

BIO- CHEMISTRY

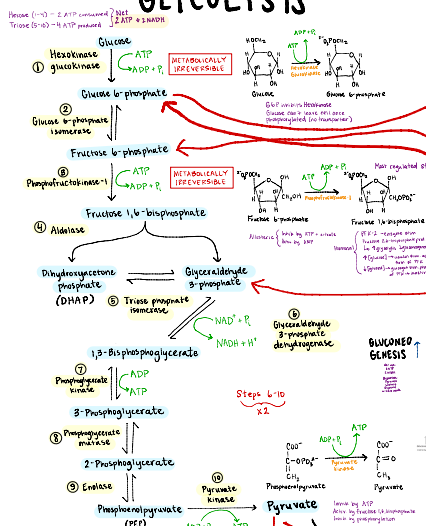
FROM K_SUNDAYSUNDAYSUNDAY

→ Ochem on pg. 13

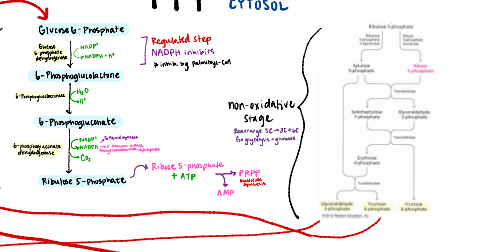
FYI...

These review sheets are from taking Biochem + Ochem at University, so some info is out of scope for the MCAT. With that said, the sheets are mostly general info + hold many relevant concepts. I hope they help!

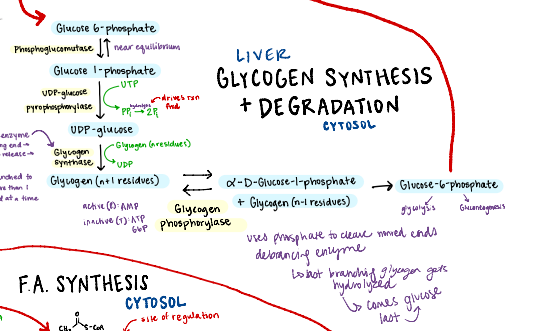
GLYCOLYSIS



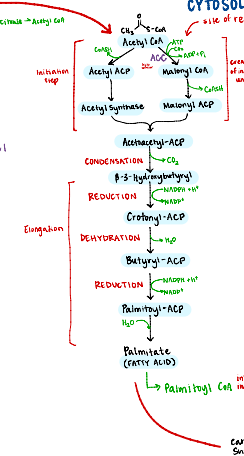
PPP CYTOSOL



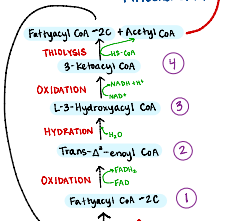
LIVER GLYCOGEN SYNTHESIS + DEGRADATION CYTOSOL



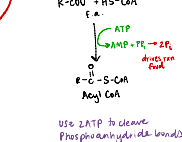
F.A. SYNTHESIS CYTOSOL



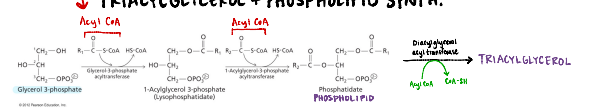
BETA-OXIDATION MITOCHONDRIA



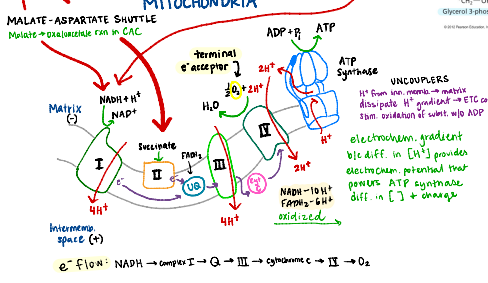
F.A. ACTIVATION



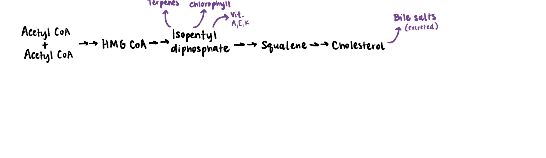
TRIACYLGLYCEROL + PHOSPHOLIPID SYNTH.



ETC MITOCHONDRIA



CHOLESTEROL SYNTHESIS



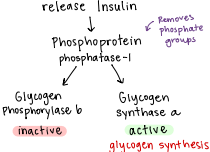
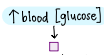
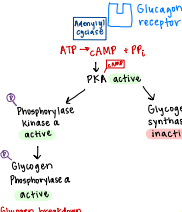
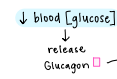
METABOLISM REGULATION

GLYCOGEN METABOLISM REGULATION

thru hormone-induced phosphorylation + dephosphorylation (con. med.)

of glycogen synthase + glycogen phosphorylase

also affected by allosteric regulators



Inhibit ATP synthase
- H⁺ gradient buildup
- CAC provides NADH, backed up
- Pyruvate → lactic acid
↳ moved to anaerobic pathway

ETC

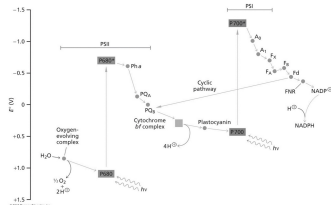
$$\Delta G^{\circ} = -nFE^{\circ}$$

(-) spontaneous (+)

CALVIN CYCLE - light independent rxn

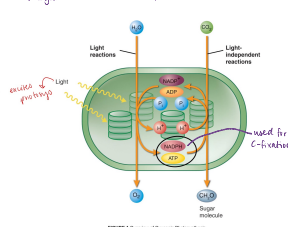
Carboxylation → Reduction → Regeneration
enzyme = RuBisCO

PHOTOSYNTHESIS



O₂ evolving complex -

biogenic to chloride bonds 4e⁻ + protons to make O₂ @ 1 atm



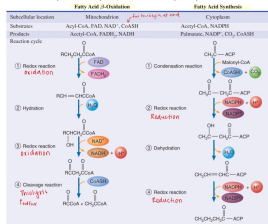
F.A. SYNTHESIS

ACC1

Acetyl CoA → Malonyl CoA

active: Citrate
↑ [glucose] insulin
inhibits: Glucagon, Epinephrine, Palmitoyl-CoA

thruway

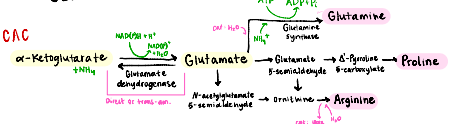


Enzyme Activation: Not in a complex like the CAC, but requires 4 ATP

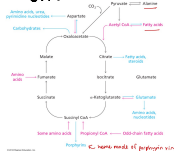
Enzyme is Fatty Acid Synthase complex, but carrier protein (ACP) must be active. 6 ATP

CH 17 - AMINO ACID METABOLISM

GLUTAMATE FAMILY



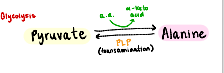
CAC



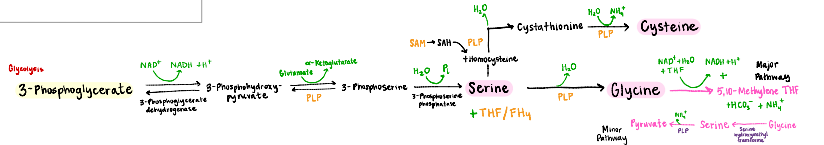
ASPARTATE FAMILY



PYRUVATE FAMILY



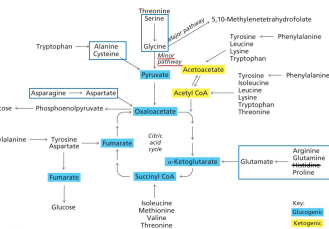
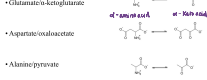
SERINE FAMILY



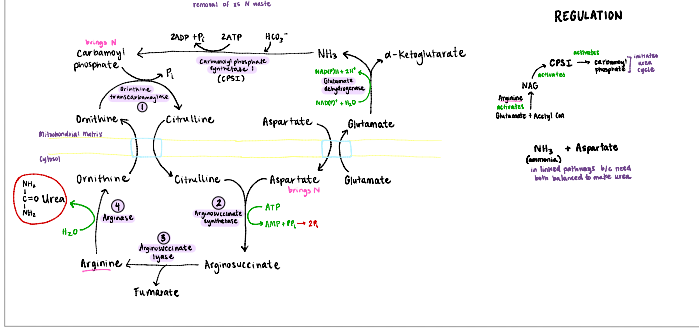
COFACTORS

- PLP - (from biotin) transamination
- THF - (from folate) transfer of 1-C substituents
- SAM - transfer of acetyl groups
- TPP - transfer multi-C units, Pyruvate → Acetyl CoA

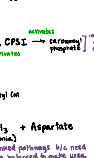
TRANSAMINATION



UREA CYCLE



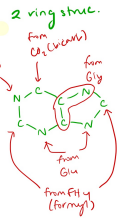
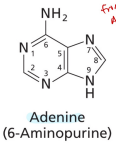
REGULATION



