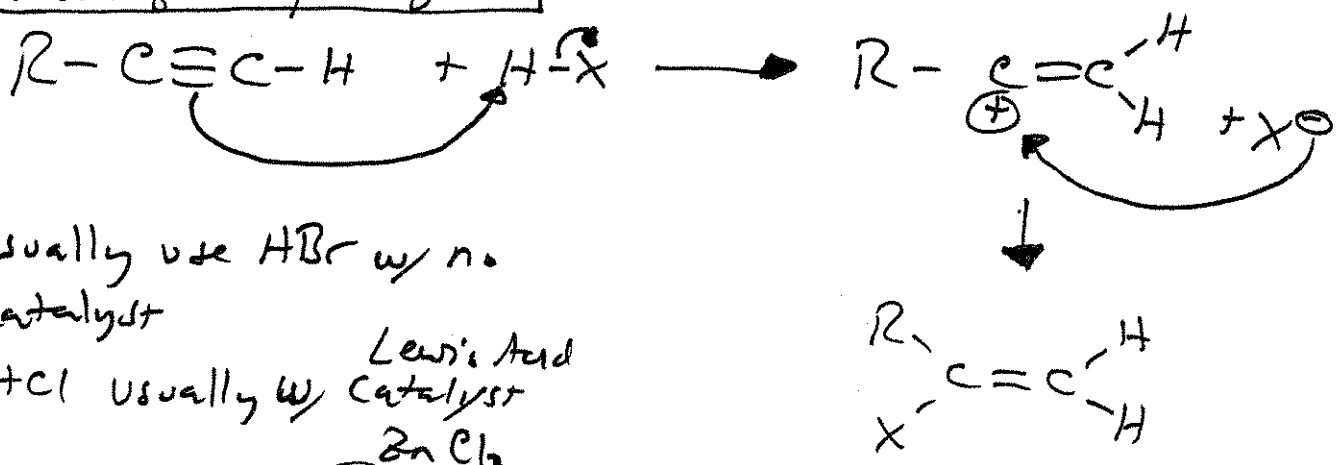
→ with 2° + 3° alkyl halides → E2 eliminations are the favored pathway

Electrophilic Addition Reactions of Alkynes

Addition of H-X (hydrogen halides)

- similar to addn of H-X to alkenes
- forms Markovnikov pdt

ex: Addn of 1st equiv. of H-X

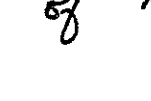


→ usually use HBr w/ no catalyst

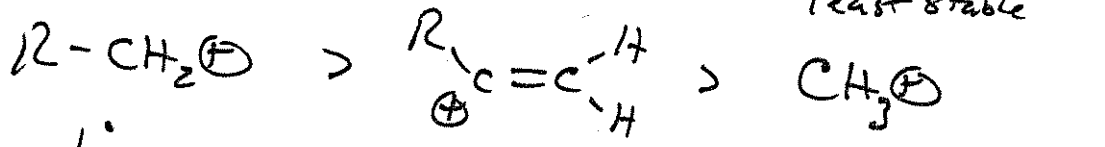
→ HCl usually w/ Lewis acid catalyst

$ZnCl_2$

$HgCl_2$

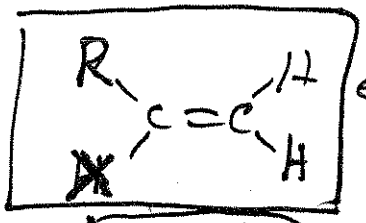
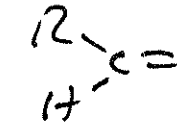
- stability of  between 1° + methyl carbocation

