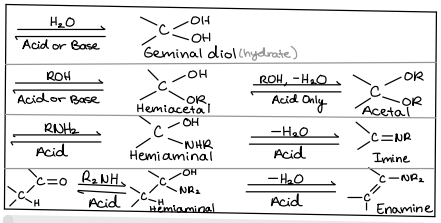
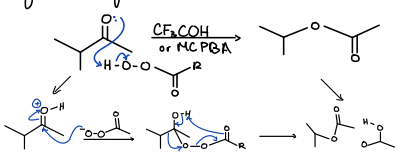


Baeyer - Villager Reaction



H > 3° > 2° > Ph > 1° > methyl

Protecting Groups:

OH → OR — grig + OH — deprotonation, H on O acidic

acetal - HO OH H_2SO_4 ; H_2SO_4, H_2O

thioacetal HS SH $ZnCl_2$ or BF_3 ; $HgCl_2$ H_2O H_2 cond.

↳ acetals protect diols and C=O

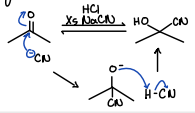
↳ raney ni, H_2 → thioacetal to alkane

Tests for aldehyde: ald → carb.

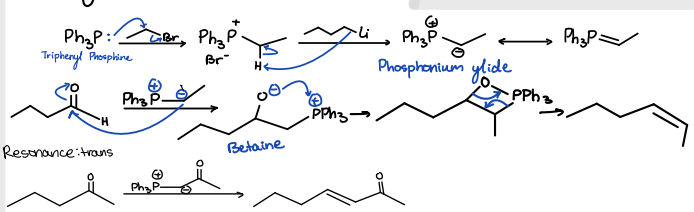
Cu^{2+}, NaOH, H_2O — Cu_2O

Ag^+, H_2O — Ag

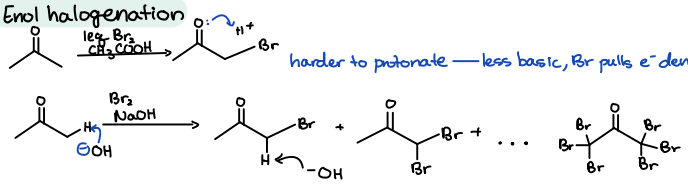
Cyanohydrin Formation



Wittig Reaction



Enol halogenation



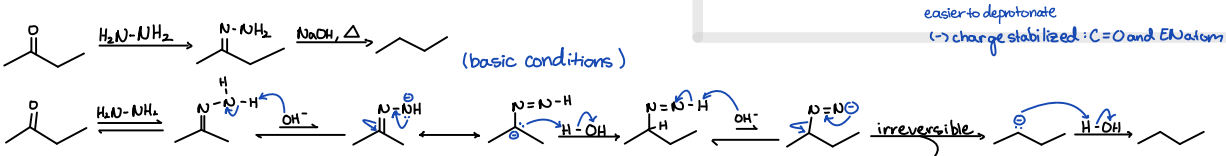
harder to protonate — less basic, Br pulls e⁻ density from C=O

easier to deprotonate

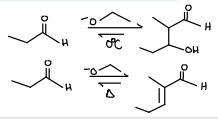
(→) charge stabilized: C=O and EN atom

full bromination at α positions

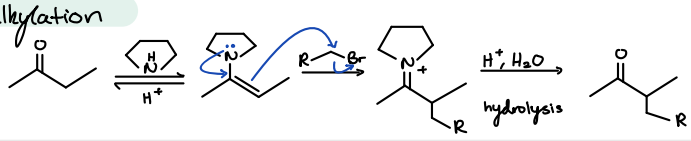
Wolff-Kishner Reaction



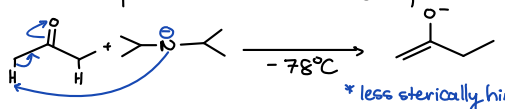
Aldol addition at low T



α-alkylation



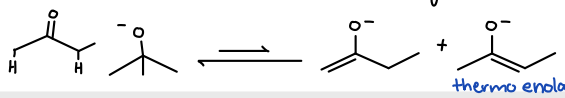
Irreversible Deprotonation → Kinetic product



