Alkene Nomenclature

(E) - Opposite side of =

(Z) - Zame side of =

Based on priority of groups

Configuration

(R) - clockwise

(S) - counterclockwise

(+/-) for light reflection

Elimination vs. Substitution

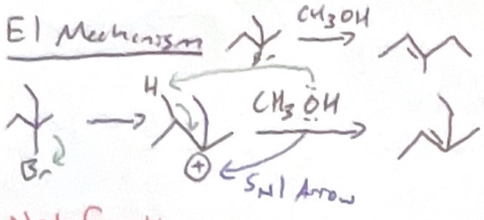
E1 prefers heat

- E1 and S_N1 compete, not favorable
- E2 and S_N2 are selective; S_N2 cannot react with 3°

E1: 3° > 2° > 1° S_N1: 3° > 2° > 1° All but S_N2 follow Carbocation stability rules!

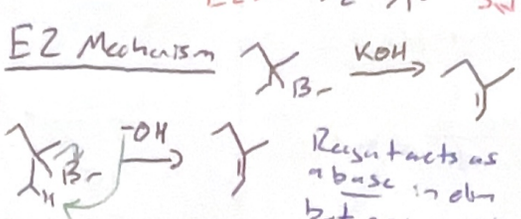
E2: 3° > 2° > 1° S_N2: 1° > 2° >> 3°

E1 Mechanism



Not favorable; rearrangements and S_N1 can occur, products yield

E2 Mechanism



Reactant acts as a base in elim but nucleophile in sub.

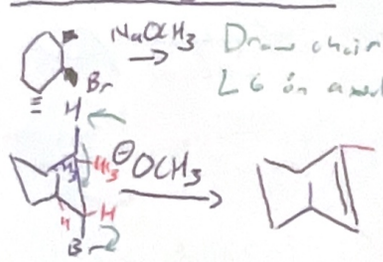
Anti coplanar H abstracted to reduce LG and base interference.

Zaitsev vs. Hoffman

Zaitsev: = ends upon more substituted Carbon, resonance alkyl groups donate e- density and increase stability

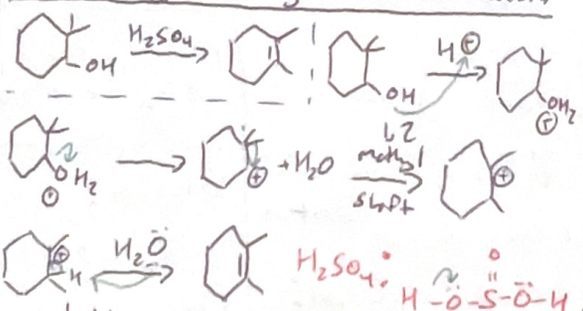
Hoffman: = on less substituted. Use bulky base ($KOtBu$) to accomplish

E2 with Cyclohexane

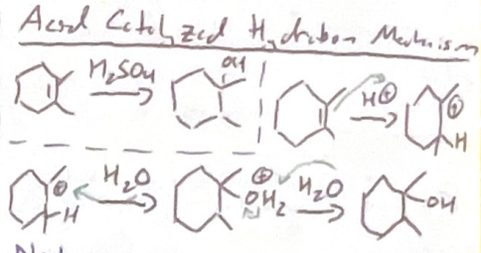


Draw chair and place LG on axial position

Acid Catalyzed Dehydration Mechanism



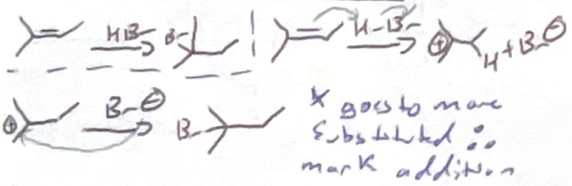
Acid Catalyzed Hydration Mechanism



Not same as reactant to left as C⊕ already stable here.

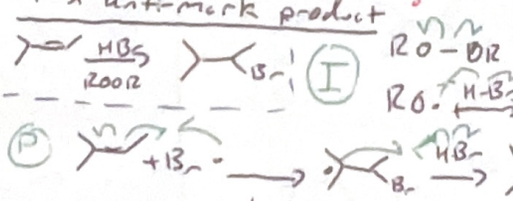
Reversible and happens in equilibrium!!