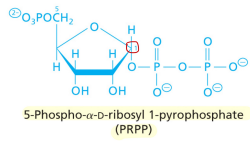
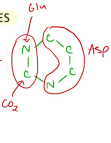
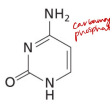
NH₃ + Aspartate (ammonia) in liver pathways has to be balanced to make urea

CH 18 - NUCLEOTIDE METABOLISM

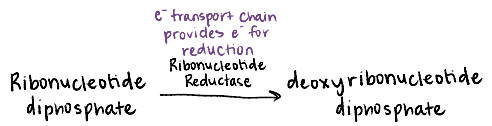
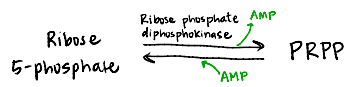
THE MAJOR PURINES



THE MAJOR PYRIMIDINES



needed for nucleotide synthesis



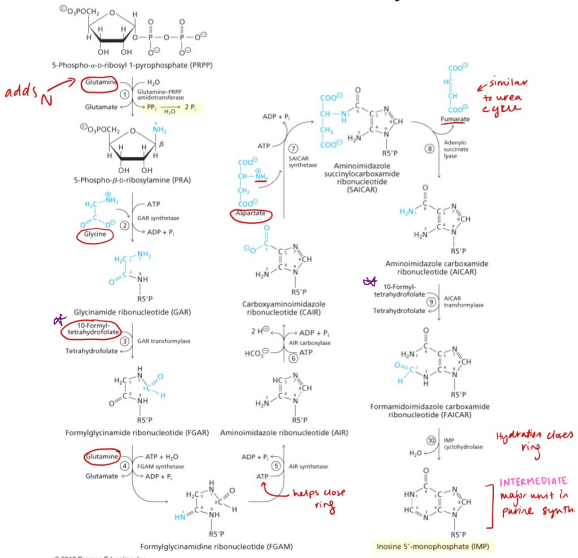
Purine Synthesis

- 10 steps to inter. mediate
- more energetically expensive (7 ATP equiv)
- needs PRPP
- uses PRPP as scaffold
- major intermediate: IMP
- 2 ring structure

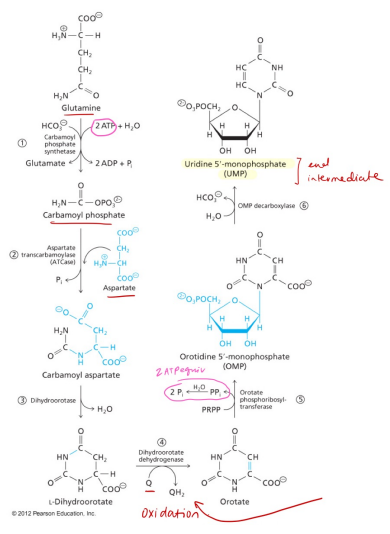
Pyrimidine Synthesis

- 6 steps to inter. mediate
- less energetically expensive (4 ATP equiv)
- needs PRPP
- 1st ring is built, then added onto PRPP
- major intermediate: UMP
- 1 ring structure

PURINE SYNTHESIS

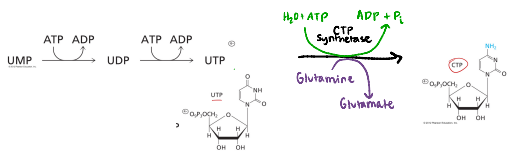
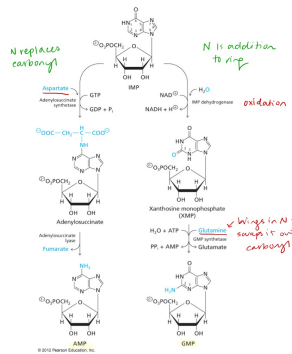


PYRIMIDINE SYNTHESIS



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PURINE REGULATION

Major inhib: IMP + AMP + GMP
Feedback inhib.

PYRIMIDINE REGULATION

Activate: ATP + GTP
Inhib: UTP + CTP

Cofactors:

- Methylene THF - adds methyl dUMP \rightarrow dTMP
- THF - Purine syn. adds formyl grp
- 5,10-Pyrimidine syn. oxidation
- NADP⁺/NADPH - Pyrim. catabolism
- FAD - part of e⁻ chain to make deoxy

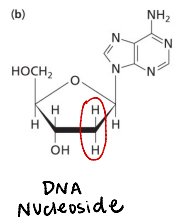
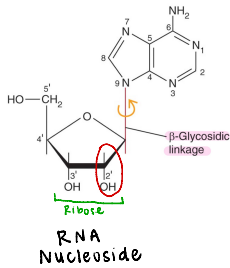
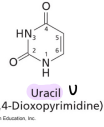
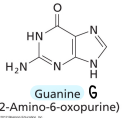
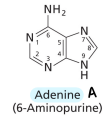
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CH 19 NUCLEIC ACIDS

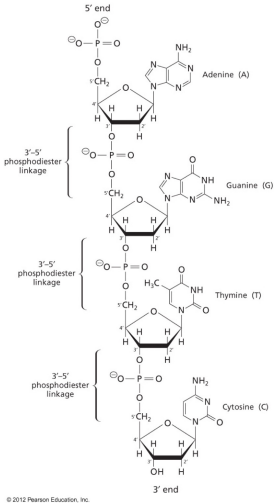
Nucleotide has ribose + base + phosphate

THE MAJOR PURINES

THE MAJOR PYRIMIDINES



1° STRUCTURE 5' → 3'



DNA 3° structure stabilized by noncovalent interactions

- H-bonds**
btwn base pairs
GC stronger than AT b/c T orbital overlap
- Stacking interactions**
btwn adjacent pairs on each strand
- Hydrophobic effects**
favorable, places bases on interior
- Charge-charge interactions**
(-) phosphate backbone, stabilized by (+) Mg²⁺ or cationic proteins w/ Lys + Arg side chains

- ↑ # base pairs ↑ stacking strength
- ↑ # H bonds ↑ E req to denature
- C-G > A-T

DNA 4° STRUCTURE

DNA helix wraps around histone
Histones condense
Condensed fibers supercoil into chromatin
Stored in chromosome
* (-) DNA backbone has favorable association w/ (+) a.a. Lys + Arg in Histones

BASE PAIRING

RNA A=U C≡G
DNA A=T C≡G
more H-bonds btwn C+G

DNA melting curve



is sigmoidal b/c cooperativity
like a zipper - more likely to dissociate into separate strands as more strands separate (↓ stacking int. + H bonds ↑ separation of strands)

NUCLEIC ACID HYDROLYSIS

RNA more reactive than DNA b/c have hydroxyl group on 2'C
↳ can undergo alkaline hydrolysis, DNA needs ↑ temp + nucleases

Nucleases - cleave DNA @ palindromic sequences
exo - cleaves ends
endo - cleaves w/in sequence

	DNA	← sugar →	RNA
	deoxyribose		ribose
	double-stranded	← form →	single stranded
	helix (B, A, Z)		fold, loops, twists, hairpins (padding)
↑ more RNA	RNA template storage + more stable	← roles →	protein template, regulation + more reactive
	stays in nucleus	← location →	can traverse out of nucleus
	Yes; w/ histones + chromatin formation	← archived? →	No
	A-T G-C	← bases →	A-U G-C

good b/c signal needs to be degraded

BIOCHEMISTRY GUIDE EXAM 1

$$\Delta G = \Delta H - T\Delta S$$

favorability $-\Delta G$ Enthalpy $-\Delta H$ Entropy $+\Delta S$
 favorable rxn = spontaneous
 ΔS drives protein folding

$$pH = -\log[H^+] = \log \frac{1}{[H^+]}$$

$$pK_a = -\log K_a = \log \frac{1}{K_a}$$

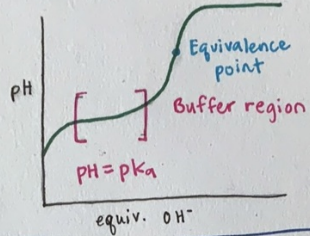
smaller pK_a = stronger acid

- IMF's**
- Charge-charge
 - Ion pairs (salt bridges)
 - Van der Waals
 - Dipole-dipole
 - Hydrogen bonds
 - Dipole-induced dipole
 - Induced dip.-Induced dip.
 - London dispersion
 - Hydrophobic effect

HENDERSON-HASSELBACH

$$pH = pK_a + \log \frac{[A^-]}{[HA]} = pK_a + \log \frac{[\text{Proton acceptor}]}{[\text{Proton donor}]}$$

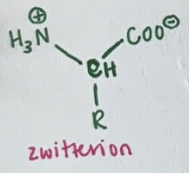
BUFFERS



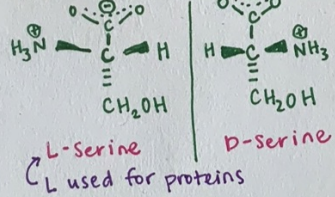
Buffers resist changes in pH around their $pK_a \pm 1$ pH unit