Kinetic enolate

* less sterically hindered H - faster

Reversible Deprotonation → Thermodynamic product

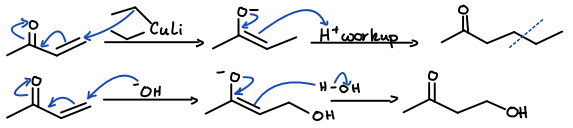


thermo enolate

α-β unsaturated C=O

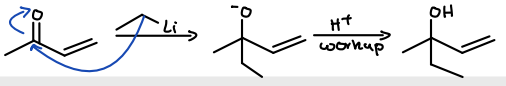
1,4 addition — Nu^- that add reversibly — thermo prod.

- H_2O, OH^-, RO^-, ROH, RNH_2, R_2NH, RS^-, RSH, R_2CuLi, CN^-, enolates



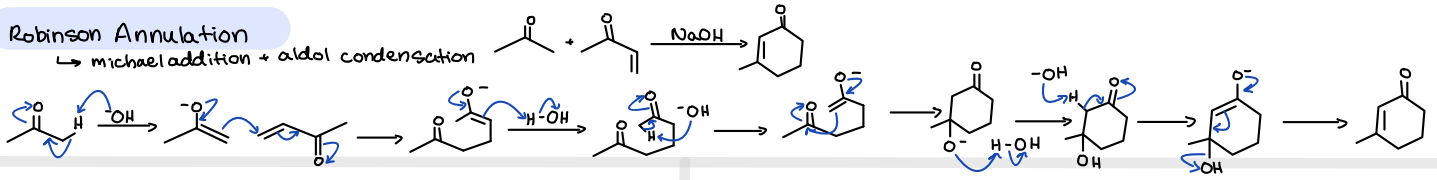
1,2 addition — Nu^- that add irreversibly — kinetic prod

↳ $LiAlH_4$, H_2N-NHR, H_2N-OH, R-Li (inconsistent: $NaBH_4$, R-MgBr)

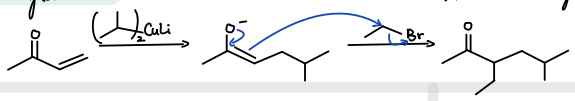


Robinson Annulation

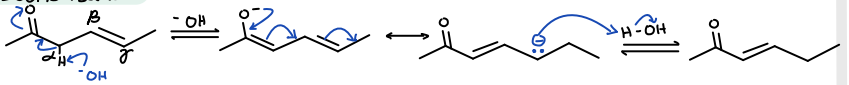
↳ michael addition + aldol condensation



Dialkylation — enolate intermediate can be trapped w/ alkylhalide



Isomerization

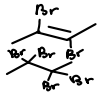


Alkyne Reactions

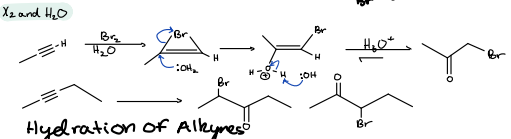
HBr - geminal dibromide

Halogen addition

- 1eq. Br_2, Xs LiBr, CCl_4
- Xs Br_2, Xs LiBr, CCl_4



X_2 and H_2O



Hydration of Alkynes

Hg cat - $HgSO_4$, H_2SO_4, H_2O

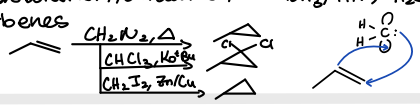
Hydroboration - Oxidation — 1) Cy_2BH 2) NaOH, H_2O_2, H_2O