H-X markovnikov product



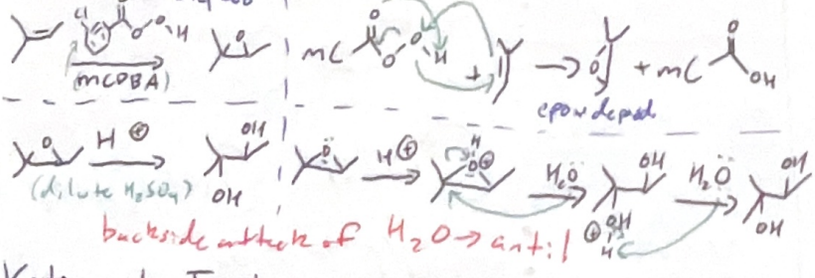
* goes to more substituted ∴ mark addition

H-X anti-mark product

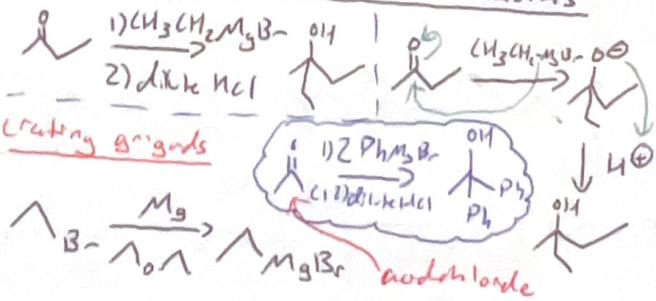


Br is added before H here, so the product is anti-mark with X on less substituted C.

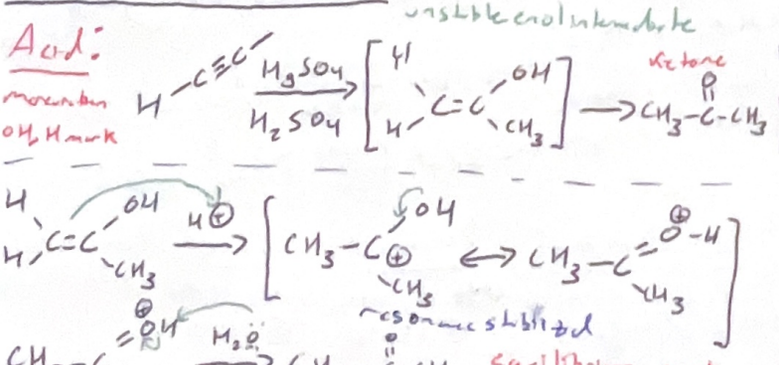
Epoxidation and Peroxide Ring Opening (acid-catalyzed)