AMINO ACIDS

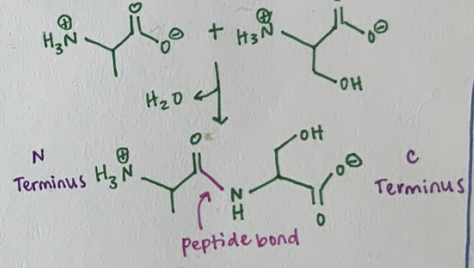
a.a. structure



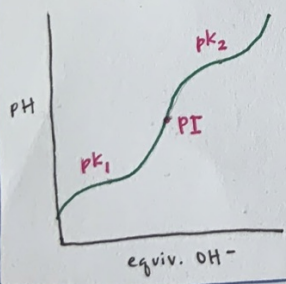
a.a.'s are chiral



Peptide bonds link a.a.'s



a.a.'s are ionizable, titration

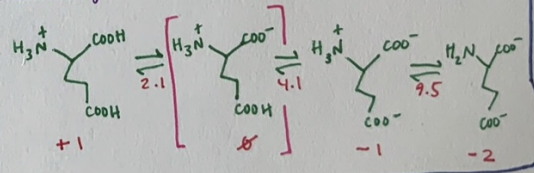


PI = isoelectric point

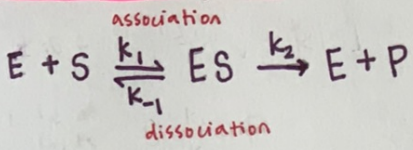
PI = pH @ net neutral charge

$$PI = \frac{pK_1 + pK_2}{2}$$

$pH < pK_a$
protonated



ENZYME KINETICS



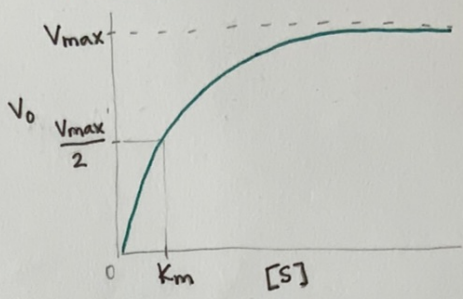
Michaelis-Menton Equation

$$V_0 = \frac{V_{max} [S]}{K_m + [S]}$$

[S] req. to reach 1/2 V_{max} measures binding affinity of E+S

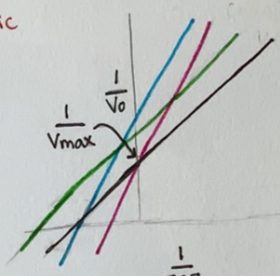
$$K_m = \frac{1}{2} V_{max} \quad \downarrow K_m \uparrow \text{affinity}$$

Michaelis-Menton



Lineweaver-Burk equation

$$\frac{1}{V_0} = \left(\frac{K_m}{V_{max}} \right) \frac{1}{[S]} + \frac{1}{V_{max}}$$



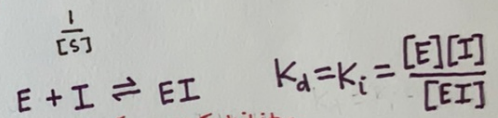
Competitive Inhibition
Uncompetitive Inhibition
Noncompetitive Inhibition
 $x=0, y = \frac{1}{V_{max}}$
 $y=0, x = \frac{1}{K_m}$

Catalytic Constant - k_{cat}

$V_{max} = k_{cat} [E]_{total}$ $\frac{1}{k_{cat}} = \text{time for 1 catalytic event}$
Speed \downarrow $\frac{k_{cat}}{K_m}$ } enzyme efficiency
affinity \uparrow $\uparrow k_{cat} \uparrow E \text{ speed}$

Enzyme Regulation

- Genetic Control** - expression of E
long time scale
- Covalent Regulation** - binding to or removing a.a. side chain
quick time scale
- Noncovalent Regulation** - allosteric modifiers
quick time scale
- Compartmentalization** - Phys. separation by cell components
long term soln.
- Allosteric Regulation**

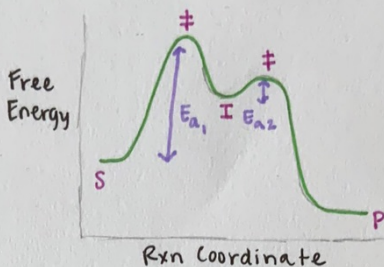
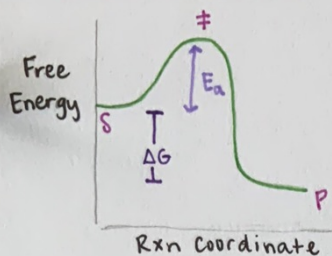


$\downarrow K_i \uparrow$ affinity b/w E + I
aff. by where I binds $\rightarrow V_{max}$ K_m \leftarrow aff. by when I binds

	Competitive I binds E	\emptyset	\uparrow
Under $V_{max} + K_m \downarrow$	Uncompetitive I binds ES	\downarrow	\downarrow
"None" $K_m = \text{no change}$	Noncompetitive I binds E or ES	\downarrow	\emptyset

ENZYMES
 \uparrow rxn rate fwd + rev.
Does not affect ΔG
Not consumed

RXN DIAGRAMS



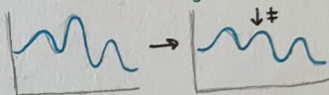
ENZYME CATALYTIC MODES

Proximity + Orientation

- specific positioning of S + other reacting grps
- ΔS less unfav. than soln. cat. rxn
- Induced fit

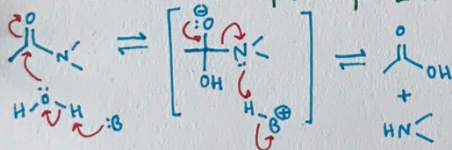
Transition State Stabilization

- stabilize ‡ $\downarrow E_a$
- E binds ‡ more tightly than S



Acid-Base Catalysis

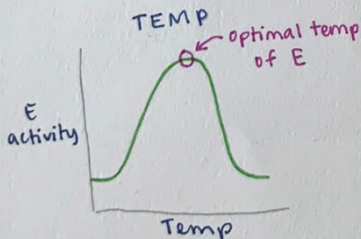
- Creates better Nuc, Elec⁺, + L.G.



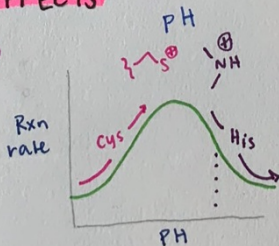
Covalent Catalysis

- Covalent bond btwn E+S creates more reactive I

TEMPERATURE + PH EFFECTS



\uparrow temp \uparrow rxn rate until
E is denatured



Cys: \uparrow pH \uparrow E activity
His: \uparrow pH \downarrow E activity

CH7 - ENZYME COFACTORS

Cofactors = helpers
Enzymes use cofactors b/c ↑ reactivity beyond what a.a.'s provide

COMMON ROLES IN CATALYSIS

- Binding + orientation
- Lewis acids
- Redox centers
- Group Transfer

COFACTOR SOURCES

- Synthesis from simple precursors
- Metal ions
- Vitamins } From diet

COFACTORS

Essential ions
mostly metal ions

Activator ions
loosely bound
Stim. E w/ req. for metal ion

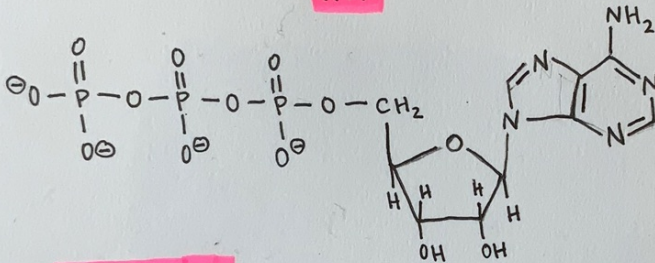
Metal ions of metalloenzymes
tightly bound
bind E at active site

Coenzymes
org. compds.

Cosubstrates
loosely bound
S in E catal. rxn.
Recycled
Dissociate from ac. site

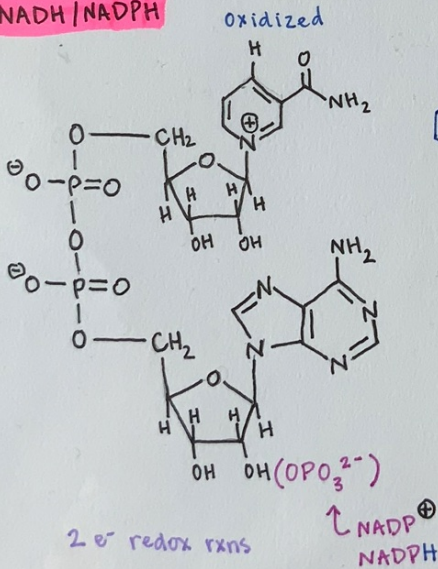
Prosthetic groups
tightly bnd.
remains bound to E thru rxn

ATP



Transfer of phosphoryl or nucleotidyl grps can transfer diff. secs.

