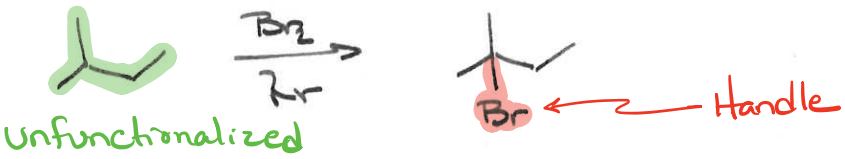
Common Themes

Functionalization – Addition of functional group

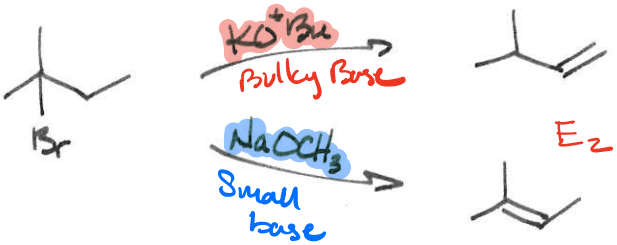


Free radical bromination

New * 

Allylic bromination

Formation alkenes



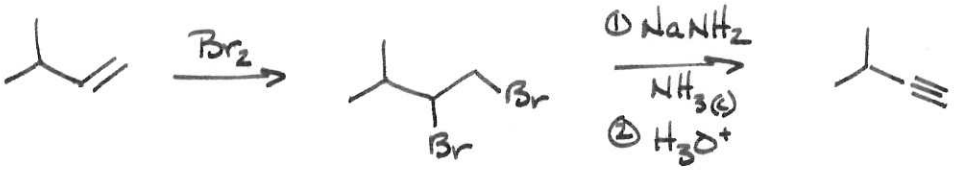
E_2

Bulky Base (KO^+Bu, LDA)

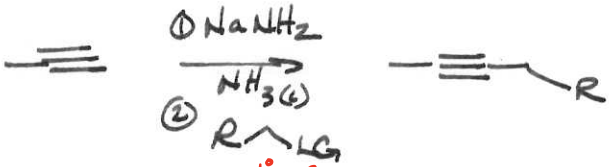
Small base (NaOMe, NaOEt)

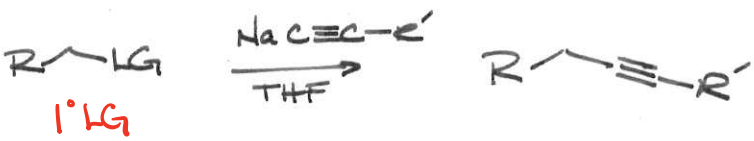
* Allows for migration of functional group.