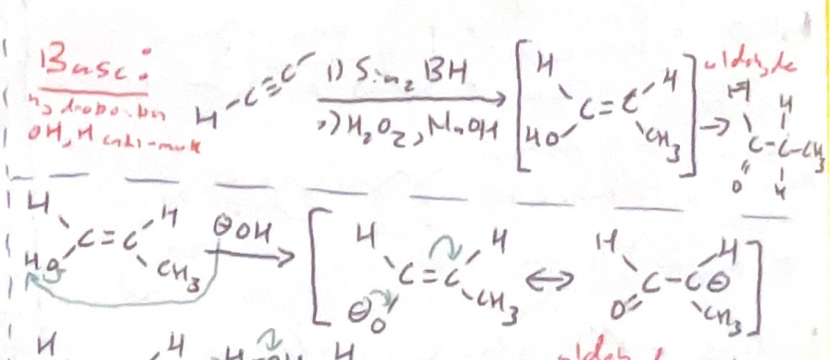


Grignard Reactions and Mechanisms

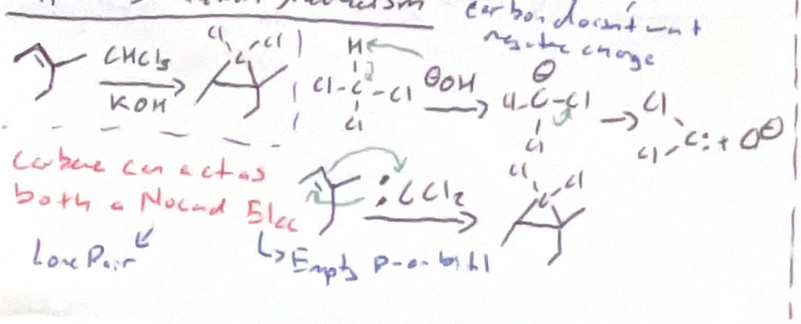


Keto-enol Tautomerism

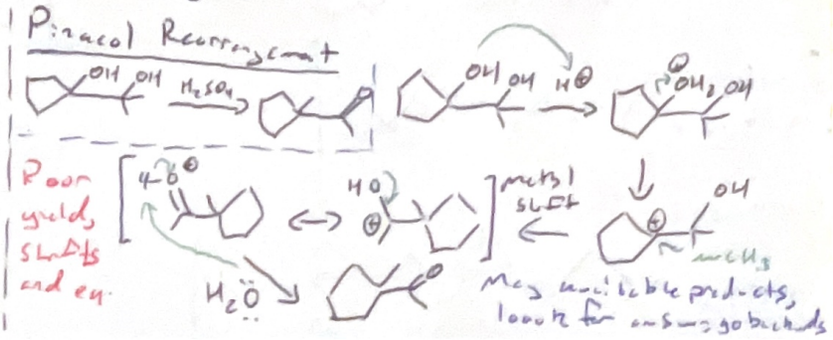




Alpha Elimination Mechanism



Pinacol Rearrangement

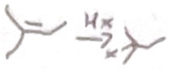


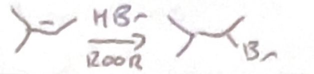
Rxn Names/Table

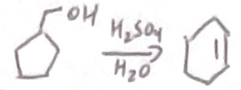
(legend: = alkenes, = alcohols, = alkynes)

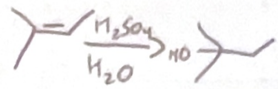
Pyridine: 

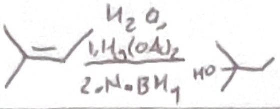
Gilman Reagent / Lithium Dialkyl Cuprate: Ph_2CuLi

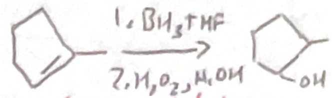
Mark HX Addition: X on more substituted; H added first


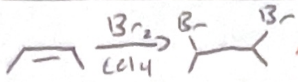
Anti-Mark HX Addition: X on less substituted; ROOR → X added first


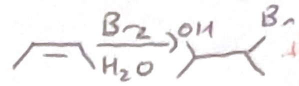
Acid Catalyzed Dehydration • H_2O removed from reactant in E1 fashion • can rearrange; methyl/hydride shift


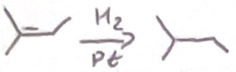
Acid Catalyzed Hydration • OH added in mark fashion • rearrangements possible


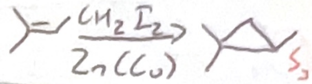
Oxymercuration/Demercuration • Adds OH in mark fashion, can't rearrange • Anti Addition


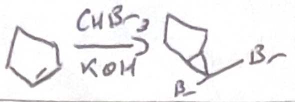
Hydroboration: Adds OH in anti-mark fashion, can't rearrange. One step, favored in synthesis. Syn addition


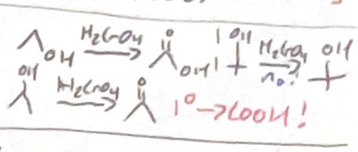
Halogen Addition • Adds 2 X across double bond • Anti


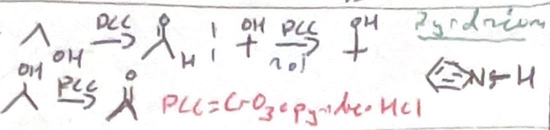
Halohydrin Formation • Adds X and OH to opposite sides of double bond • Anti


Catalytic Hydrogenation • Adds H_2 across double bond. Same for alkynes. Syn of H_2


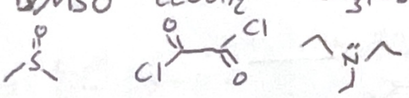
Simmon's Smith • Adds cyclopropane across a double bond. Syn


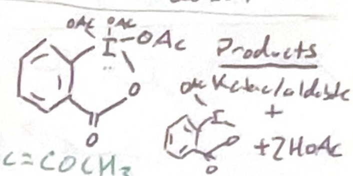
Alpha Elimination • Adds CX_2 across a double bond. Syn


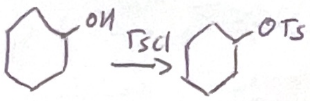
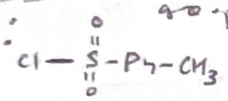
Chromic Acid • Uses a heavy metal to oxidize alcohols. $H_2SO_4 + Na_2Cr_2O_7 \rightarrow H_2CrO_4$. 1° → COOH!