most stable



1° least stable

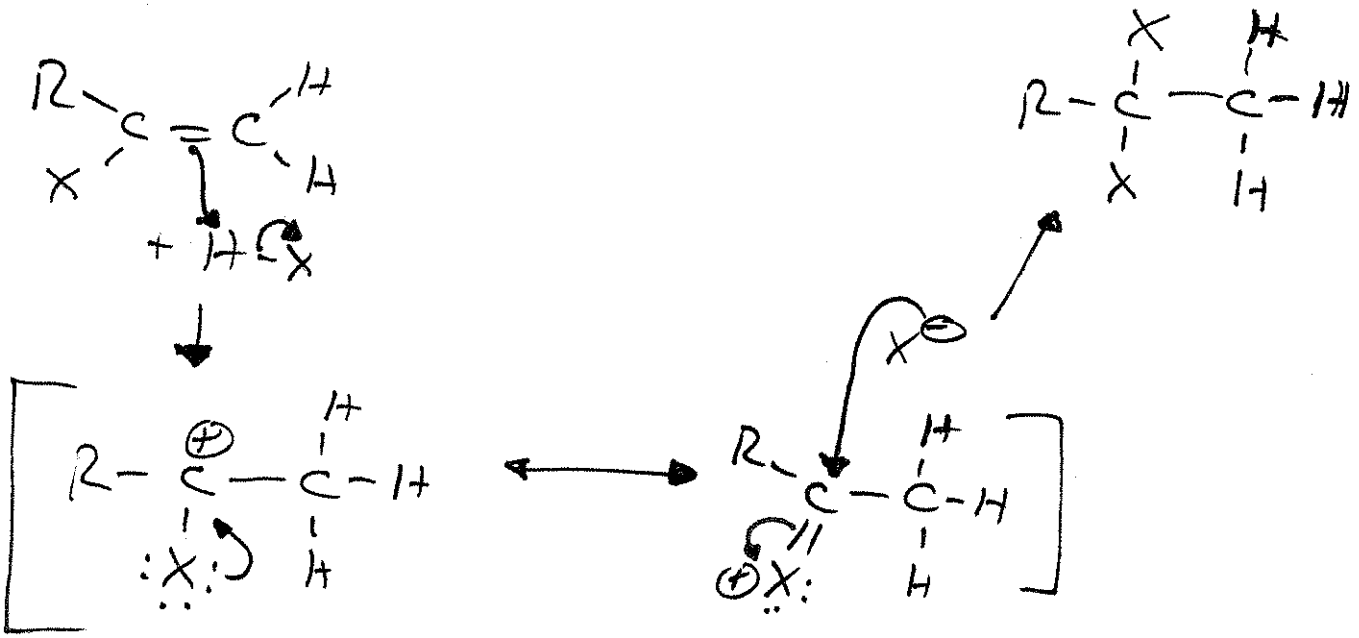
methyl

 ← Pdt from 1st H-X addn is less reactive than  Why?

π-bond e⁻ density less available for rxn

- Because X is electron withdrawing & pulls e⁻ density away from alkene double bond.

Addition of 2nd equivalent of H–X



resonance stabilization of carbocation
(octet around all atoms)

Addition of H_2O to Alkynes

acetaldehyde

$$H-C\equiv C-H \xrightarrow[\substack{H_2SO_4\\ HgSO_4\\ \text{or}\\ Fe_2(SO_4)_3}]{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H$$

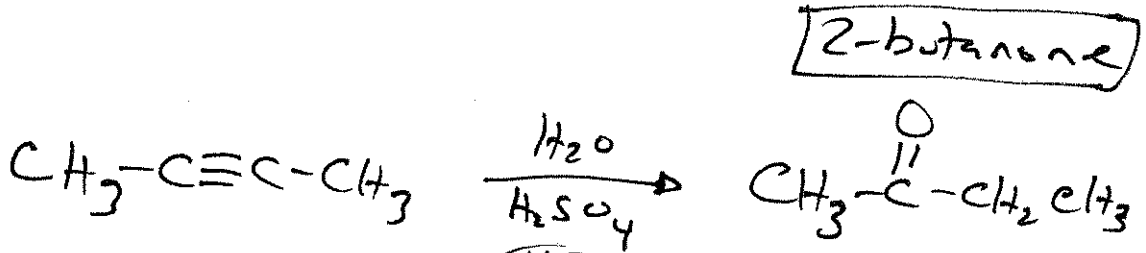
mercury or iron salts (catalysts)

$$R-C\equiv C-H \xrightarrow[\substack{H_2SO_4\\ HgSO_4}]{H_2O} R-\overset{O}{\overset{\|}{C}}-CH_3$$

