

Lecture - Alkynes

IEA = ionic electrophilic addition

Learning Objectives

Reactions of Alkynes:

IEA ① Addition of $HX \Rightarrow HCl, HBr, HI$ ← IEA know mechanism
- Markovnikov orientation

IEA ② Addition of $X_2 \Rightarrow Br_2, Cl_2$ (no $\Delta/h\nu$)! IEA

IEA ③ Addition of H_2O (oxymercuration) - can use $R-OH$ instead of H_2O (IEA)
- know keto-enol tautomerization!
- acid catalyzed
- base catalyzed

④ Hydroboration

⑤ Addition of H_2 (Reduction)

- full reduction
- partial reduction by cis-addition (Z-product)
- " " " trans-addition (E-product)

⑥ Oxidative Cleavage (w/ $KMnO_4$ or O_3)

⑦ As nucleophiles

we can build larger organic molecules!

- substitution with 1° halides
- as bases w/ 2° halides (E 3°)
- addition to carbonyls ($R-CHO$ or $R-C(=O)R$)

Synthesis of alkynes - dehydrohalogenation of vicinal halides
- " " " geminal "

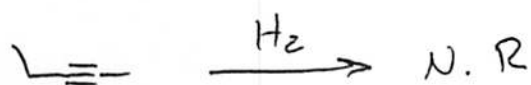
→ and coupling an acetylide w/ a 1° alkyl halide

APPLICATION: Synthesis of larger organic molecules! (from smaller building blocks)
- Modification of functional groups!

Alkynes

Reductions

⑤ Addition of H_2 (using a catalyst)



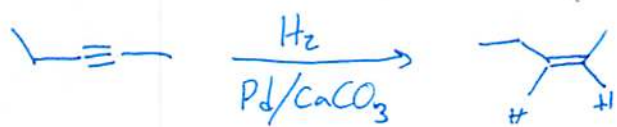
• Full Reduction!

• Catalyst can be:
Ni, Pt, Pd, or PtO

Lindlar's catalyst

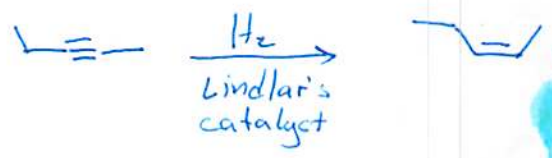
To stop at the alkene, we need to "poison" the catalyst.
with CaCO_3 or BaSO_4 /quinoline.

This catalyst is called "Lindlar's Catalyst" \Rightarrow Pd/CaCO_3



cis-addition ONLY!!
to make the Z-alkene.

could also write:

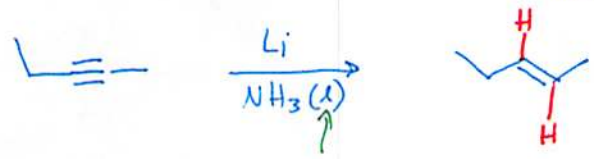


Can we make a trans-alkene?

- You Bet!!