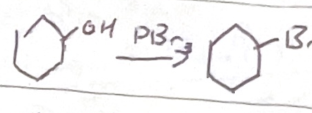
PCC: (pyridinium chlorochromate) Controllable oxidation reaction. $PCC = CrO_3 \cdot pyridine \cdot HCl$. Pyridinium


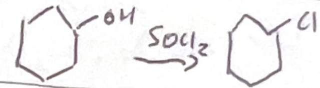
Bleach: Same as PCC. $NaOCl, H_2O$ on TEMPO. 1° → Aldehydes, 2° → Ketones, 3° → No reaction

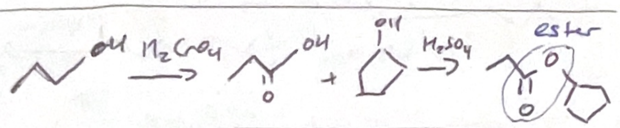
Swern Oxidation • Uses aprotic solvents as main reagent. Same rxns as PCC. DMSO, $(COCl)_2$, Et_3N:

$(COCl)_2$ is big, greasy; Et_3N: is hindered base

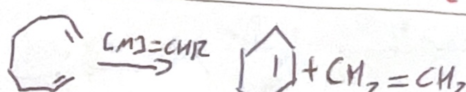
Dess-Martin Periodinane (DMP) • Takes place under mild conditions • excellent yield. Same rxns as PCC. Products: Ketone/aldehyde + ... + 2HOAc. $Ac = COCH_3$


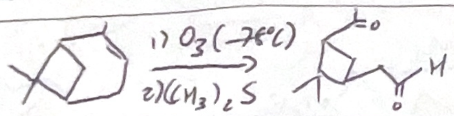
Tosylates: Converts OH into a great leaving group!

TsCl:


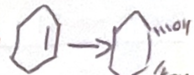
Replacing OH w/ Br: PBr_3. High yield, better than HBr, no rearrange!


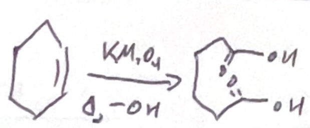
Replacing OH w/ Cl: $SOCl_2$. Use instead of $ZnCl_2$


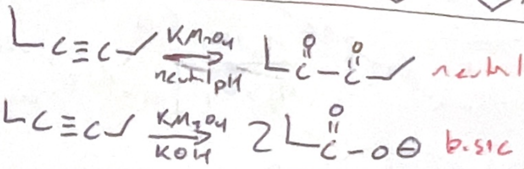
Fischer Esterification • ester


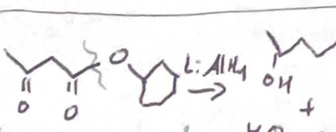
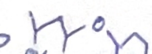
Olefin Metathesis: Removes $CH_2=CH_2$


Ozonolysis • Cleaves double bond to aldehydes. 1) O_3 (−78°C) 2) $(CH_3)_2S$


Syn Dihydroxyl Addition • works w/ either OsO_4 • or cold, dilute $KMnO_4$, ^-OH


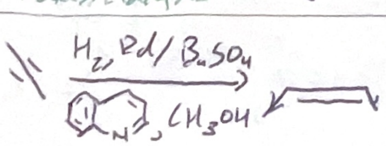
$KMnO_4$ Cleavage • Occurs if $KMnO_4$ is heated too much. Oxidizes further than ozonolysis


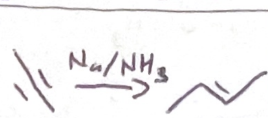
$KMnO_4$ w/ Alkynes: glycol from alkenes, diketone from alkynes. neutral / basic


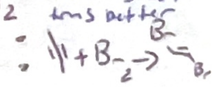
Lithium Aluminum Hydride • Ester destroyed → two alcohols. Cleaves esters, reduces ketones/aldehydes

$NaBH_4$ →


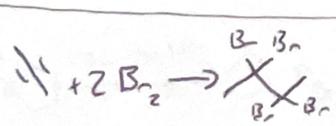
Alkyne Elimination: Need geminal or vicinal dihalides. Turns halides into alkynes

Terminal	Internal
Use $NaNH_2$ @ 150°C	Use KOH @ 200°C

Lindlar's Catalyst • Alkynes to alkenes with cis (Z) stereo!


Trans alkenes from Alkynes


1 mol X_2 to alkyne: cis/trans, but trans better


2 mol X_2 to alkyne


Williamson Ether Synthesis • Tosylates works too. S_N2