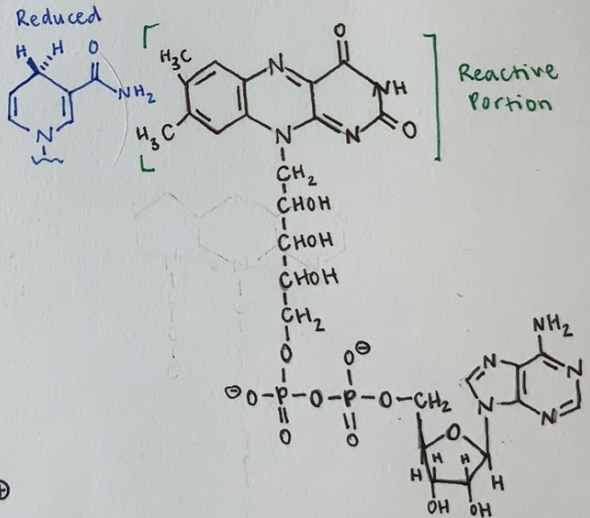
NADH/NADPH



2 e⁻ redox rxns

↑ NAD⁺
NADPH

FAD/FMN

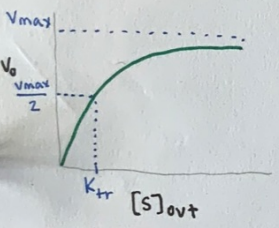


1 and 2 e⁻ redox rxns

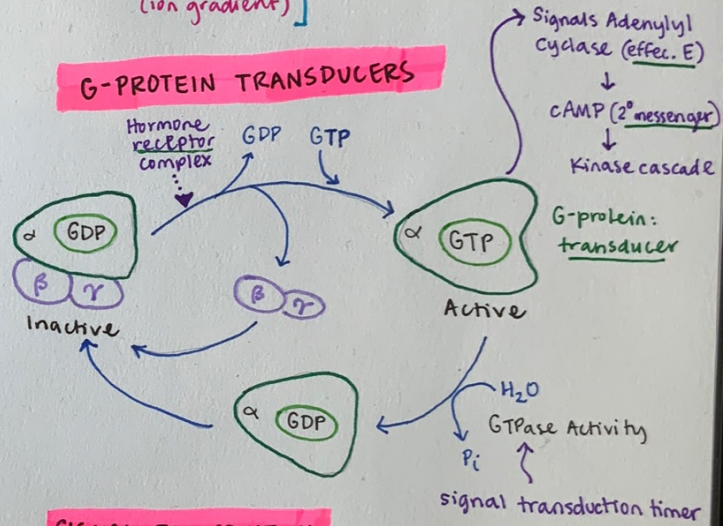
MEMBRANE TRANSPORT

	Protein carrier	Saturable w/ substr.	w/ cont. gradient	E input req.	
SIMPLE DIFFUSION	No	No	Down	No	PASSIVE Favorable ΔS effect
CHANNELS	Yes	No.	Down	No	
CARRIER-MEDIATED TRANSPORT	Yes	Yes	Down	No	
ACTIVE TRANSPORT					ACTIVE Use ATP
1°	Yes	Yes	Up	Yes (direct source)	
2°	Yes	Yes	Up	Yes (ion gradient)	

$$V_0 = \frac{V_{max} [S]_{out}}{K_{tr} + [S]_{out}}$$

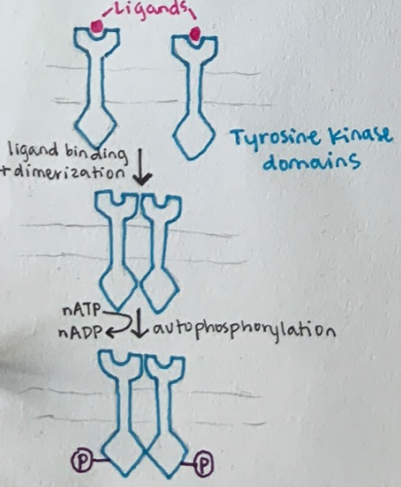


G-PROTEIN TRANSDUCERS

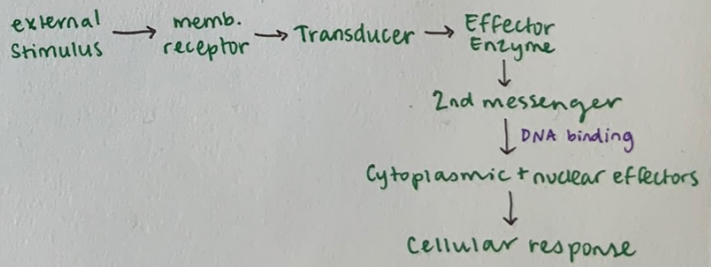


TYROSINE KINASE

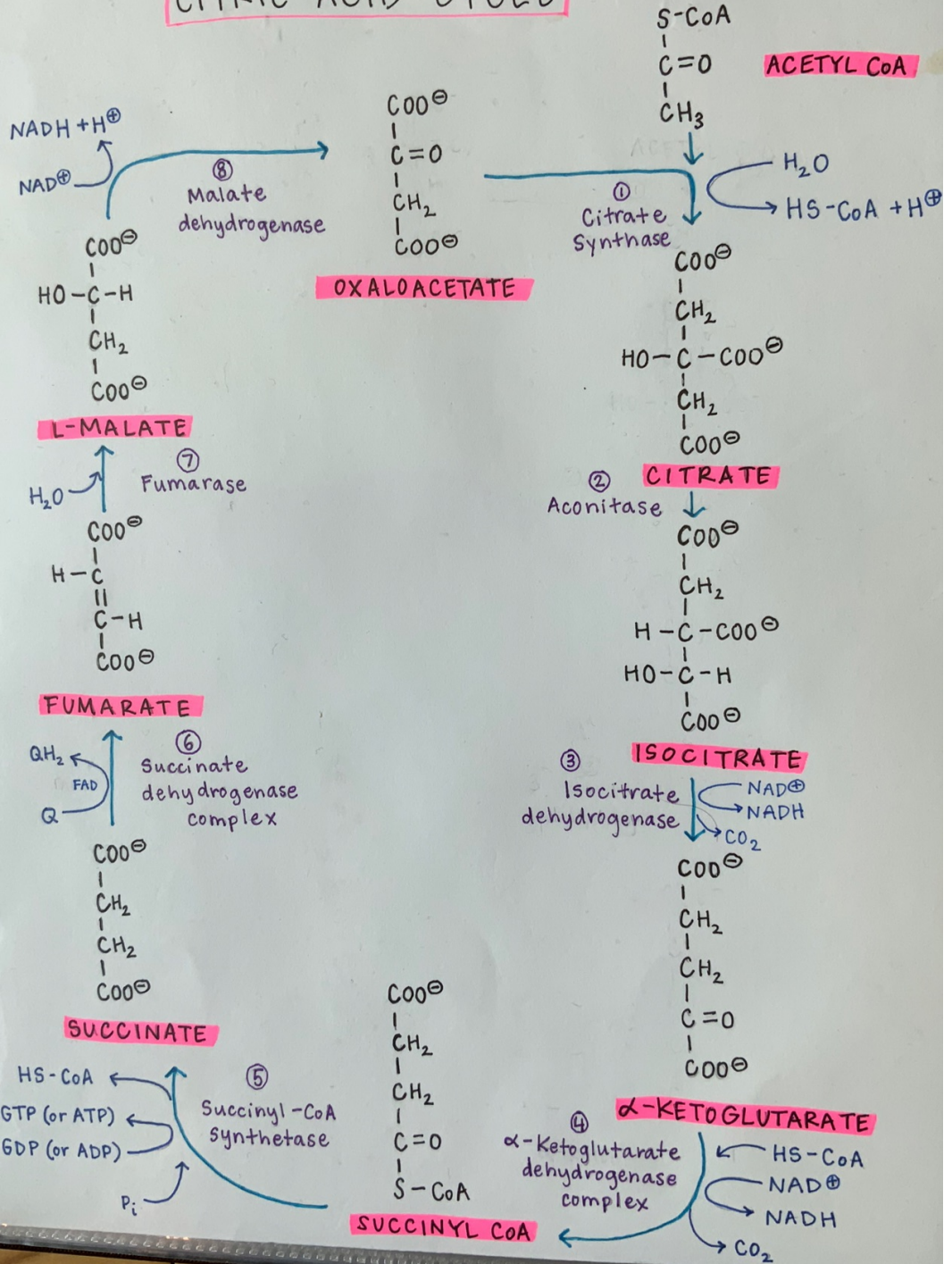
Memb. receptor, transducer, + effector Enzyme all-in-1