Alkene Reactions

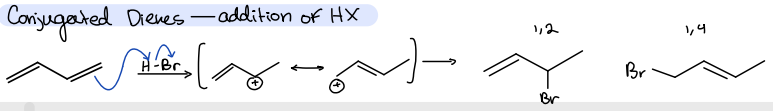
- O_3, $(CH_3)_2S$
- OsO_4, H_2S, H_2O_2 → syn addition OH

Trans → syn, cis → anti

- Oxymercuration / Demercuration — 1) $Hg(OAc)_2$, H_2O 2) $NaBH_4$, NaOH, H_2O
- Hydroboration / oxidation — BH_3, THF, H_2O_2, NaOH, H_2O
- Carbenes



Conjugated Dienes — addition of HX

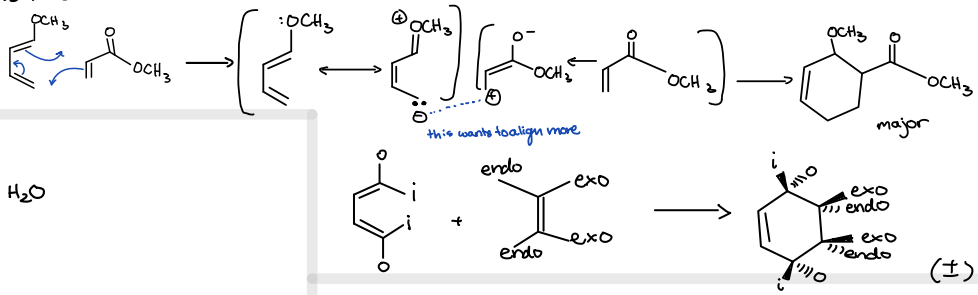


1,2 = Kinetic control
Faster, low temp

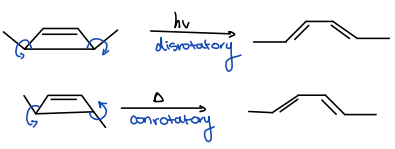
Thermodynamic control — which prod. is more stable
↳ more sub. alkene: more stable

* 1,3 orientation minor

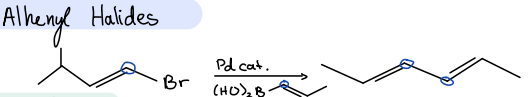
Diels Alder



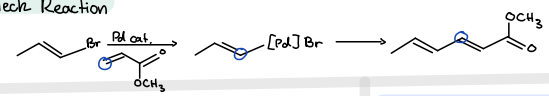
# π e⁻	Δ	hv
2, 6, 10	dis	con
4, 8	con	dis



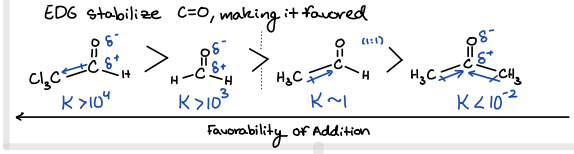
Alkenyl Halides



Heck Reaction



EDG stabilize C=O, making it favored

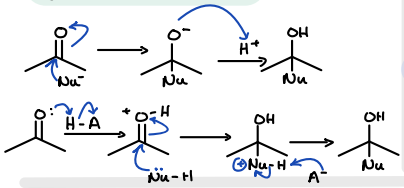


+ tough to isolate hydrates

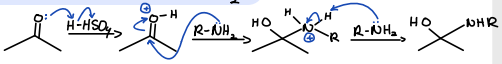
Hemiacetals can be isolated only w/ fav. equilibrium — certain aldehydes 5mem rings, 6 mem cyclic hemiacetals

