CHM2120 A Lecture 21 Dec 4, 2012

- last sapling assignment Due Dec 12th.

Today – No new content!

Review - key mechanism, key concepts & key reactions

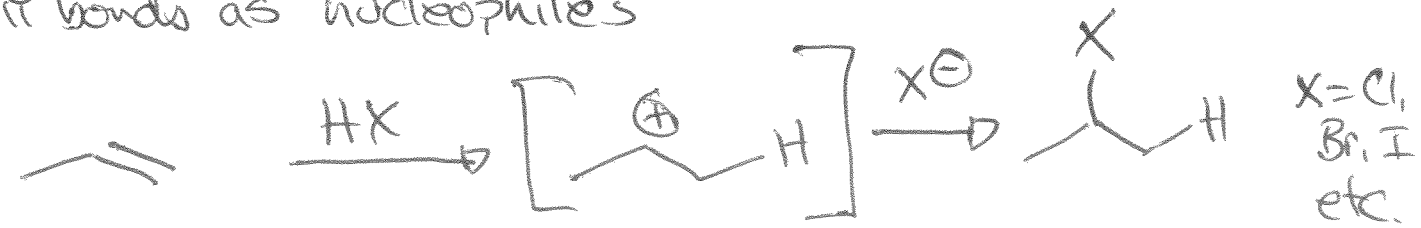
CHM1321

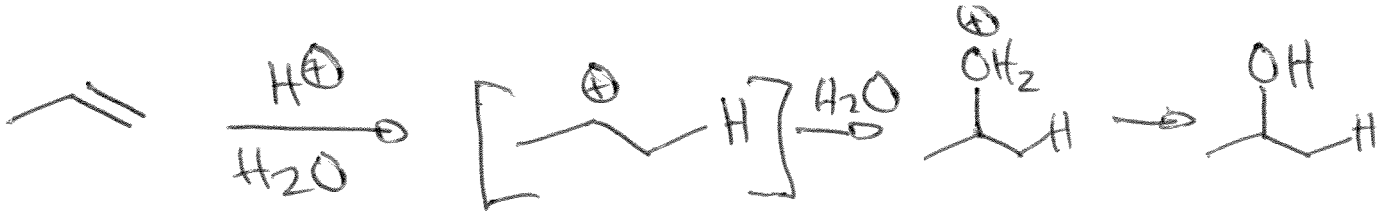
Mechanisms: π bonds as nucleophiles, EAS, addition of strong nuc to carbonyls.

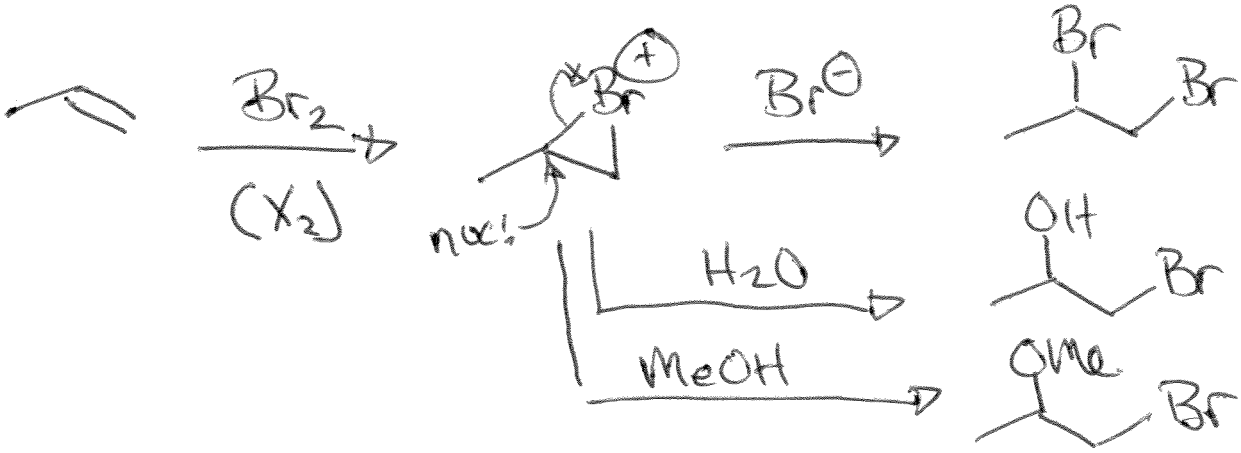
concepts: acid-base chemistry (pka), electrophilicity, nucleophilicity, regiochemistry