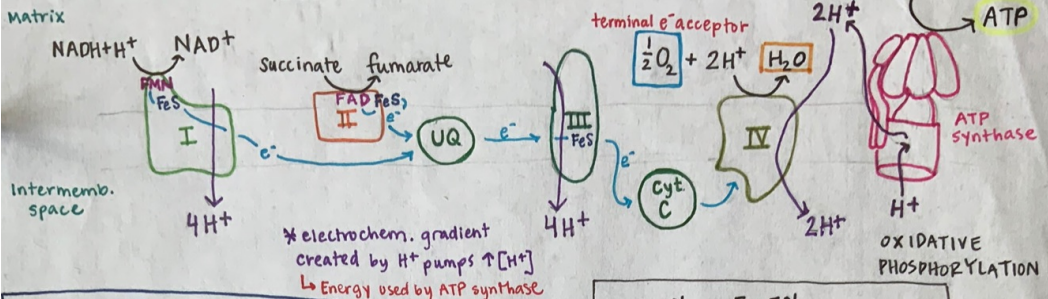
SIGNAL TRANSDUCTION



CITRIC ACID CYCLE



ELECTRON TRANSPORT CHAIN



COFACTORS
 All complexes use Prosthetic Grps
 NADH → FMN → FeS → Q* → Cyt → O₂
 Succinate → FAD → FeS → Q* → Cyt → O₂
 *cosubstrate
 b, c, c₁, c, a, a₃

$$\Delta G^{\circ} = -nF\Delta E^{\circ}$$

more (-) E^o e⁻ donor
 more (+) E^o e⁻ acceptor
 for -ΔG^o, must have +ΔE^o

NADH comes from:

- Citric Acid Cycle - in Mit. Matrix
- Glycerol phosphate shuttle
- Malate-aspartate shuttle (used more)
- Bring NADH into mitochondria

ORGANIC

CHEMISTRY

FROM K_SUNDAYSUNDAYSUNDAY

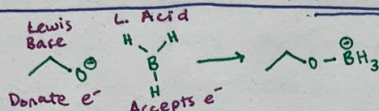
CH 1. MOLECULAR GEOMETRY + HYBRIDIZATION

HYBRID.	#e ⁻ pairs	VSEPR Geometry	Bond Angle	Examples
sp ³	4	Tetrahedral	109.5°	
sp ²	3	Trigonal planar	120°	
sp	2	Linear	180°	$H-C \equiv C-H$

ACIDITY

- C → H₃O⁺ > H₂O
- A → electroneg. HF > H₂O
Atom size HU > HF
- R] →
- D] →
- I → Polar bond
- O → Hybridization
 $\equiv C-H > =C-H$
sp sp²

CH 2. ACID-BASE



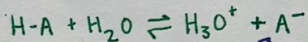
pKa

St. Acids	Protonated O	Carbox. Acids	Protonated N	Alcohols
HCl H ₂ SO ₄	R-OH ₂ ⁺ H ₃ O ⁺		R-NH ₃ ⁺ +NH ₄ ⁺	R-OH H ₂ O
-5	-2	5	10	15

Lower pKa = stronger Acid

Equilibrium lies away from stronger Acid

Ketones	SPC	Amines	sp ² C	sp ³ C
	$\equiv C-H$	R-NH ₂		
20	25	35	45	55



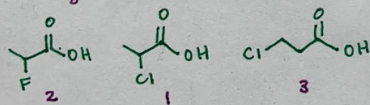
More stable A⁻ = stronger HA

- electroneg. = stable
- ↓ larger = stable

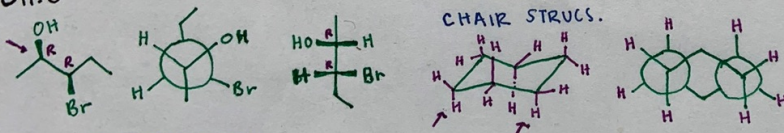
(-) charge stabilized by eneg. atoms - close to charge, more, T, eneg.

$K_{eq} = 10^{(product\ pKa - reactant\ pKa)}$

Charge Atom
Resonance
Delocalize
Inductive
Orbital

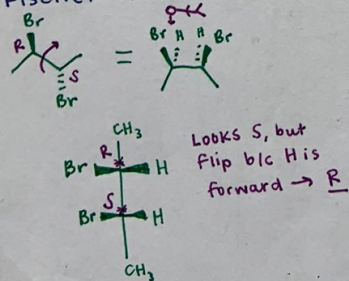


CH.3



- Most stable = lowest E
- fewest axial groups
- smaller grp. axial
- tert-butyl never axial

FISCHER PROJECTION



BASICITY

*stability of charge (not whole molec.)

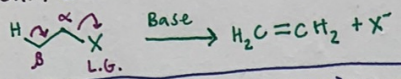
(-) > Neutral

Less stable > More stable

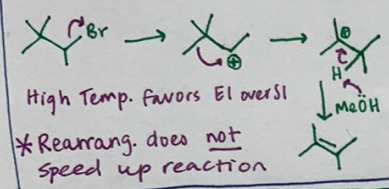
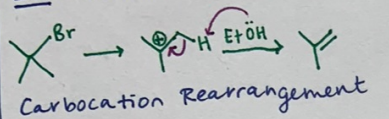
Resonating lone pair not available

EDG's > EWG's

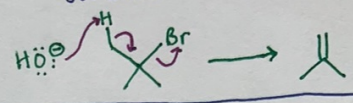
CH.7 ELIMINATION REACTIONS



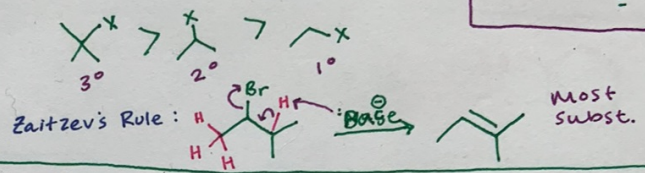
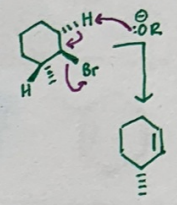
E1 - Form most stable (subst.) Alkene



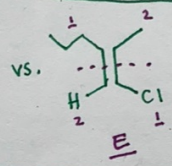
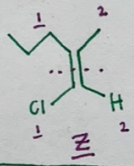
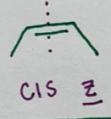
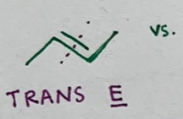
E2 - Form more stable (subst.) alkene
St. Base + Hindered L.G.



H must be ANTI to LG



ALKENE STEREOCHEMISTRY



Z - highest priority on zee zame zide

E - highest priority on opposite sides

GOOD L.G.
Cl Br I OTs on sp^3C

(-) CHARGED

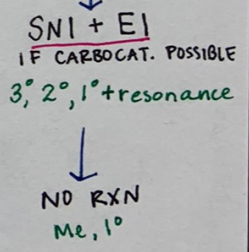
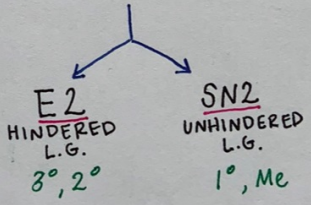
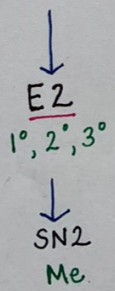
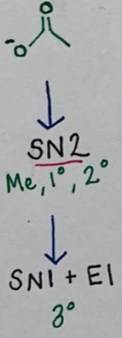
NEUTRAL

NON-BASIC NUCLEOPHILE
 $\text{RS}^- \text{X}^- \text{CN}^- \text{N}_3^-$

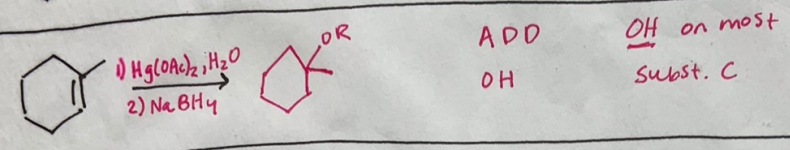
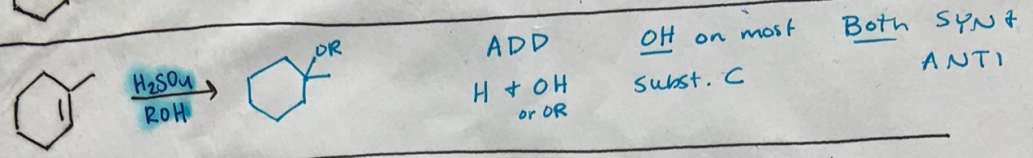
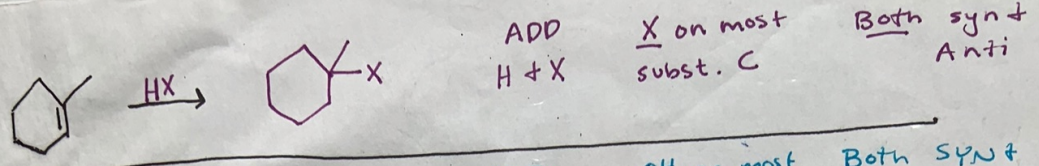
BIG BULKY BASE
CC(C)(C)[O-]

STRONG BASE / NUCLEOPHILE
CC(O-) CC(OH) CC(NH2)

