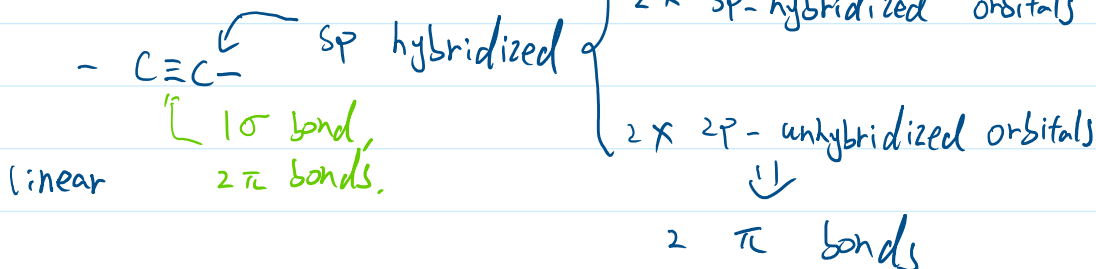


Alkynes

Alkynes

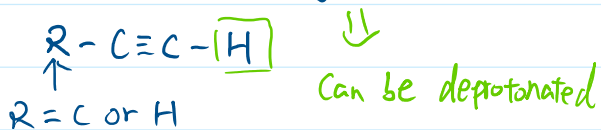


π -bonds (overlapping 2p-orbitals)

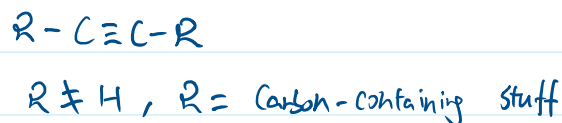
\hookrightarrow Nucleophile \rightarrow isolated π -e $^-$ density is reactive
 $\downarrow\downarrow$
 no resonance

2-types of Alkynes:

Terminal Alkynes



Internal Alkynes



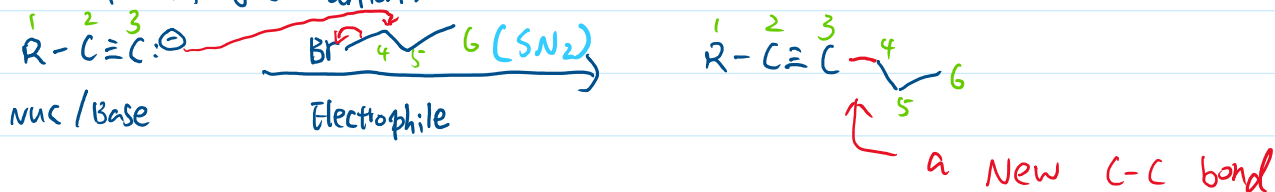
Recall; the \uparrow s-character, the more stable the anion.
 so \rightarrow the terminal alkyne is relatively acidic.

1 alkyne for 1 NaNH_2 = 1 equiv



Because pKa = 38 $>$ pKa \approx 25, the e.g. will favor the right side
 $10^{13} = 10^{(38-25)}$

Terminal Alkyne anion:

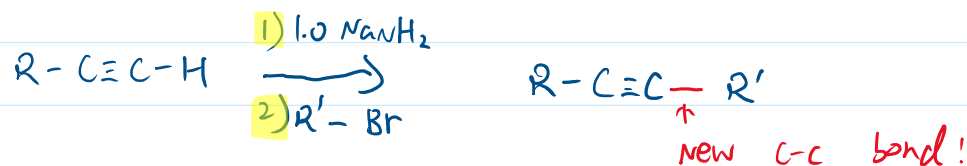


The **ONLY** reaction to make a new C-C bond (yet)



