

Chapter 24 — chemoselectivity

Regioselectivity vs. chemoselectivity vs. stereoselectivity

Carbonyls as electrophiles

Salmefamol synthesis

Reagent control of selectivity: chemoselective carbonyl reductions

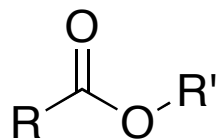
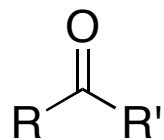
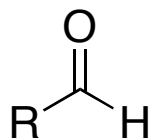
More reductions

Oxidizing alcohols

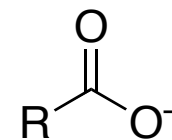
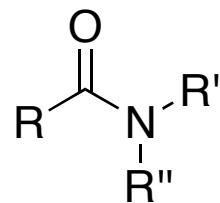
Summary of protecting groups

Carbonyls as electrophiles

more electrophilic...



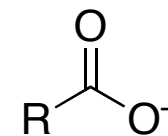
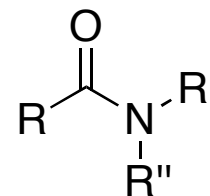
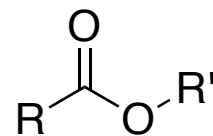
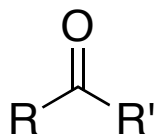
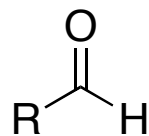
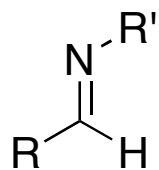
...less electrophilic



Carbonyl reduction by hydride reagents

more electrophilic...

...less electrophilic



————— H₂, Pd

————— NaCNBH₃

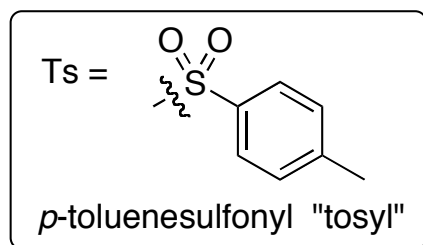
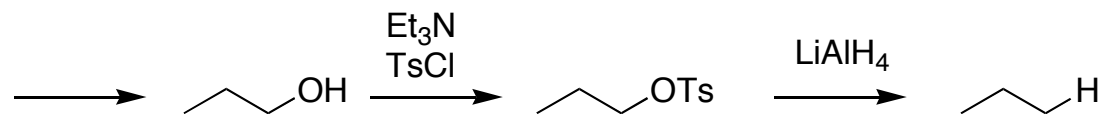
————— NaBH₄ —————