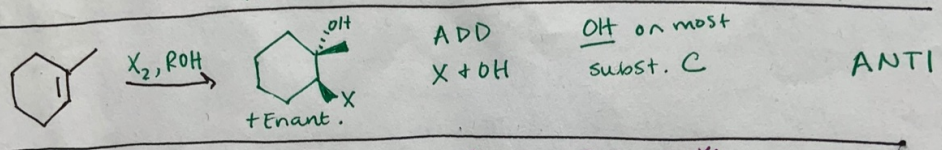
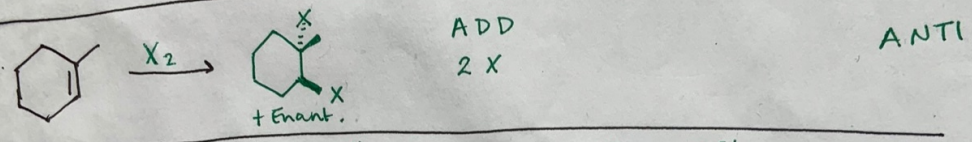
WEAK BASE / NUCLEOPHILE
CC(OH) H2O



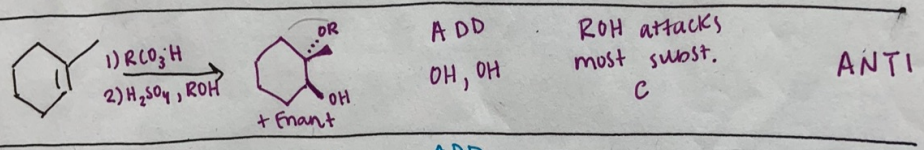
HYDRO-
HALOGENATION
OXYMERCURATION
HYDRATION



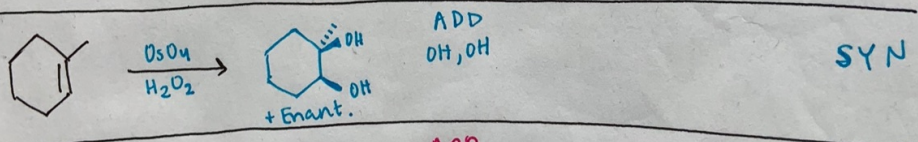
HALOGENATION



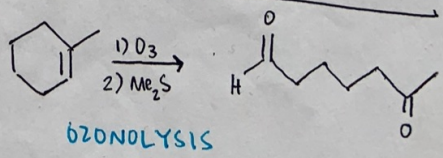
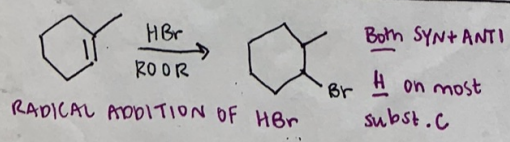
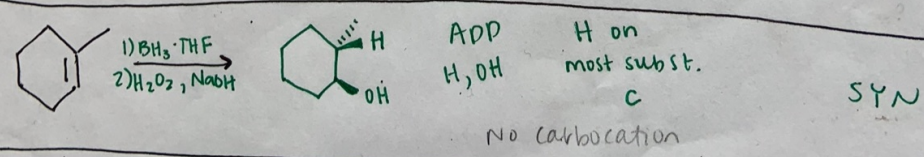
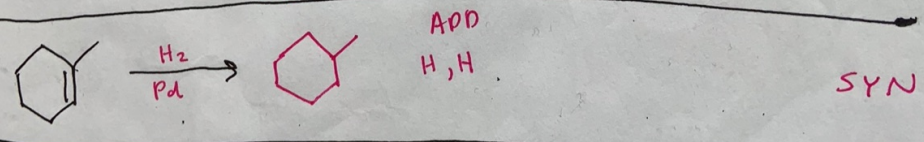
ANTI-
DIHYDROXYLATION



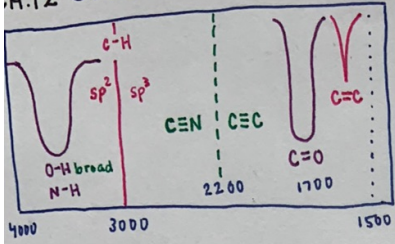
SYN-
DIHYDROXYLATION



HYDROBORATION
HYDROGENATION



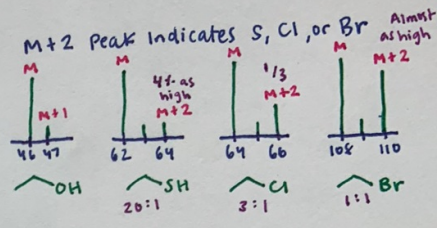
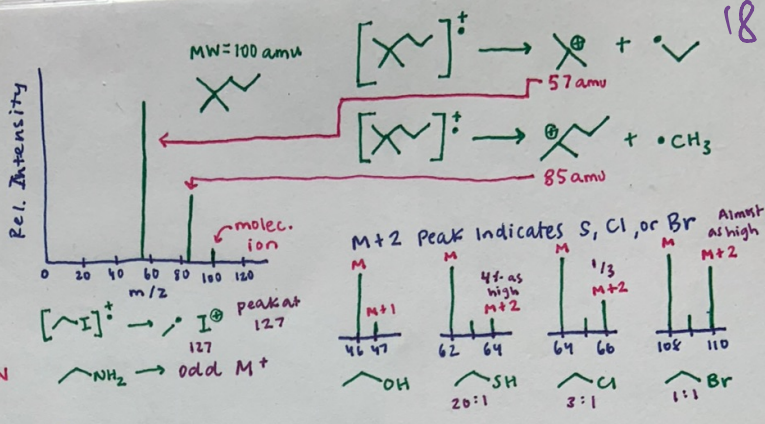
CH.12 SPECTRA



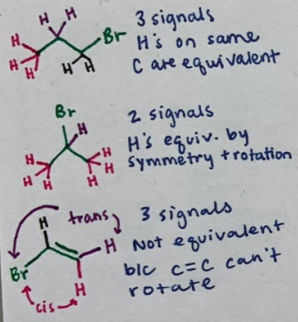
ELEMENTS OF UNSATURATION

$$E_{ou} = \frac{1}{2} (2 \cdot \uparrow C + 2 \cdot \uparrow H - \uparrow X + N)$$

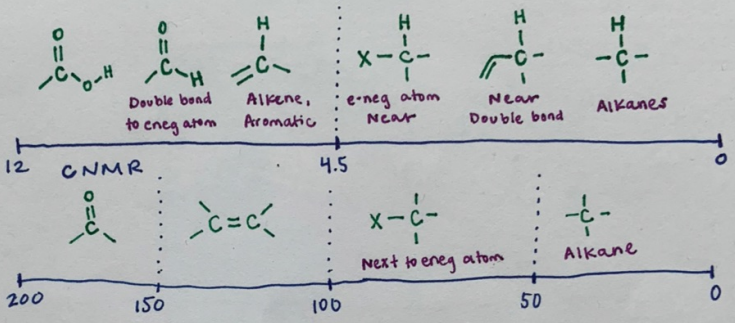
 Rings or double bonds



CH.13 NMR

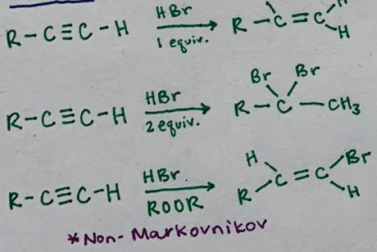


HNMR

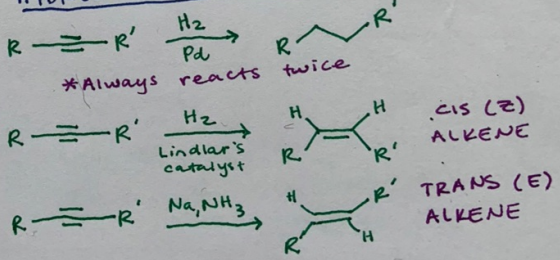


CH.9 ALKYNES

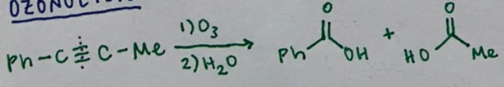
ADD H-X



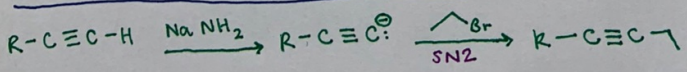
HYDROGENATION- ADD H2



OZONOLYSIS

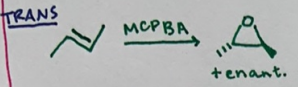
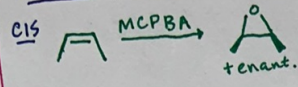


TERMINAL ALKYNES AS NUCLEOPHILES

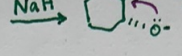
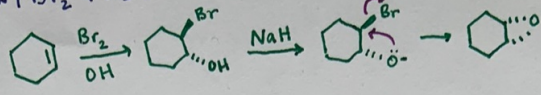


CH.14 ETHERS + EPOXIDES

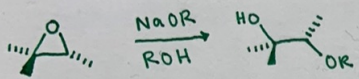
EPOXIDE SYNTHESIS



w/ Br₂ + H₂O

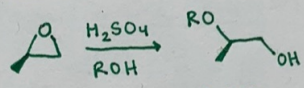


REACT W/ BASIC NUCLEOPHILES



* Attack Least subst.

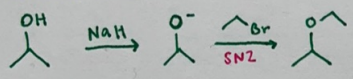
ACIDIC CONDITIONS



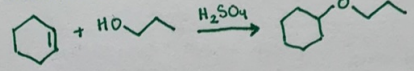
* Attack Most Subst.