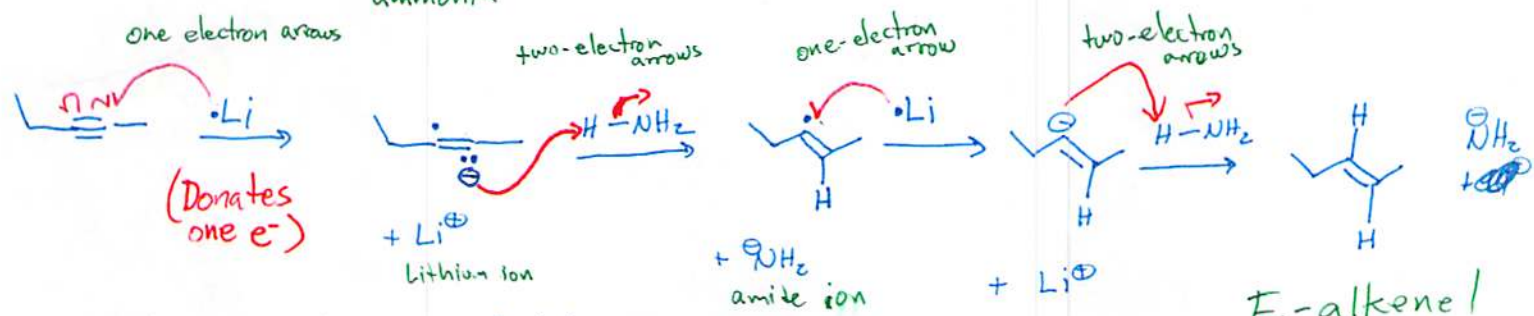
Dissolving metal reduction

"anti addition"



liquid ammonia

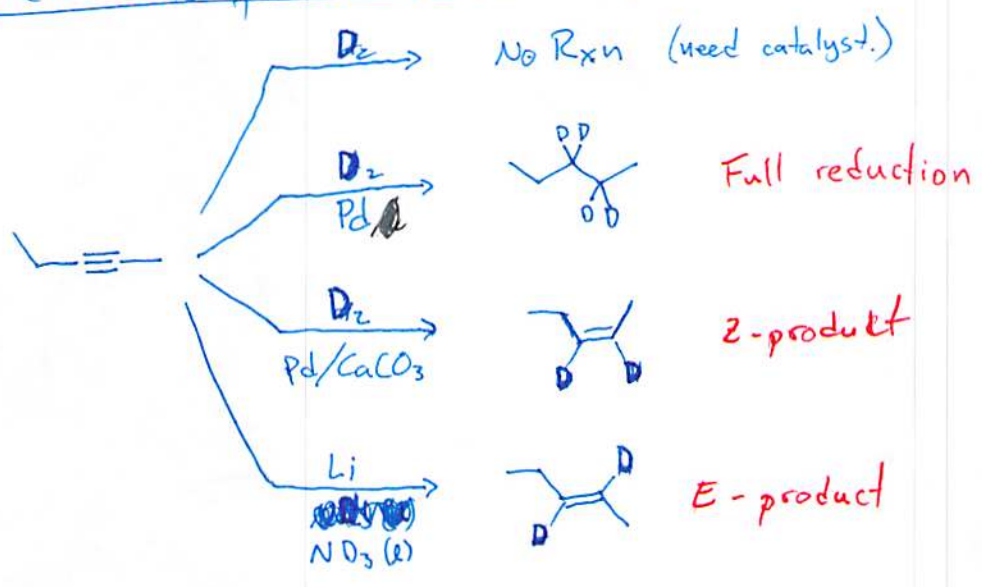
The mechanism is complex.
-I will only show you to know what's going on. not so for an exam.



E-alkene!

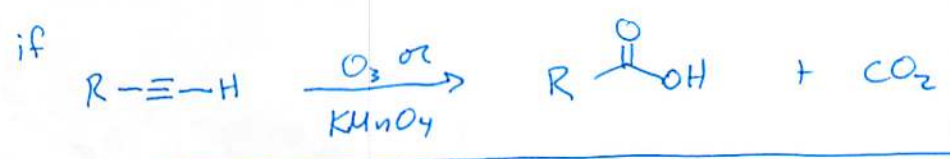
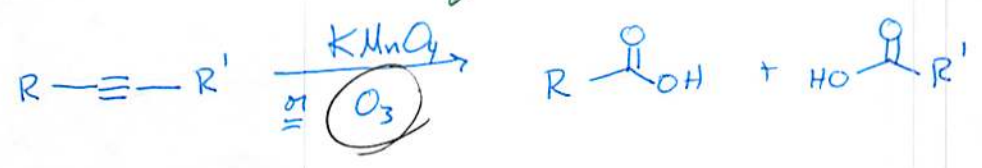
The E-alkene product is formed
Because the rxn happens stepwise, as oppose to the previous case.