Formation alkynes



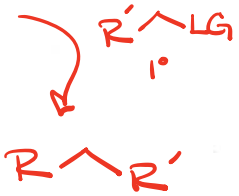
Making New C-C bonds





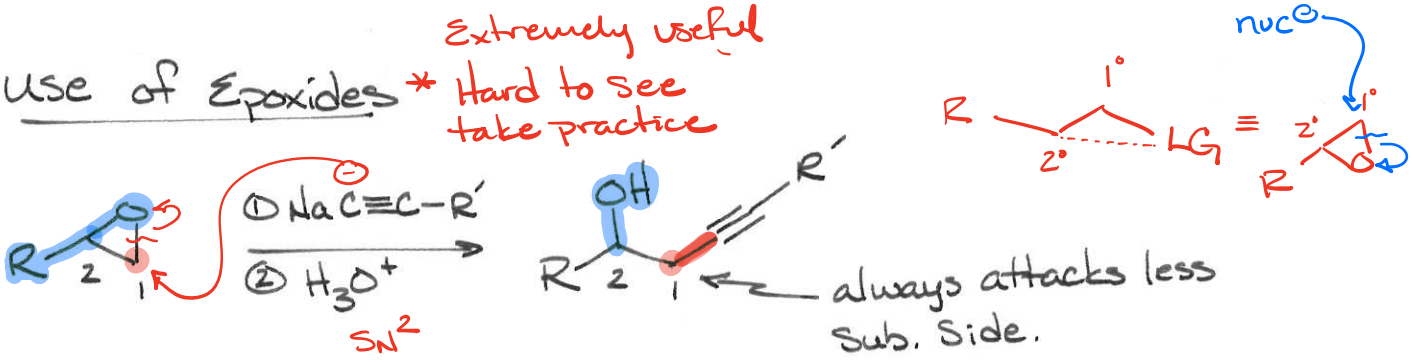
Grignard Rxn

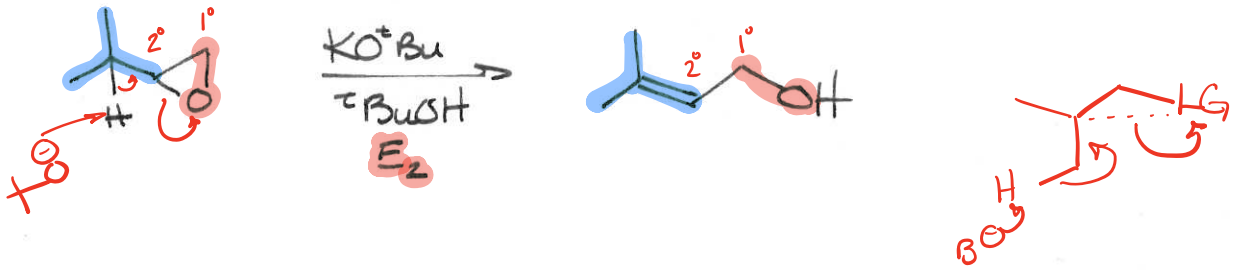
R-X $\xrightarrow{Mg}$ R-Mg-Br



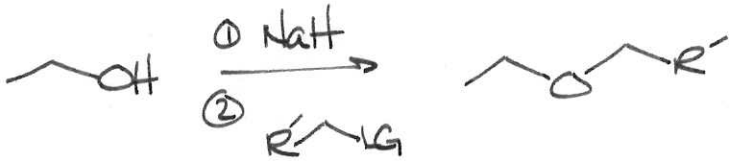
Use of Epoxides

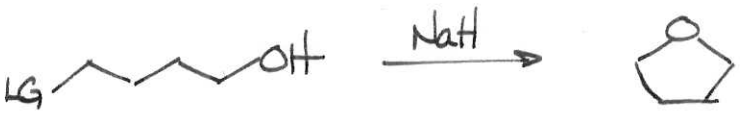
Extremely useful * Hard to see take practice