ETHER SYNTHESIS

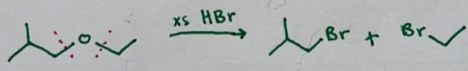
WILLIAMSON



ALCOHOL + ALKENE

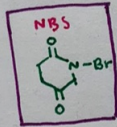
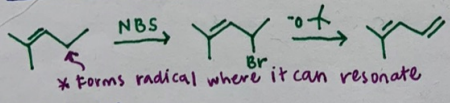


REACT W/ H-X

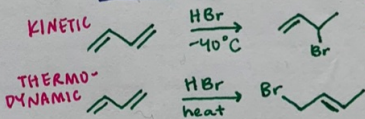


CH.15 CONJUGATED DIENES

SYNTHESIS OF DIENES - E2



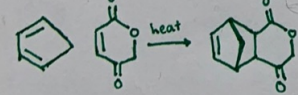
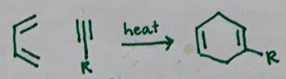
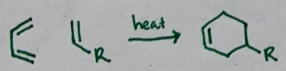
ADDITION OF H-X



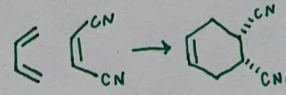
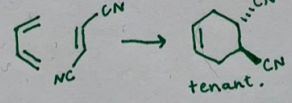
* More stable Carbocation

* More stable Alkene + Product

DIELS-ALDER



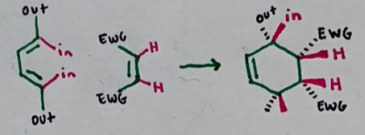
Stereochemistry



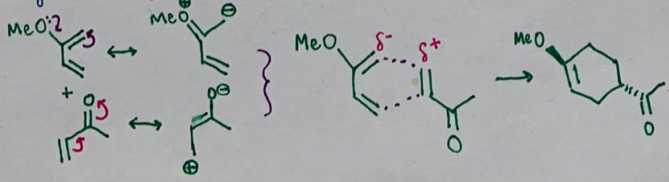
* Diene must be s-cis

* Dienophile must have EWG

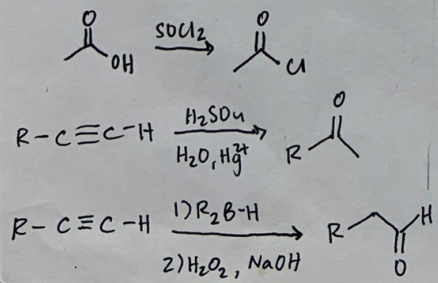
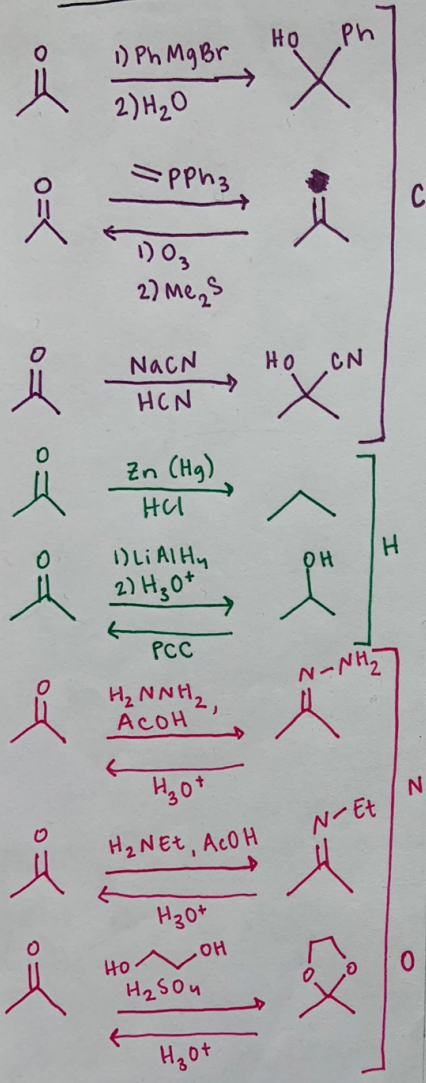
* Endo Rule:



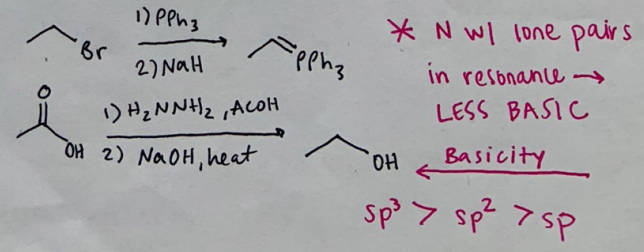
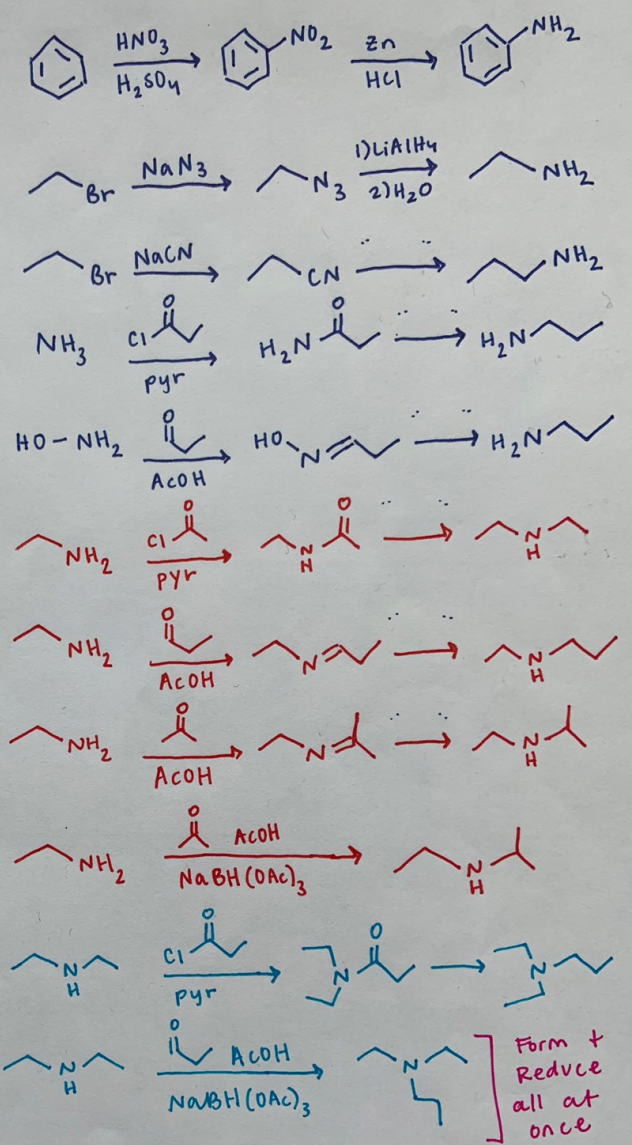
Regioselectivity * Place charge on reactive C



CH.18 KETONE REACTIONS

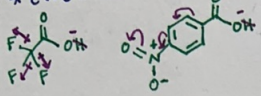


CH.19 AMINE REACTIONS 21

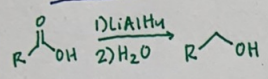


CH. 20 CARBOXYLIC ACIDS

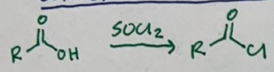
*EWG's make Acid more acidic



REDUCTION

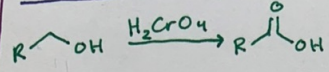


CONVERT TO ACID CHLORIDE

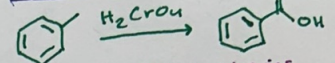


SYNTHESIS OF CARBOXYLIC ACIDS

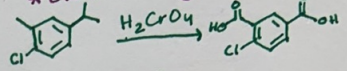
OXIDIZE 1° ALCOHOL



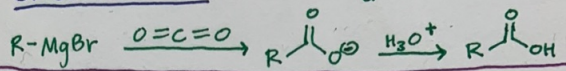
BENZYLIC OXIDATION



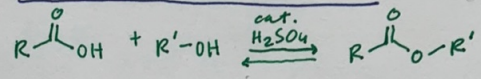
*Cleaves longer chains



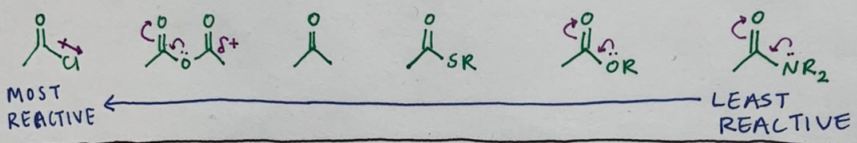
GRIGNARD + CO₂



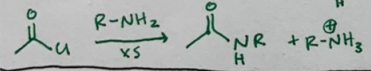
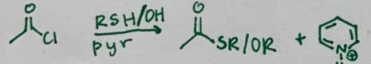
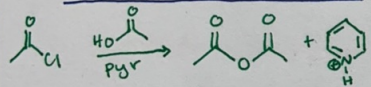
FISCHER ESTERIFICATION