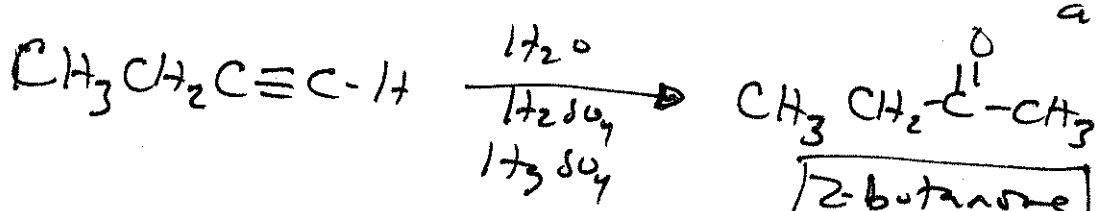
ketone

- In this reaction only acetylene will give an aldehyde all other alkynes will give a ketone as a product

ex:



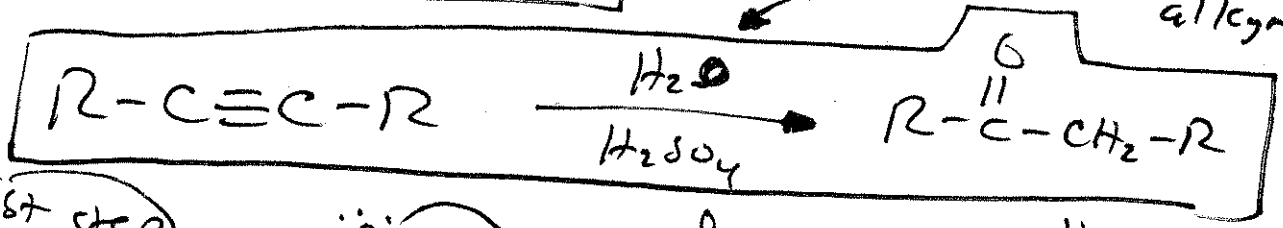
H_3SO_4 - don't always need a catalyst with internal alkynes



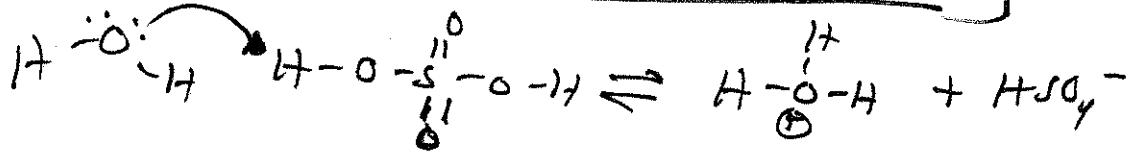
methyl ethyl ketone (MEK)