we need a base

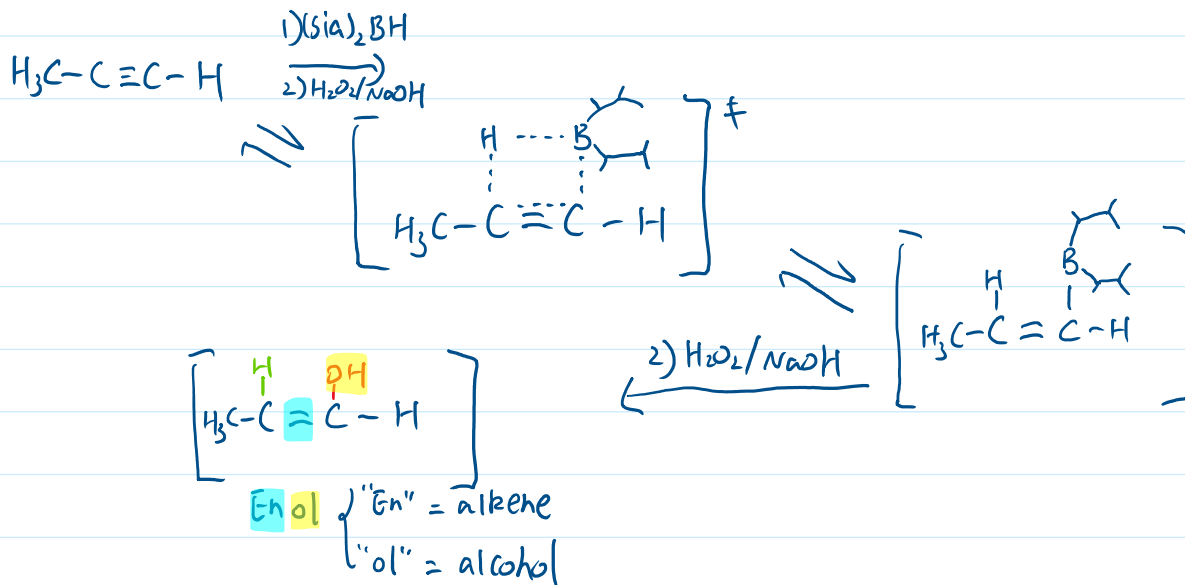
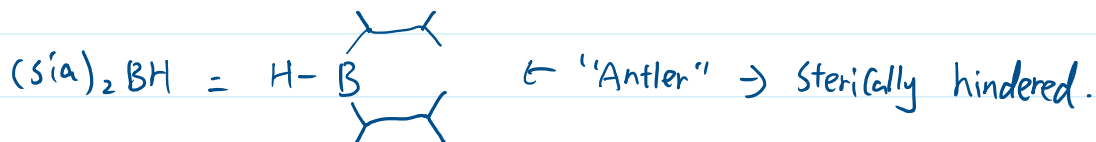
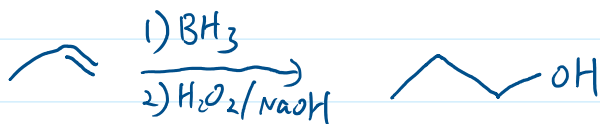
to make $\text{R}-\text{C}\equiv\text{C}:\ominus$, π -bonds along cannot make a C-C bond!



order of addition matters!

Hydroboration-oxidation of alkynes

Recall:



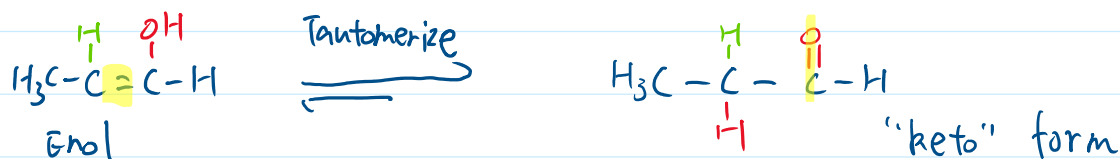
Time out:

• 01 = alcohol

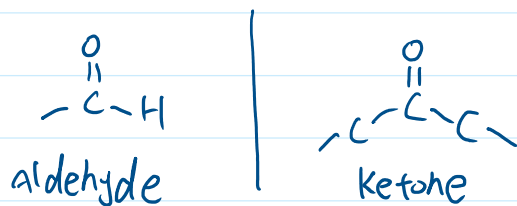
Time out:

Enols are not stable \rightarrow they "react" further through a process called "tautomerization"