Key elements of reduction (Rxn #5)



6 Oxidative Cleavage

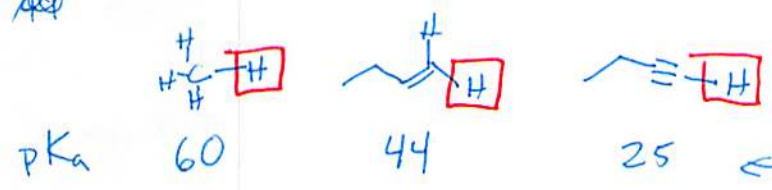
one or the other (Don't list both at the same time)



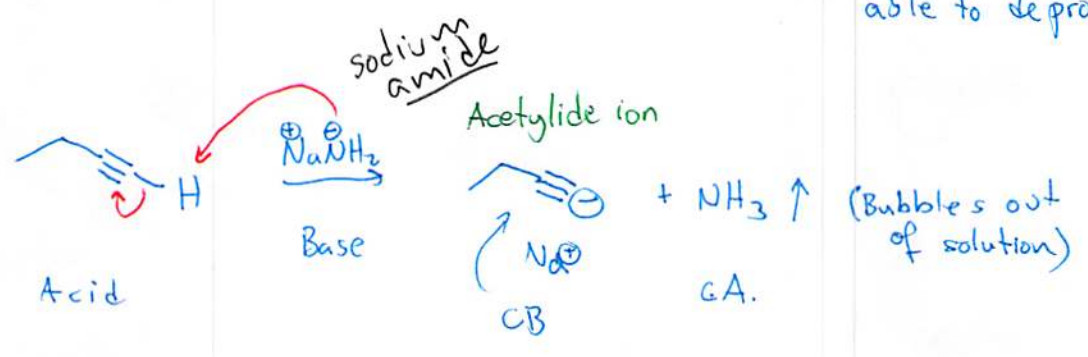
NO Aldehydes! through this oxidation.

7 As Nucleophiles

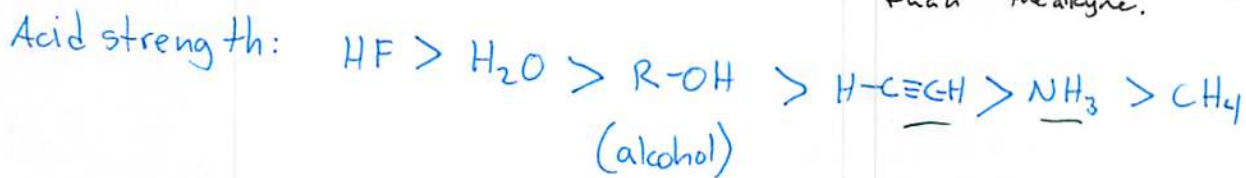
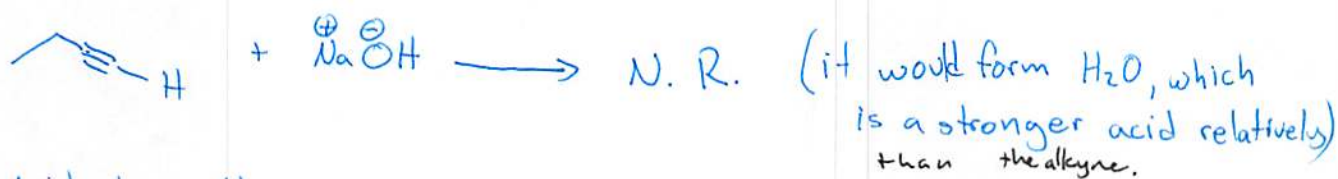
Remember?