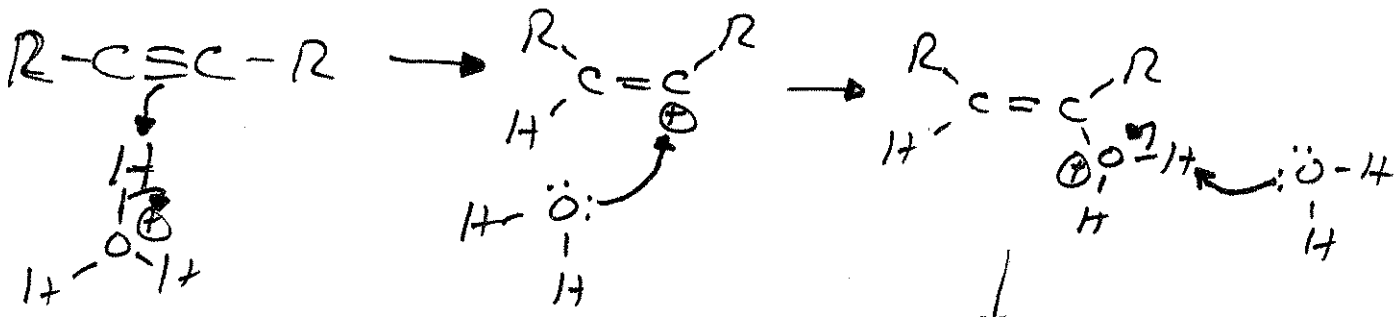
General Mechanism

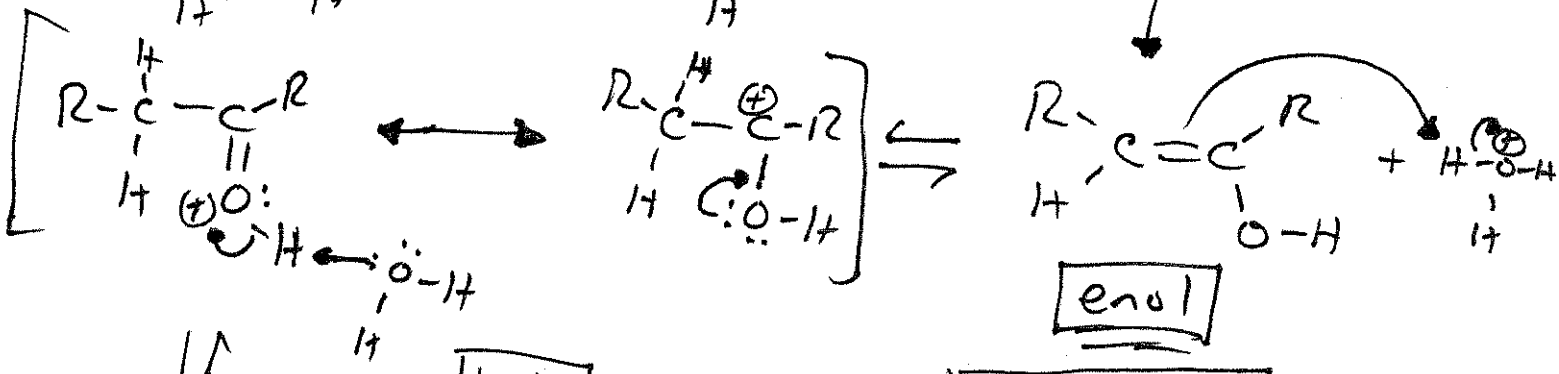
(plus H_2SO_4 if terminal alkyne)