S_N2 Rxns $R-O^{\ominus}$ nucleophile





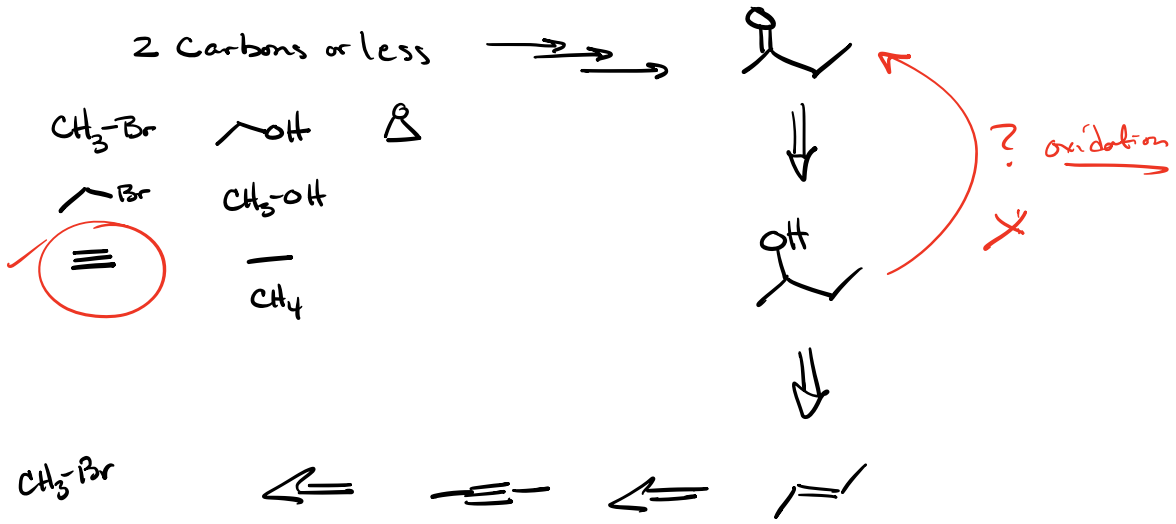
✓ S_N2 & E_2 ⟹ Can be Controlled

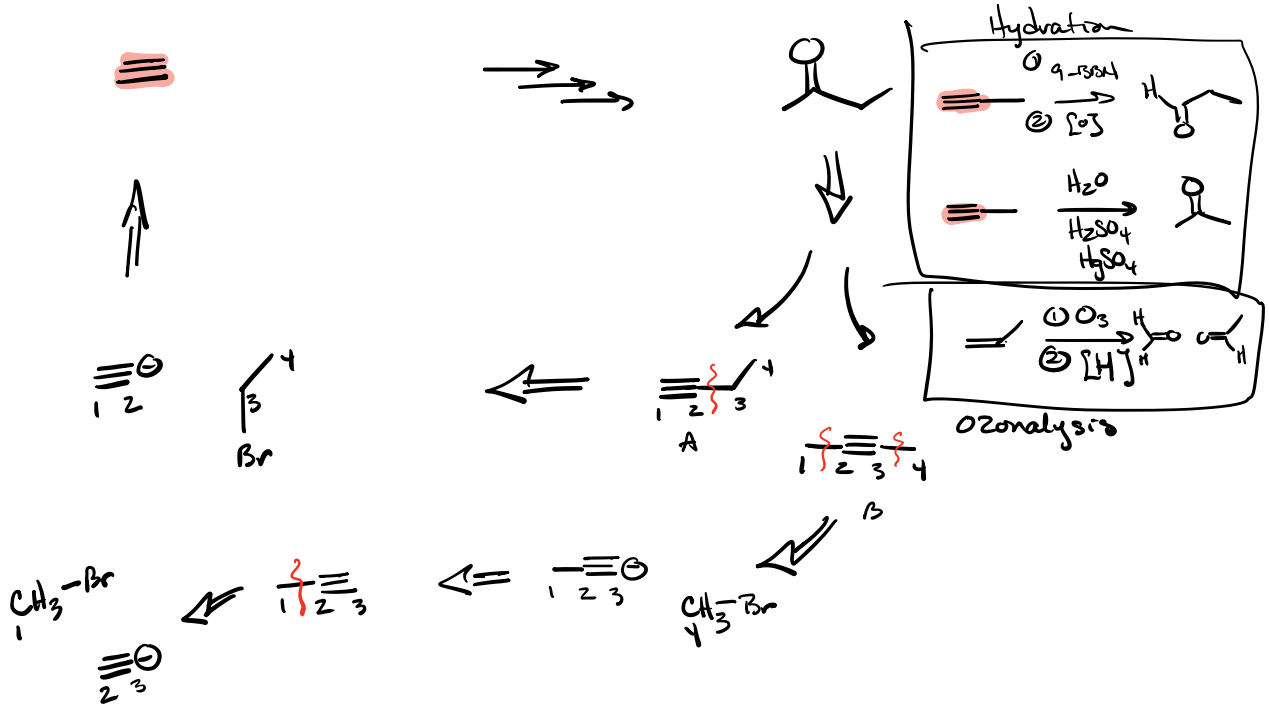
✗ S_N1 & E_1 ⟹ Hard to Control & more limited in use