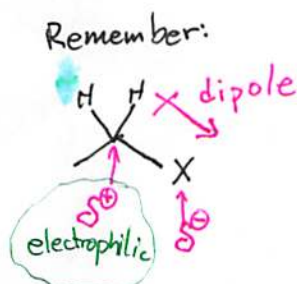
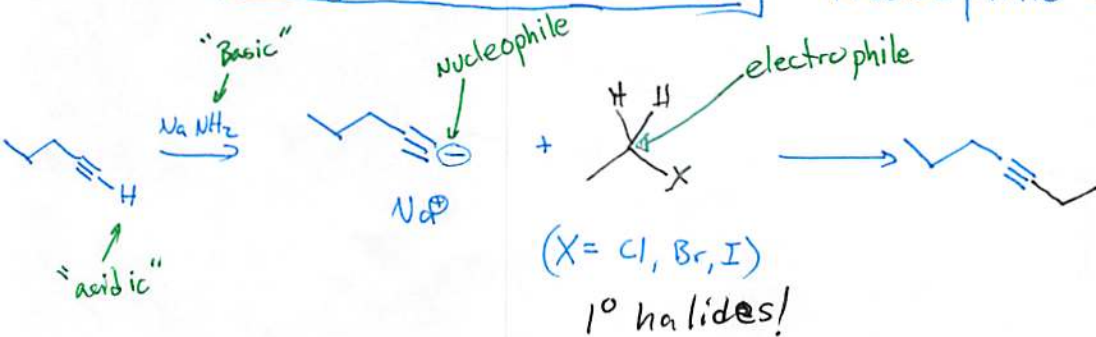
Low enough to be able to deprotonate.



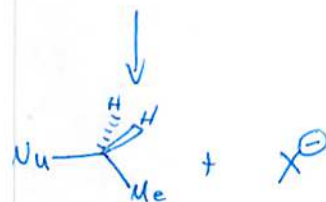
However:



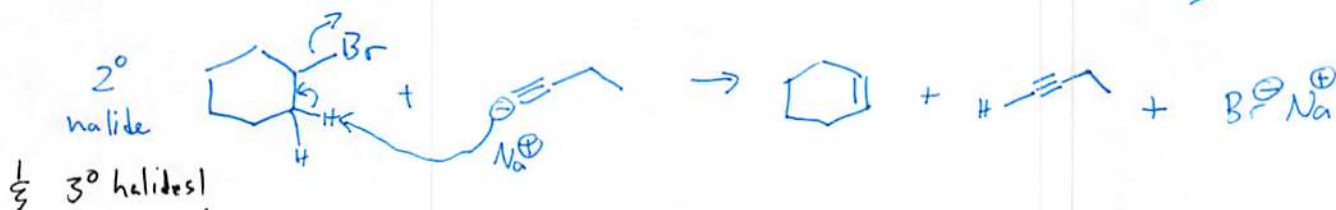
Acetylides + 1° Halides: Nucleophilic substitution. Rxn.



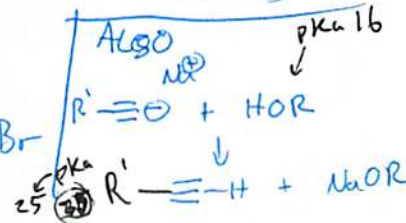
ONLY for 1° Halides!!



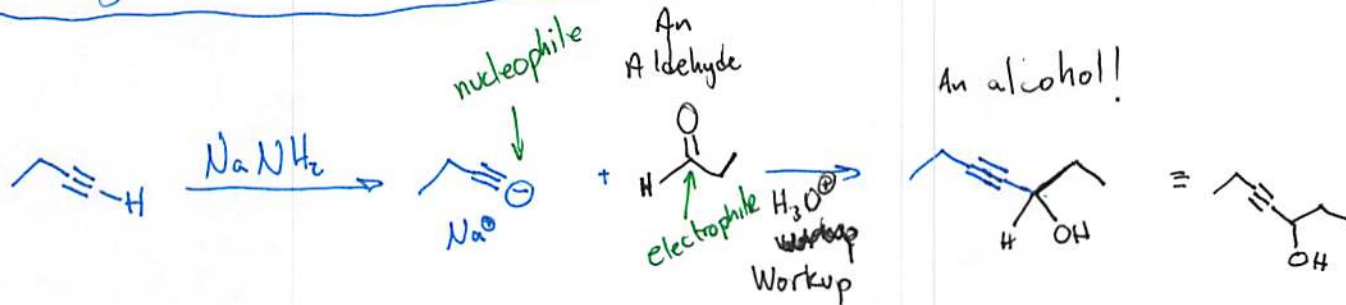
Acetylides as bases w/ 2° & 3° halides. \therefore Elimination Rxn (For now)