+ both Imine and enamine work best in mild acid

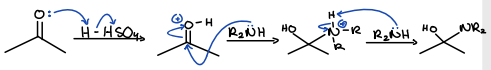
General Nu⁻ addition



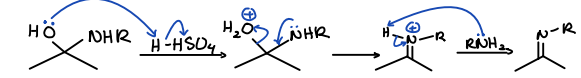
Hemiaminal Formation — RNH_2



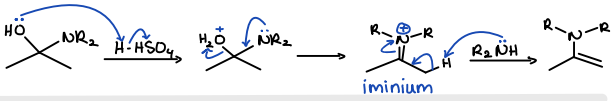
Hemiaminal Formation — R_2NH



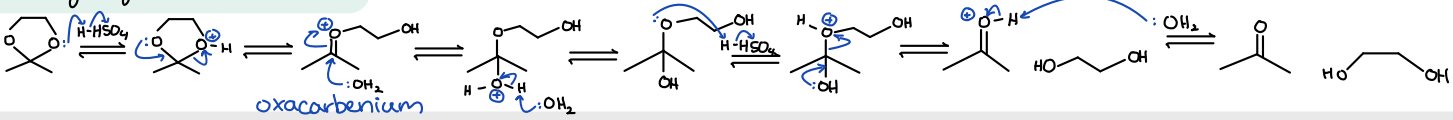
Imine Formation — RNH_2



Enamine Formation



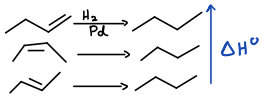
Acetal Hydrolysis — Reverse Mech.



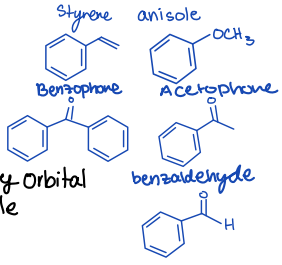
Alkenes

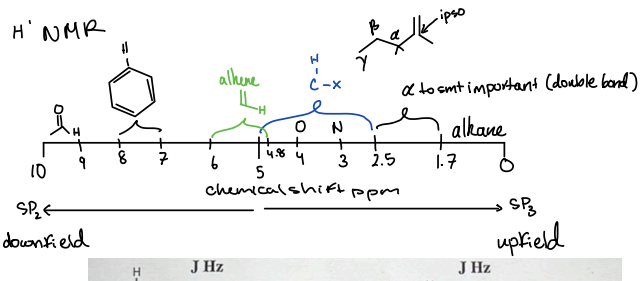
- no free rotation
- MP/BP - similar to alkanes — cis often lower than trans

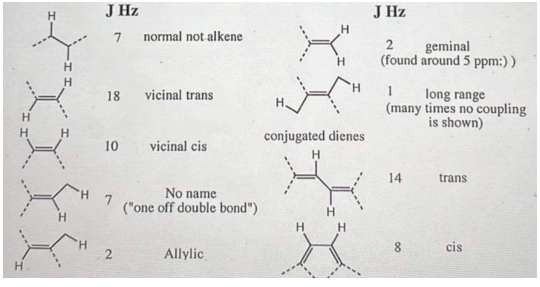
↑ΔH = less stable initial compound



- Hyperconjugation — sub donate e⁻ density into an empty orbital — more sub. alkene gen more stable
- Steric effects — Trans more stable than cis
- Local mag fields prod deshielding
  - ↳ higher $\vec{B}_{eff}$ = more deshielded
  - ↳ (4.5-6 ppm), (100-150)
- Weak Nu⁻, attack SA + E⁺, empty non bond. orb
- anti selective cat - Chiral cat. can be used to do asymmetric hyd. where only 1 chiral mole. is prod.







Alkynes

- mp, sim. bp ; Ethyne combustion at high T
- Internal = more stable than term. due to hyperconj.
- Electrophilic addition to one or both pi bonds
- Deprotonate terminal alkyne and use as Nu⁻ (pKa ~ 25)
- cylindrical movement of e⁻ produces opposing magnetic field
  - ↳ alkynes more shielded than alkenes
- Ene-diyne antibiotic/antitumor agents
  - ↳ potent causes apoptosis via radical mech → DNA dam.
- Resonance stabilization makes H more acidic + stable
- More conj → lower homo/lumo gap → higher λ_{max}
- More complicated conj — very low gap → much higher λ_{max}