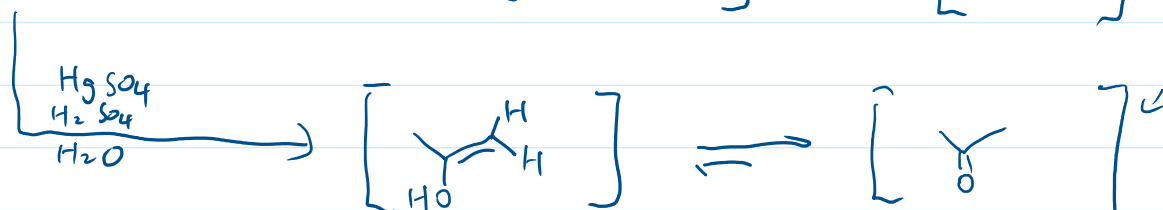
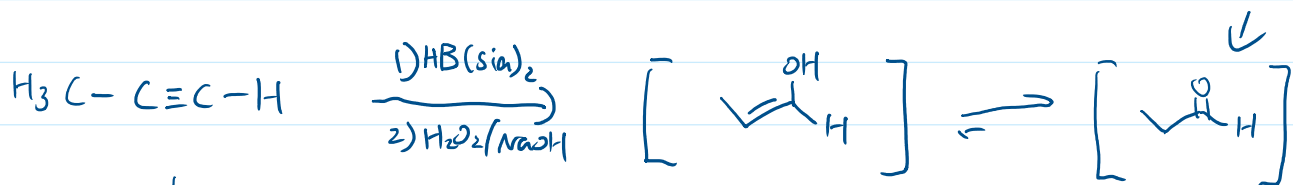
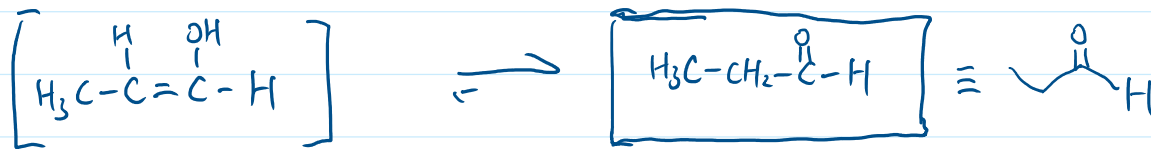
When we generate the enol form, it will spontaneously "tautomerize" to generate the more stable keto form
 $C=O$ is stronger than $C=C$ \leftarrow

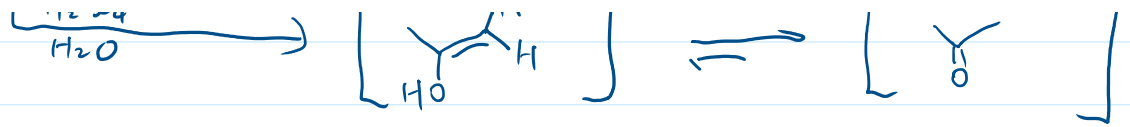


Nomenclature for $C=O$:



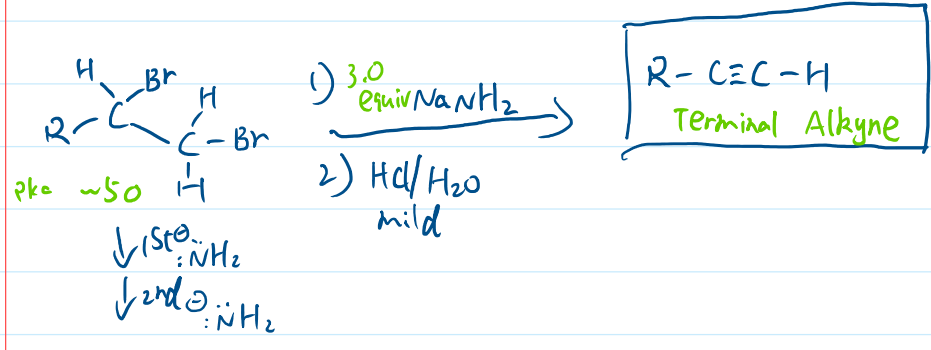
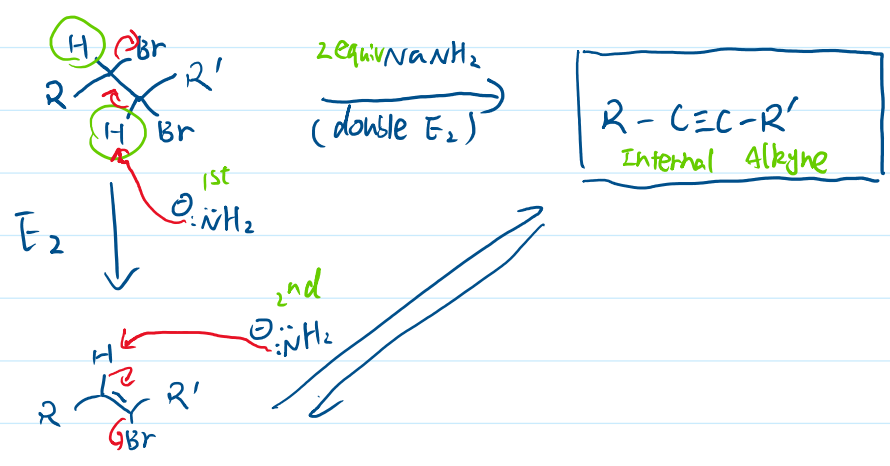
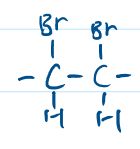
Time in:





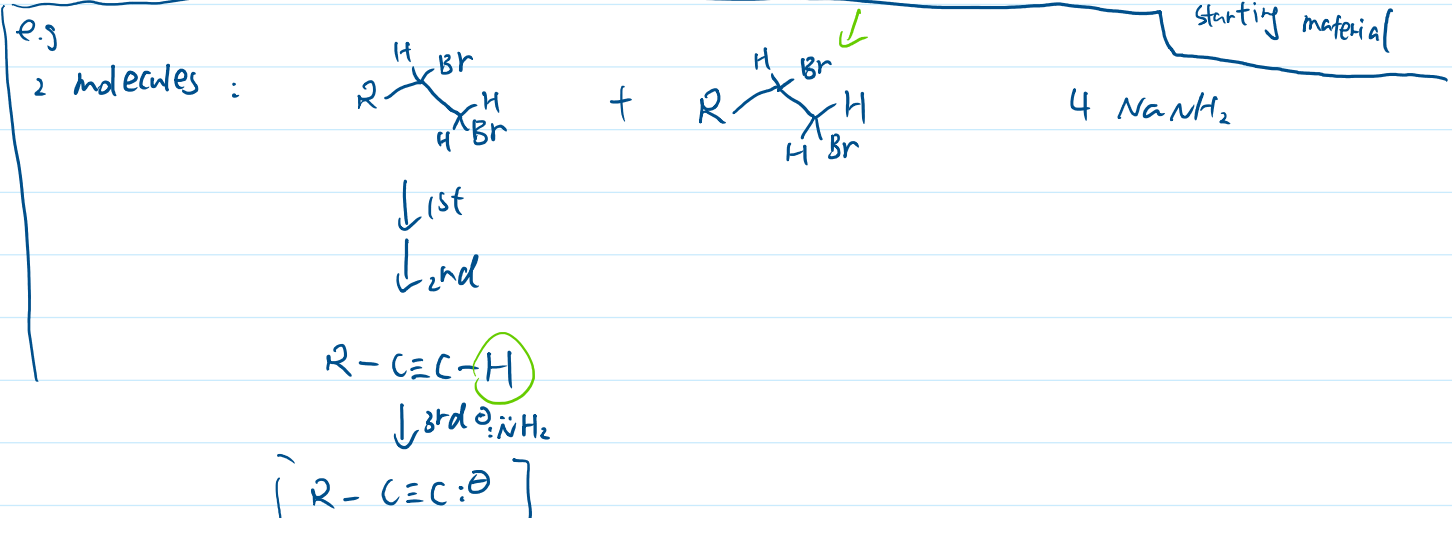
making Alkynes

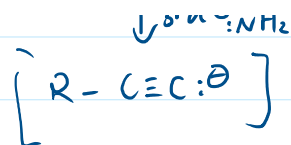
↳ vicinal Dihalides
next to "2" halogens: Cl, Br, I



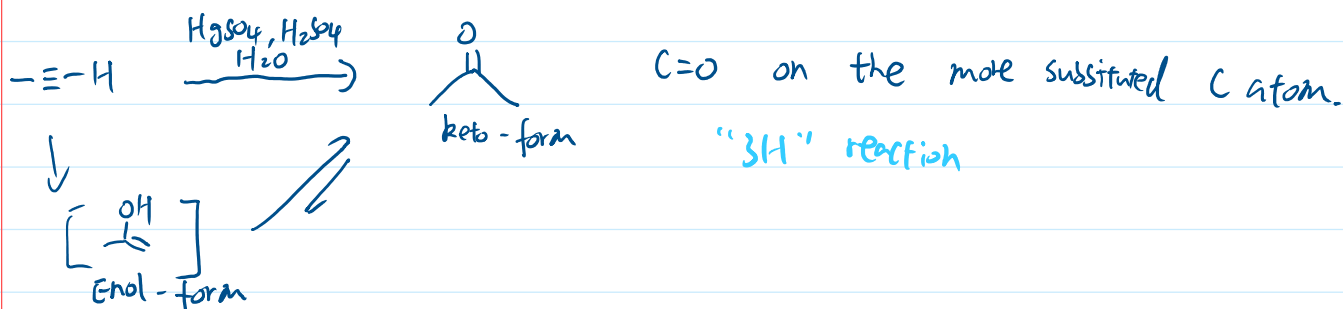
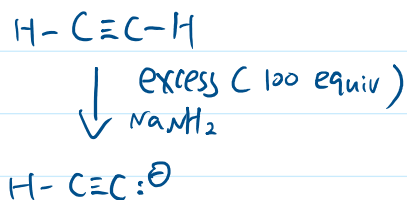
$\text{R}-\text{C}\equiv\text{C}-\text{H}$ → won't stop there! b/c the H is more acidic than the H-atoms in starting material