————— LiBH₄ —————

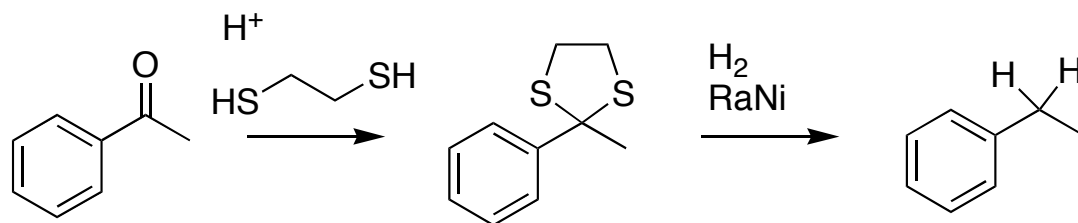
————— LiAlH₄ —————

..... BH₃ —————

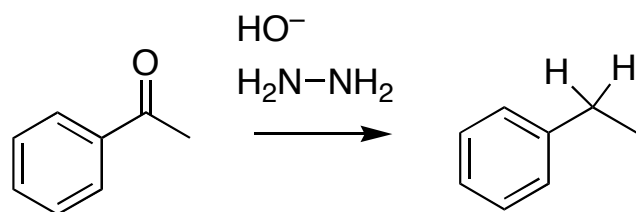
Reductive removal of functional groups



Tosylation is commonly used to convert alcohols to leaving groups

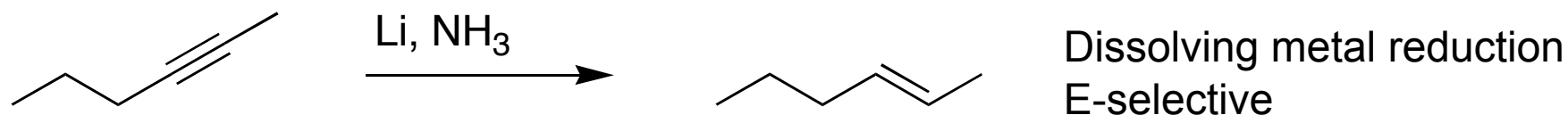
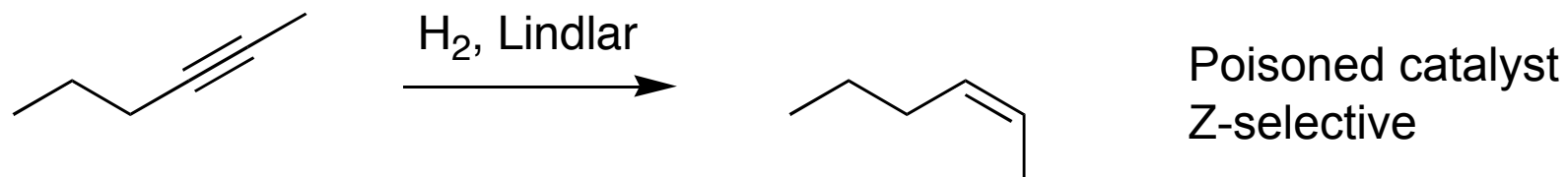
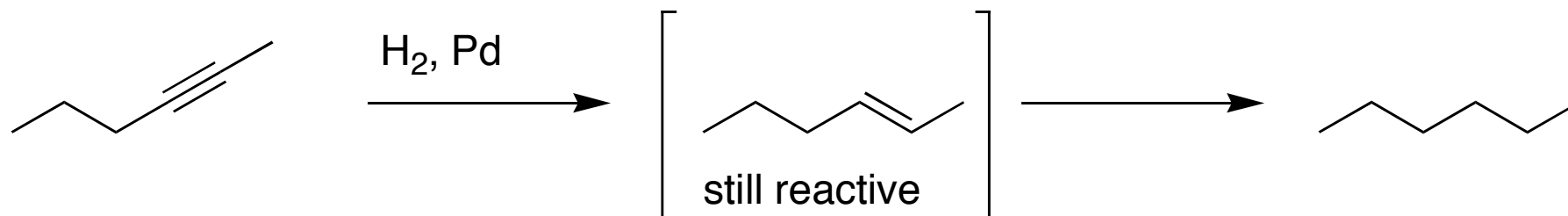


Raney Nickel is great at catalyzing the cleavage of C-S bonds

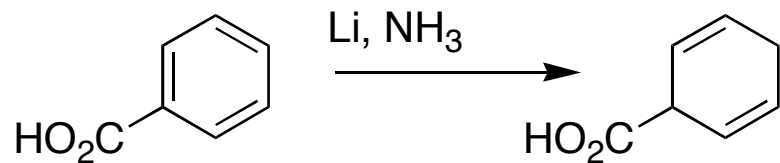
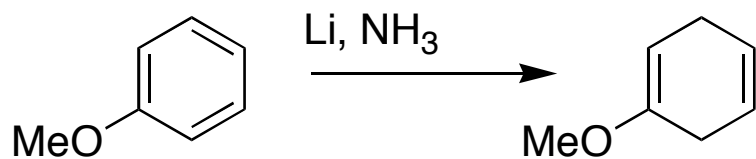
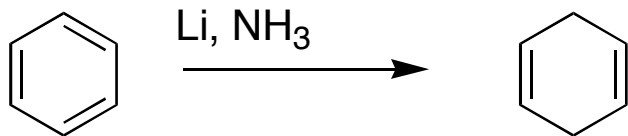


Wolff-Kishner reduction
(see class notes for mechanism)