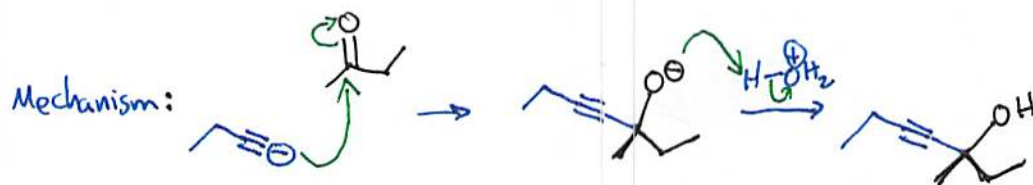
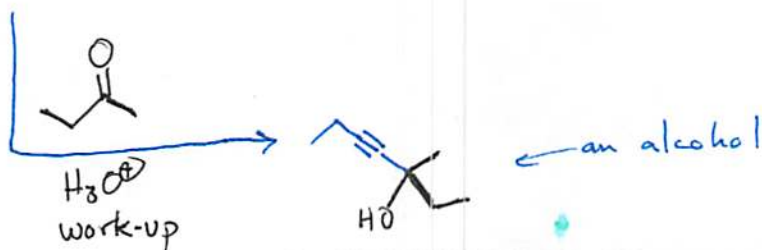
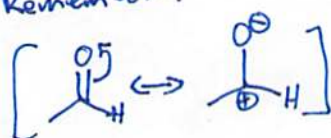
We will dig deeper into Elimination & substitution mechanisms



Acetylide with carbonyls : Nucleophilic addition

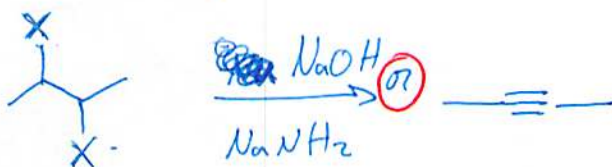


Remember:



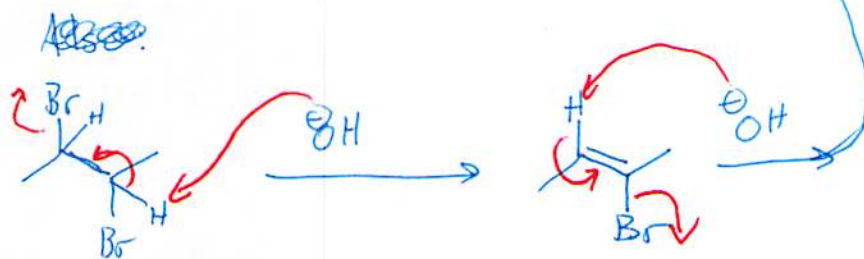
Synthesis of Alkynes

- Dehydrohalogenation of vicinal dihalides:

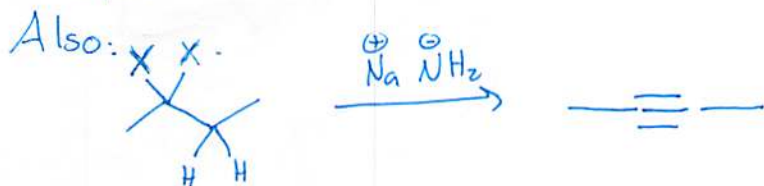


X = Cl, Br, I

Not both
at the same
time.



Geminal dihalides



X = Cl, Br, I

similar mech. as above (do on your own)

Finally; by coupling an acetylide with a 1° Alkyl halide (Rxn 7)