pk_a ~25

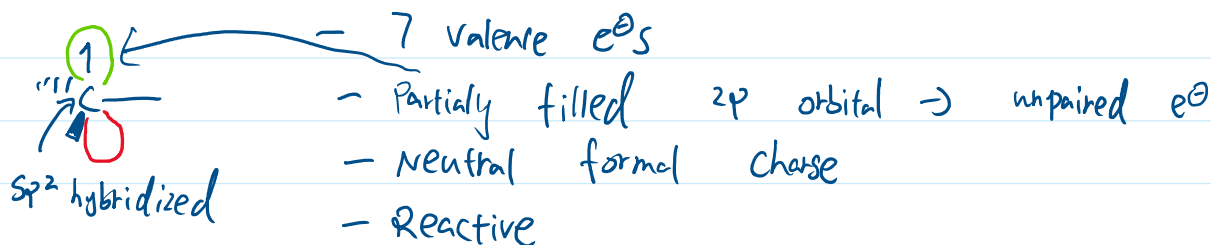




note: you can't make $\ominus : \text{C} \equiv \text{C} : \ominus$
"dianion"



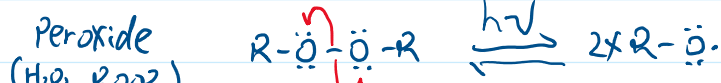
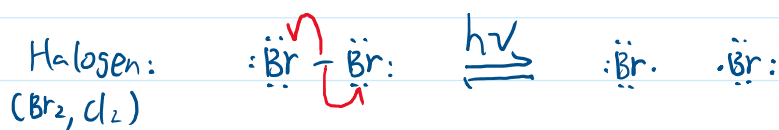
Radicals



making radicals: break a weak bond w/ heat (Δ) or light ($h\nu$)

Radical reactions start (initiate) when a radical forms

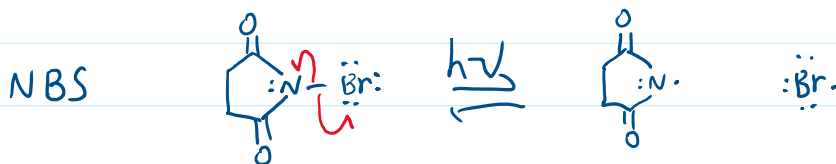
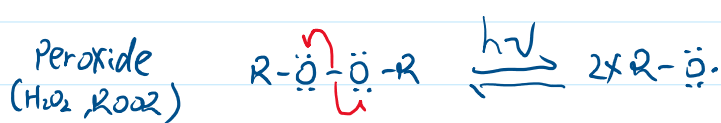
E.g.:



These radicals will react further!

They can:

① Extract an H-atom

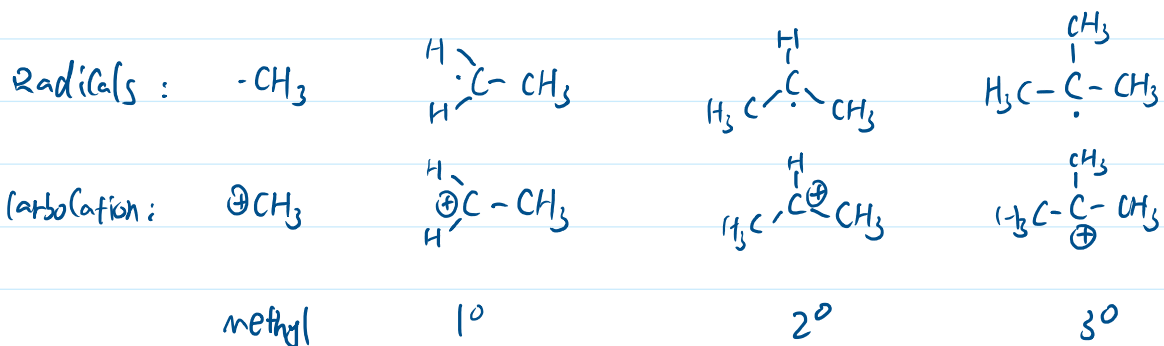


- ① Extract an H-atom
 ② Add to a double bond

Radical stability → Think stability of Carbocation, but no inductive effect

↳ Hyperconjugation

↳ Resonance (e.g.)



more substituted → more stable

Hyperconjugation: overlap of nearby σ-bonds and the empty/partially filled 2p orbital