Alkyne reductions

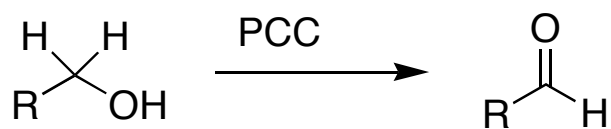
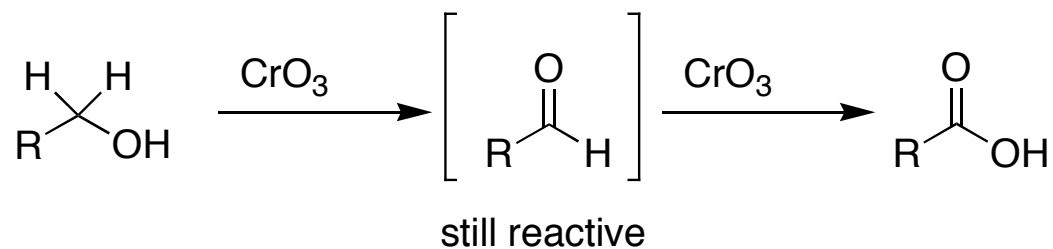
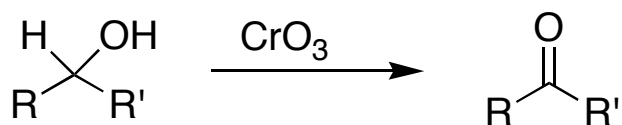
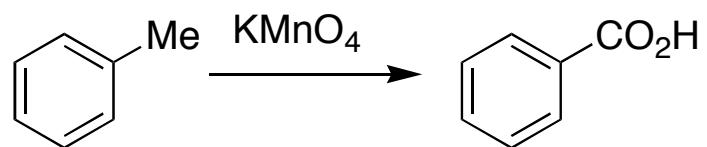


More dissolving metal reductions



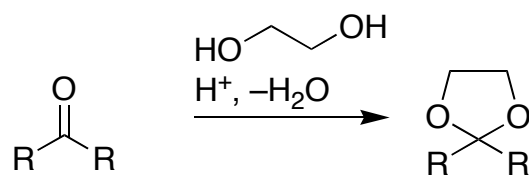
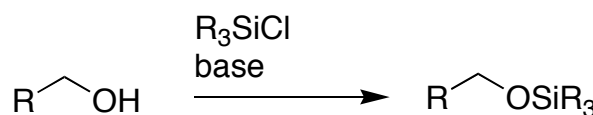
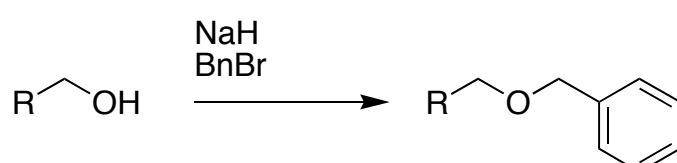
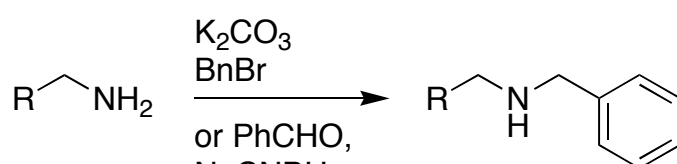
Note regioselectivity effects of
EDG and EWG

Miscellaneous oxidations



Pyridinium chlorochromate — mild, neutral oxidation that stops at aldehyde

Protecting groups 1.

Name	Addition	Protects from	Removal
acetal (dioxolane)		Protects aldehydes and ketones from nucleophiles and bases	H ⁺ , H ₂ O
silyl ether		protects alcohols from bases and nucleophiles, the bulkier versions also protect from weak acid	H ⁺ (TMS, TES) F ⁻ (all = TMS, TES, TIPS, TBDMS, TBDPS)
benzyl ether		protects alcohols from bases, nucleophiles, electrophiles, and all but the strongest acid/nucleophile combinations	H ₂ , Pd/C or HBr
benzyl amine		protects amines from bases, nucleophiles, some electrophiles, and acids	H ₂ , Pd/C (high pressure)