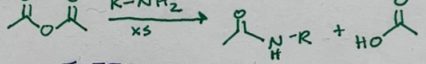
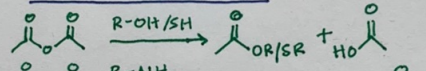
CH. 21 CARBOXYLIC ACID DERIVATIVES



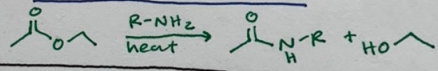
ACID CHLORIDE CONVERSIONS



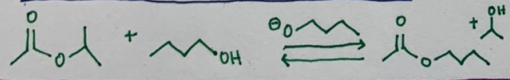
ANHYDRIDE CONVERSIONS



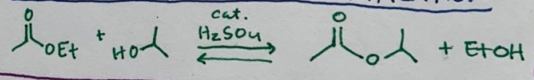
ESTER CONVERSIONS



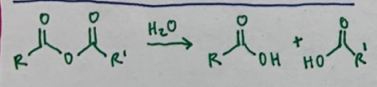
BASE-CATALYZED TRANS-ESTERIFICATION



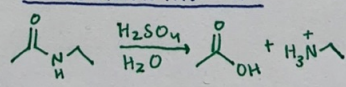
ACID-CATALYZED TRANS-ESTERIFICATION



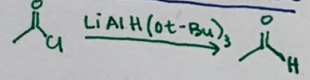
ALD CHLORIDE + ANHYDRIDE HYDROLYSIS



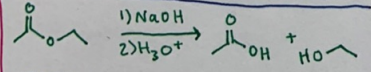
AMIDE ACIDIC HYDROLYSIS



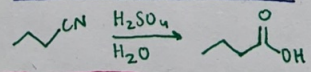
ALD CHLORIDE → ALDEHYDE



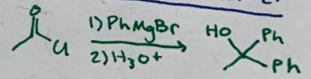
ESTER BASIC HYDRO/SAPONIFICATION



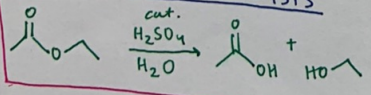
NITRILE ACIDIC HYDROLYSIS



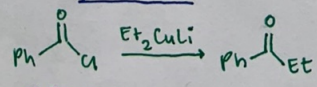
GRIGNARD: ATTACK 2°



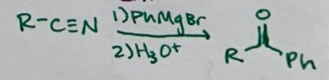
ESTER ACIDIC HYDROLYSIS



CUPRATES

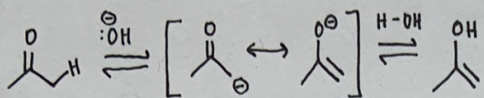


*Nitriles → Ketones React 1x

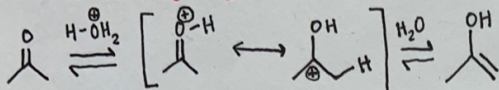


* Reacts once w/ Acid Chloride

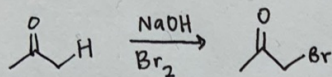
BASE-CATALYZED EQUILIBRIUM



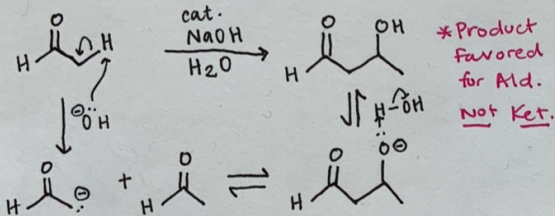
ACID-CATALYZED EQUILIBRIUM



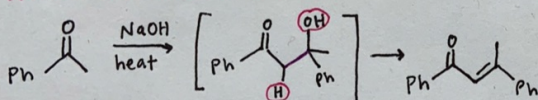
ENOLATE HALOGENATION



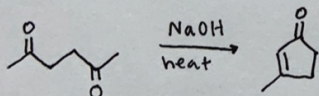
ALDOL CONDENSATION: BASE CATALYZED



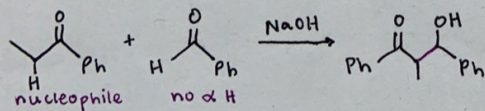
ALDOL DEHYDRATION



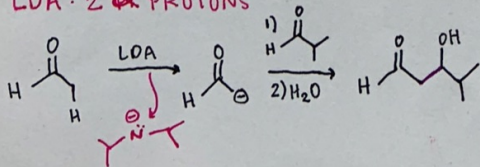
INTRAMOLECULAR ALDOL



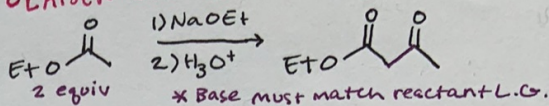
CROSSED ALDOL



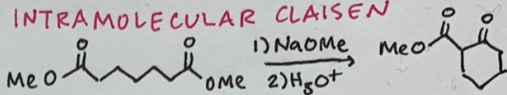
LDA: 2 α PROTONS



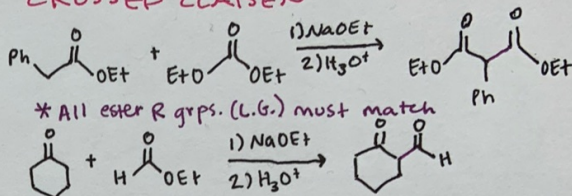
CLAISEN CONDENSATION: ENOLATE + ESTER



INTRAMOLECULAR CLAISEN

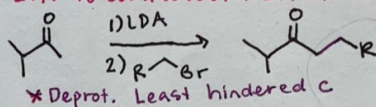


CROSSED CLAISEN

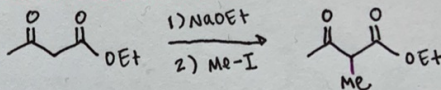


ENOLATE ALKYLATION: ENOLATE + ALKYL HALIDE

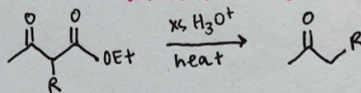
LDA TO COMPLETELY DEPROTONATE KETONE/ALDEH.



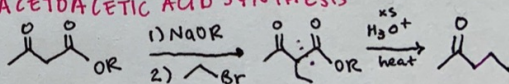
BETA-DICARBONYL COMPOUNDS



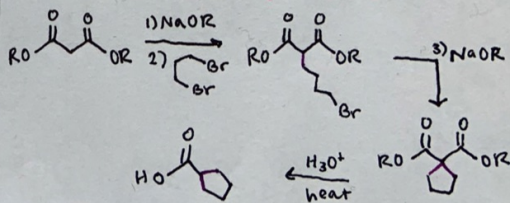
DECARBOXYLATION OF BETA-KETO ESTER



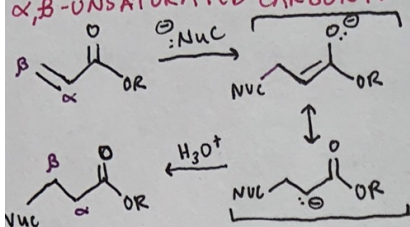
ACETOACETIC ACID SYNTHESIS



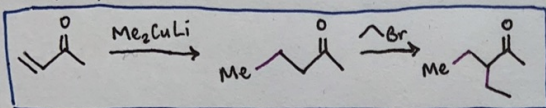
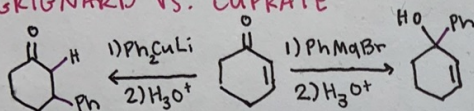
MALONIC ESTER SYNTHESIS



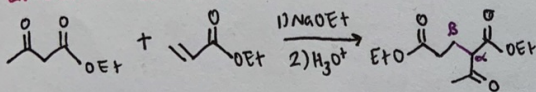
MICHAEL ADDITION
 α,β -UNSATURATED CARBONYL



GRIGNARD VS. CUPRATE

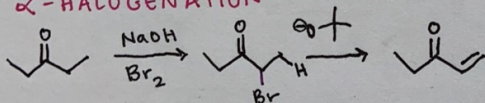


ENOLATE IN MICHAEL ADDITION

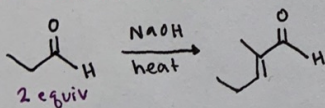


SYNTHESIS OF α,β -UNSATURATED CARBONYLS

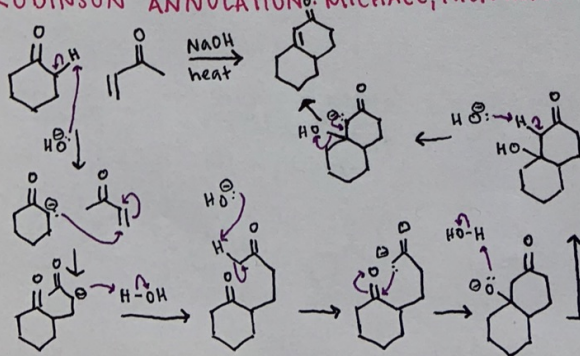
α -HALOGENATION



ALDOL/DEHYDRATION



ROBINSON ANNULATION: MICHAEL, THEN ALDOL



good luck everyone!