⟹ C^+ ⟶ Rearrangements

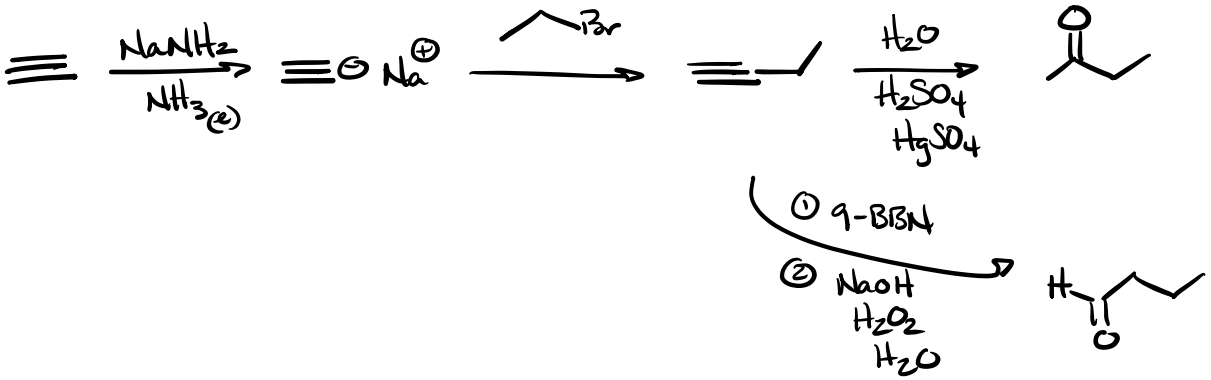
Synthesis problems

① make butanone from any reagent using carbon sources of 2 carbons or less

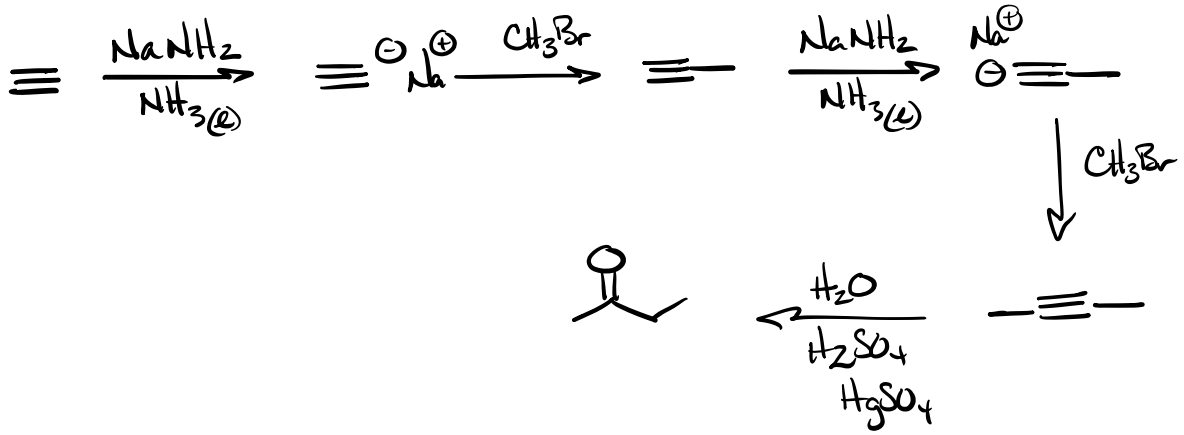


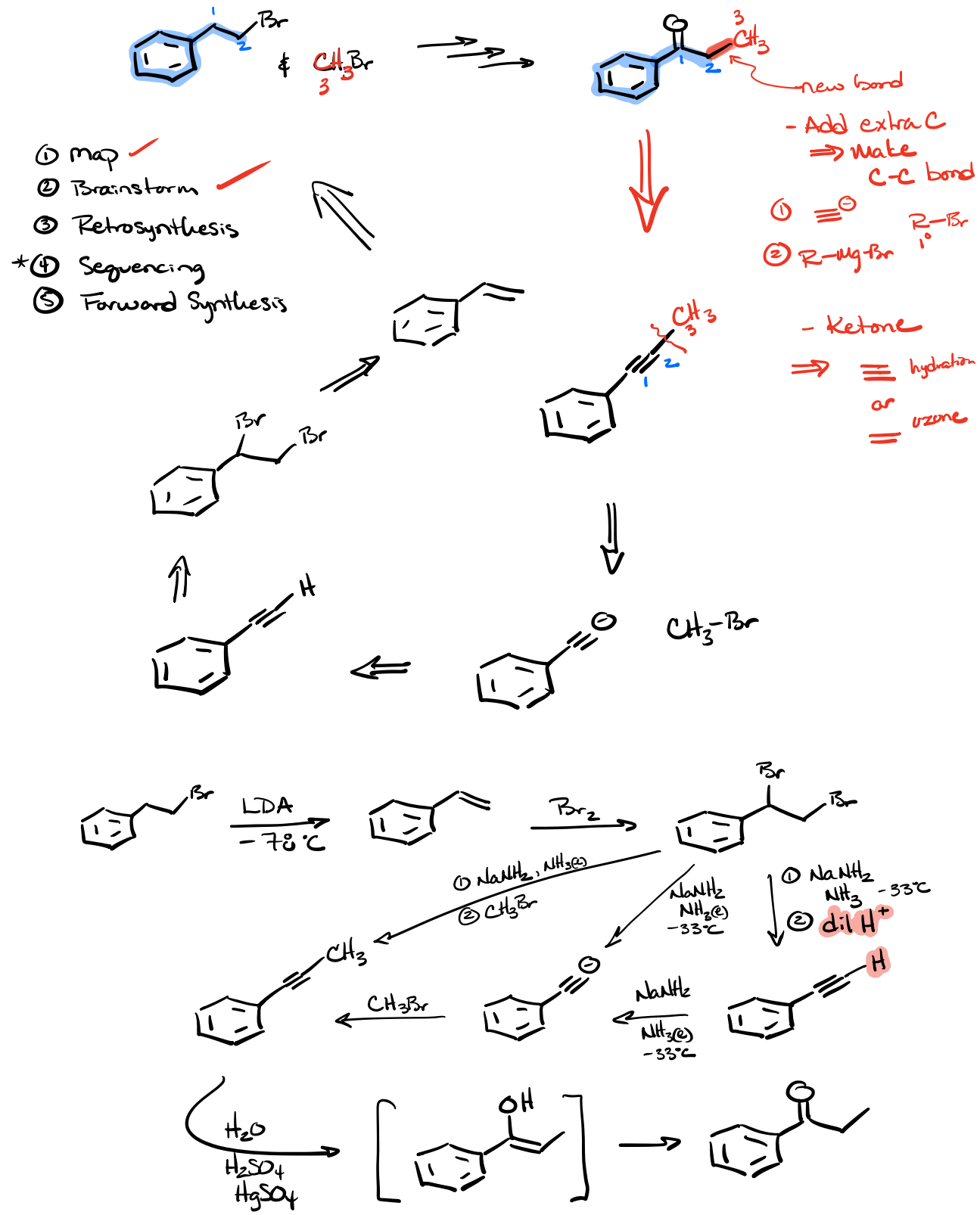


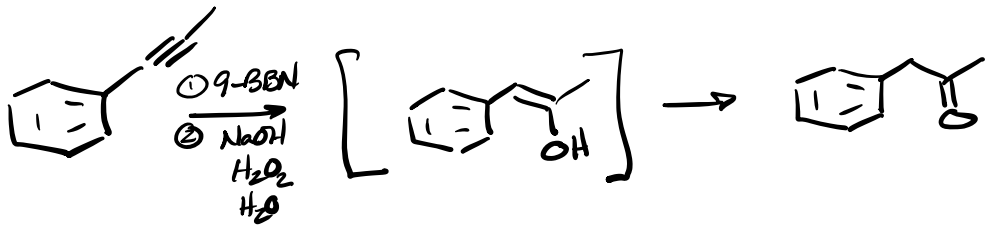
A