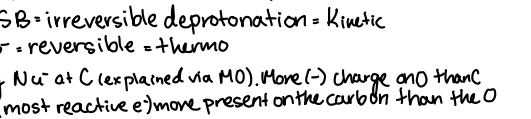
Aromatics

- Stabilizing - (4n+2) destabilizing (4n)
- Polycyc. Aro. Hydrocarbons — carcinogens like benzene — body ox. things to try to make them water soluble — ox. w/o sub. → hydrate, epoxides on aromatic hydrocarbon, DNA Nu⁻ will open epoxide - mess up DNA

Aldehydes / Ketones

Priority: Aldehyde > Ketone (oxo) > alcohol (hydroxyl)

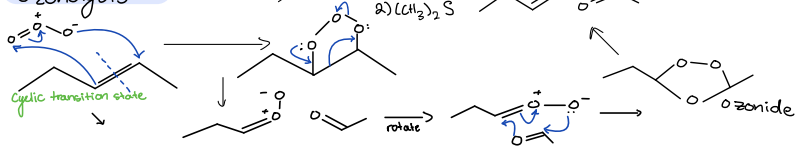
Fancy Imines
- ↳ hydroxylamine → oxime
- ↳ hydrazine - hydrazone



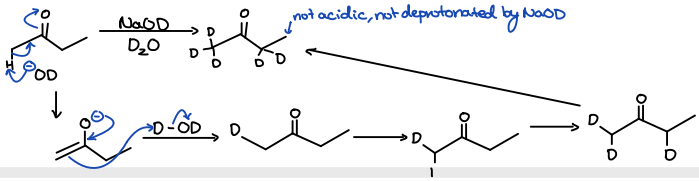
- very SB = irreversible deprotonation = Kinetic
- σ = reversible = thermo
- mainly Nu⁻ at C (explained via MO). More (-) charge on O than C homo (most reactive e⁻) more present on the carbon than the O

Aldol Rxn
1) Aldehyde has no α H (only E⁺)
2) Aldehyde B slowly added w/ Base

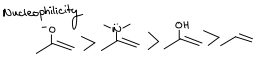
Ozonolysis

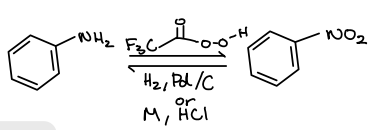


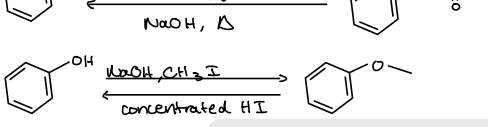
Deuterium Exchange w/ deuterated solvents



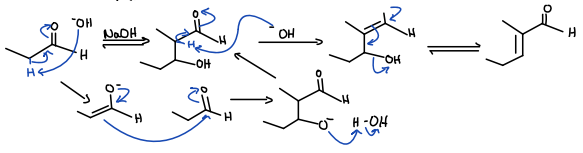
Nucleophilicity



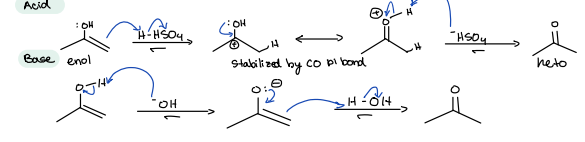




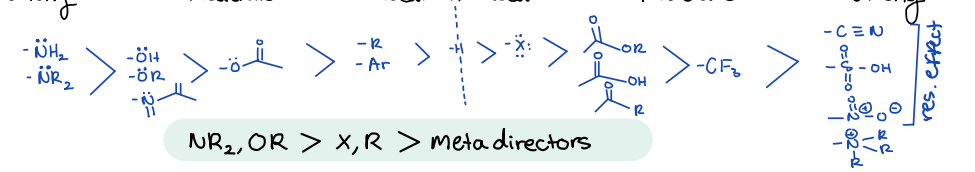
Aldol Rxn



Tautomerization



← e⁻ donating — e⁻ withdrawing →



NR_2, OR > X, R > meta directors