1st step

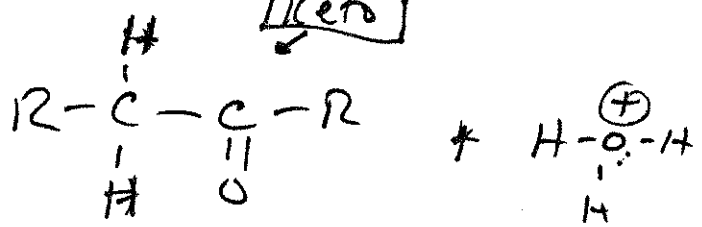






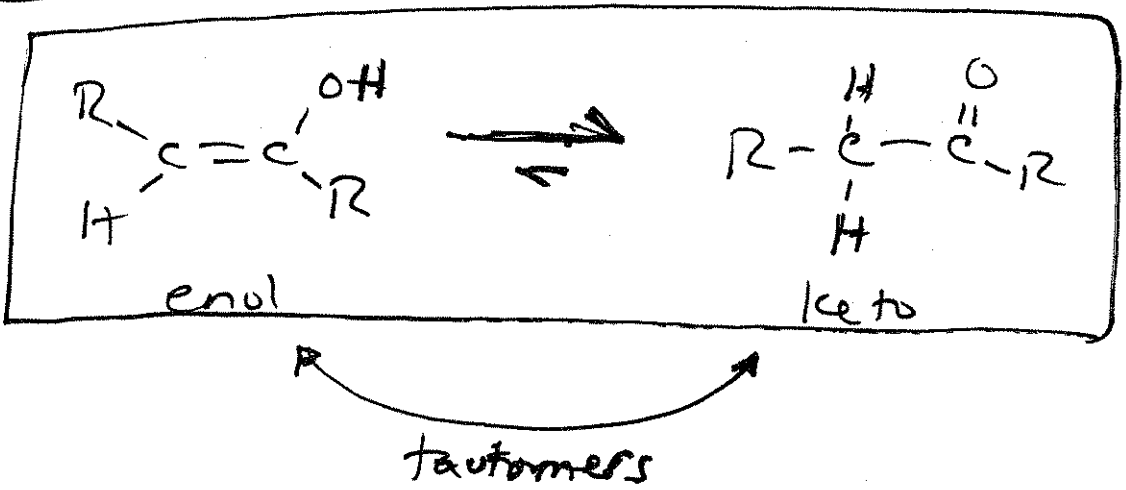
enol

keto

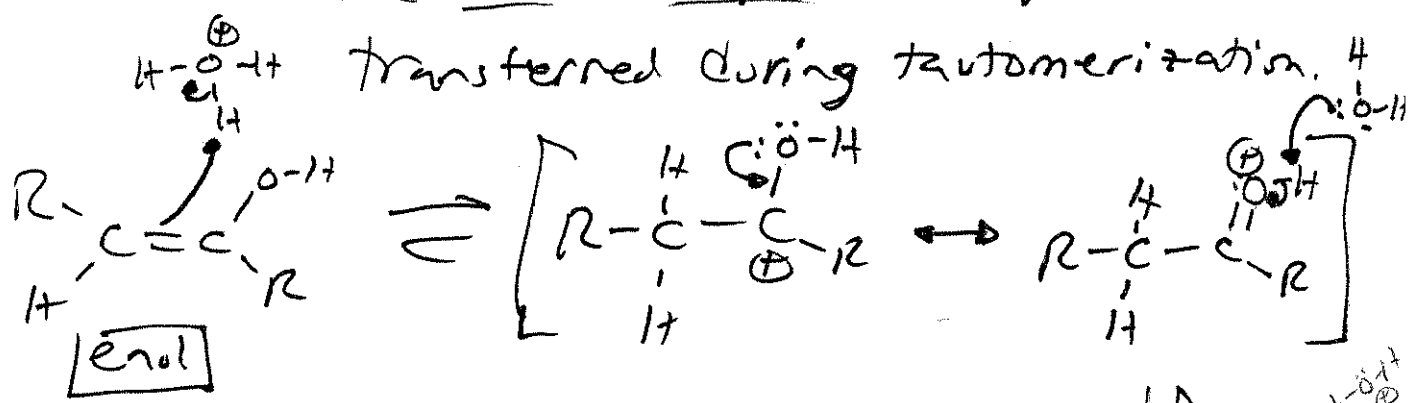


keto-enol tautomerization

Keto-enol tautomerization

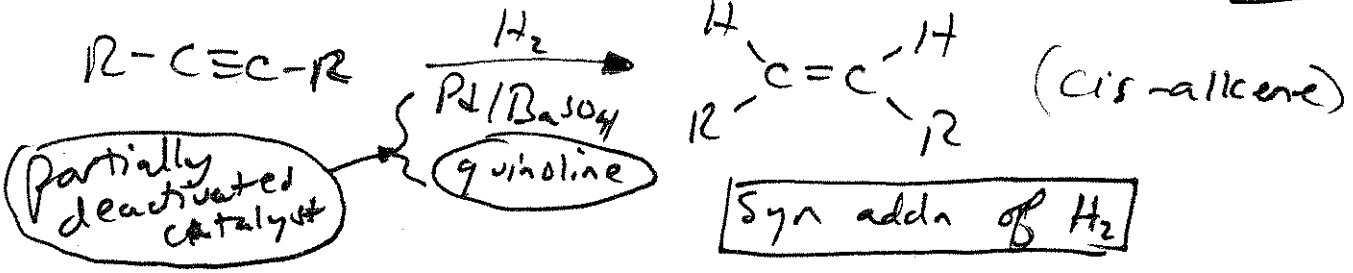


Tautomers - are NOT resonance structures of the same compound. A proton is transferred during tautomerization.



Reduction of Alkynes

- Catalytic Hydrogenation of Alkynes



- $Pd/CaCO_3$ or $Pd/BaSO_4$ w/ Quinoline gives a poisoned catalyst → makes it less reactive so it only reduces alkyne → alkene

- If one uses excess H_2 and a <u>unpoisoned</u> catalyst (Pt, Pd/C etc) will reduce alkyne to alkane (2 equivalents H_2 added)

$$R-C\equiv C-R \xrightarrow[Pt]{H_2 \text{ (excess)}} R-CH_2-CH_2-R$$

Alkynes ⟶ Alkenes using <u>Dissolving Metals</u> gives <u>Trans</u> alkenes (rather than cis-alkenes)

$$R-C\equiv C-R \xrightarrow[\text{in } NH_{3(liq)}\ (\text{Cold})]{Na \text{ or } Li} \underset{H}{\overset{R}{}}\!\!>C=C<\!\!\overset{H}{\underset{R}{}}$$

trans or E alkene

- Good News - we will skip this mechanism - you don't need to know
  - If you want to see the mechanism it's on pages 384-385 in Eg's text)

- You need to read and <u>understand</u> section 9.6 ⟶ we will start doing <u>multistep</u> synthesis soon.