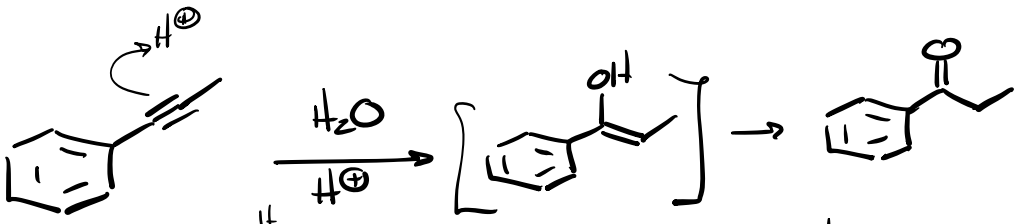

NaNH2
NH3(l)
Na
Br
H2O
H2SO4
HgSO4
① 9-BBN
② NaOH
H2O2
H2O

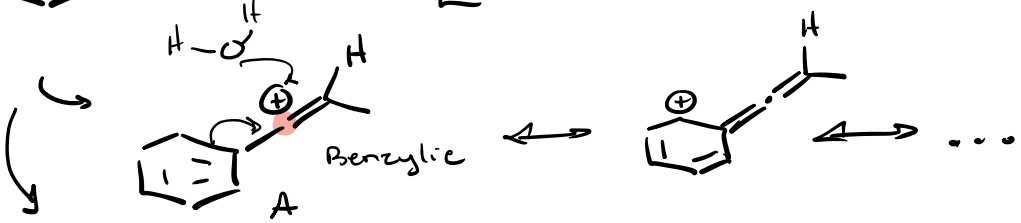
B

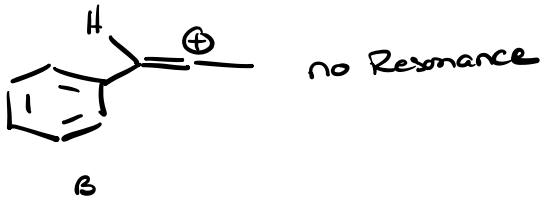

NaNH2
NH3(l)
Na
CH3Br
NaNH2
NH3(l)
Na
CH3Br
H2O
H2SO4
HgSO4

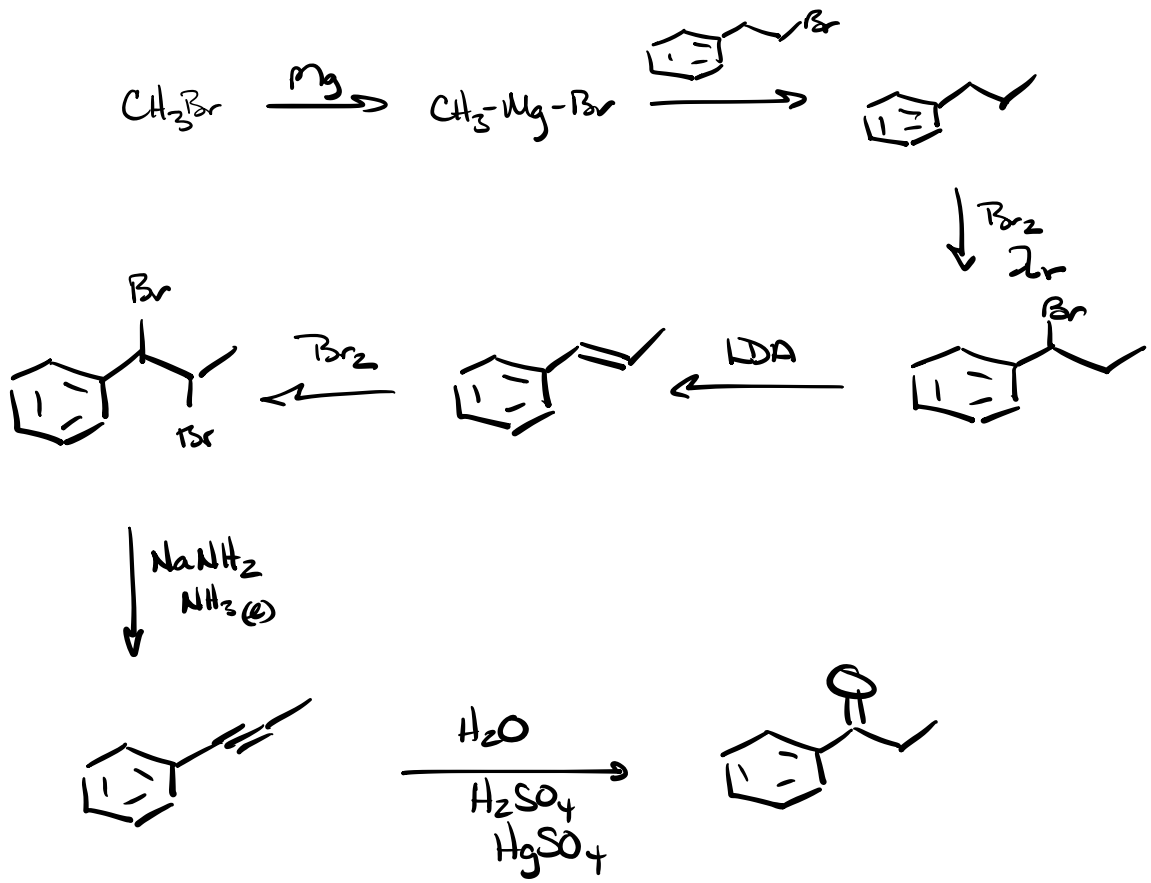

& CH_3Br
new bond
- Add extra C
⇒ Make C-C bond
① ⁻C≡
② R–Mg–Br
R–Br 1°
- Ketone
⇒ ≡ hydration
or
= ozone
① Map
② Brainstorm
③ Retrosynthesis
*④ Sequencing
⑤ Forward Synthesis
CH_3–Br
LDA
−78 °C
Br_2
① $NaNH_2$, NH_3(ℓ)
② CH_3Br
$NaNH_2$
NH_3(ℓ)
−33°C
① $NaNH_2$
NH_3
−33°C
② dil H^+
CH_3Br
$NaNH_2$
NH_3(ℓ)
−33°C
H_2O
H_2SO_4
$HgSO_4$
OH

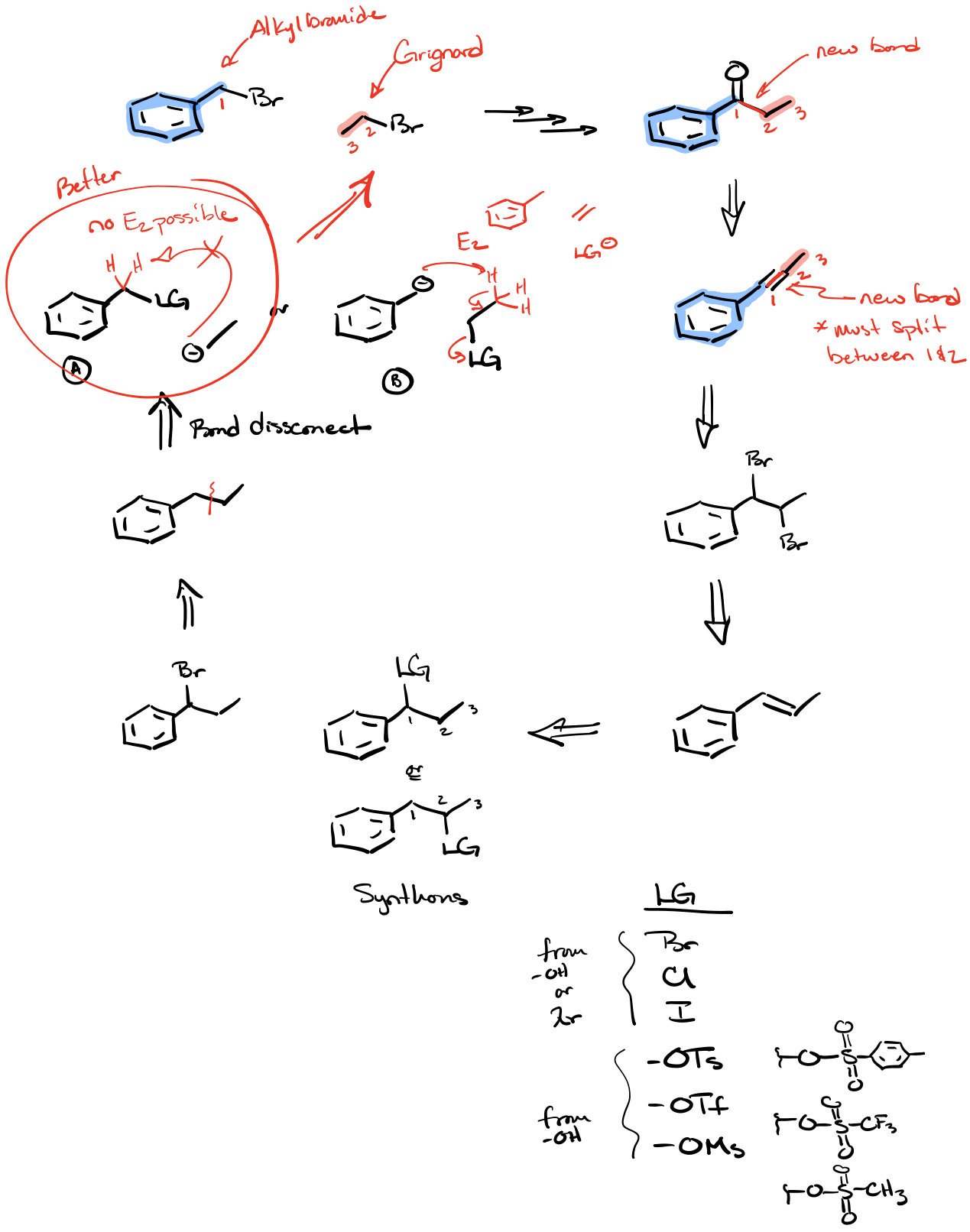

① 9-BBN
② NaOH
H_2O_2
H_2O
OH


H⊕
H_2O
H⊕
OH


H
H
Benzylic
A
...


H
no Resonance
B


CH3Br
Mg
CH3-Mg-Br
Br
Br2
2r
Br
Br2
LDA
Br
Br
NaNH2
NH3 (l)
H2O
H2SO4
HgSO4


Alkyl bromide
Grignard
new bond
Better
no E2 possible
E2
LG
new bond
* must split between 1 & 2
Bond disconnect
Synthons
LG
from -OH or -Br
Br
Cl
I
from -OH
-OTs
-OTf
-OMs

S_N2/E_2

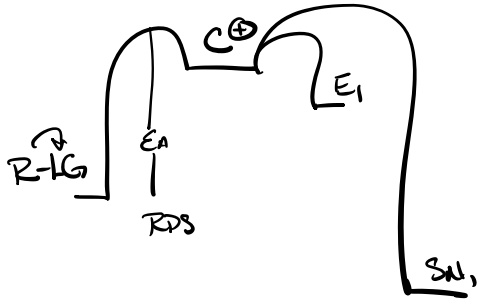
Rate $S_N2 = k[nuc][R\text{-}LG]$

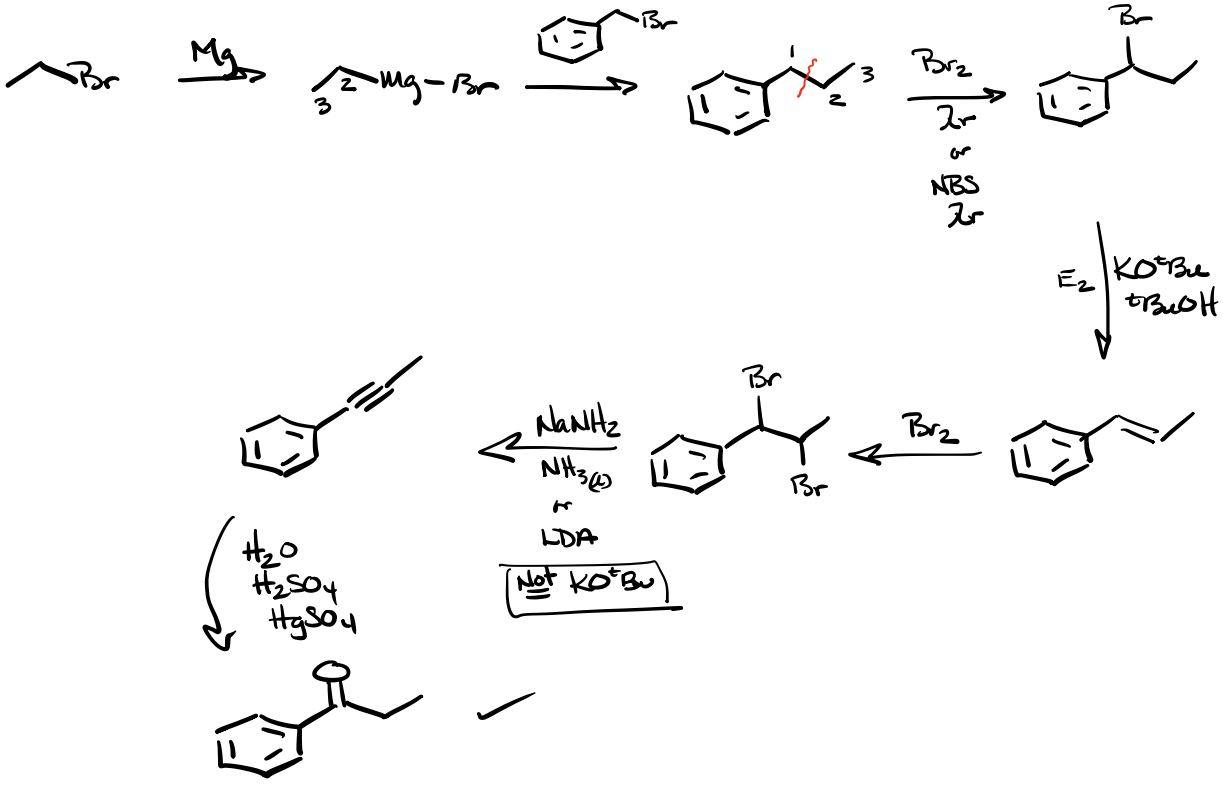
Rate $E_2 = k[base][R\text{-}LG]$

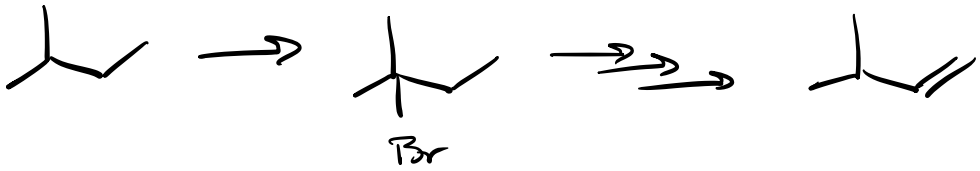
S_N1/E_1

Rate $S_N1 = k[R\text{-}LG]$

Rate $E_1 = k[R\text{-}LG]$






Br