Key rxns

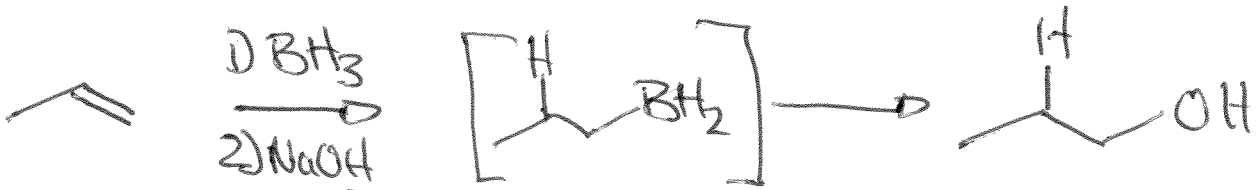
π bonds as nucleophiles

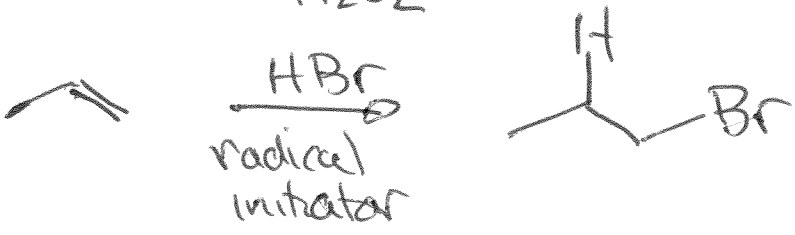




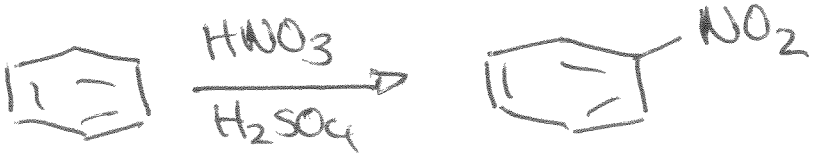


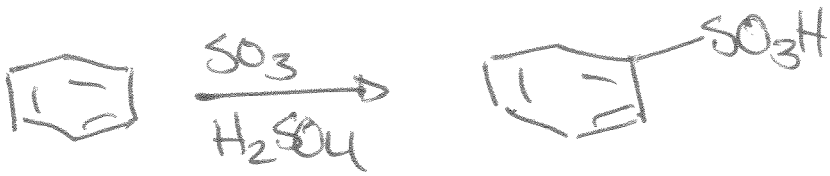
Anti. Markovnikov

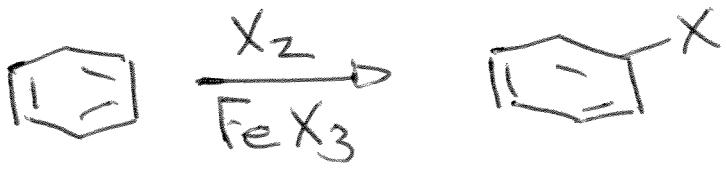




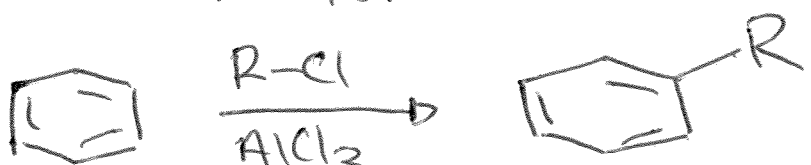
EAS



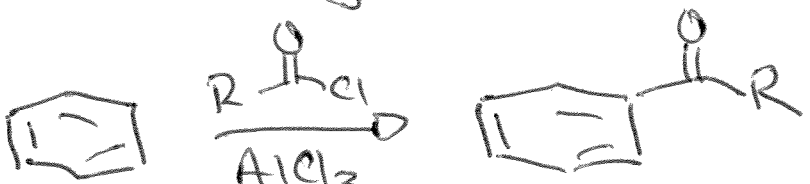




X = Cl, Br

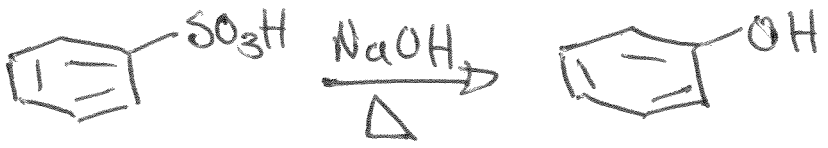


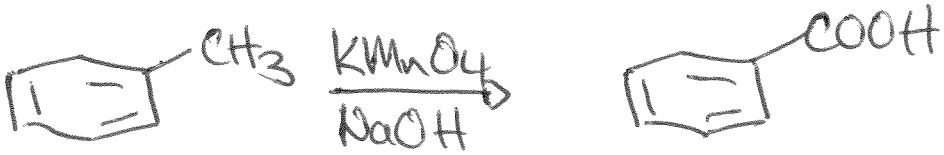
note R can rearrange to make more stable cation

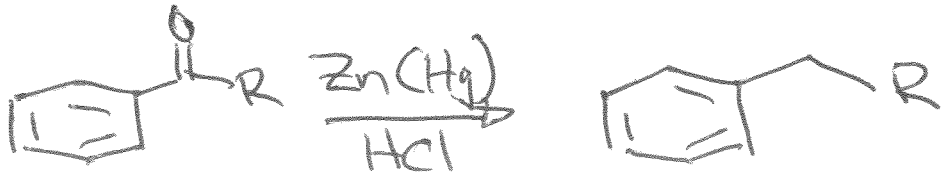


note these EAS reactions only work on aromatic rings!

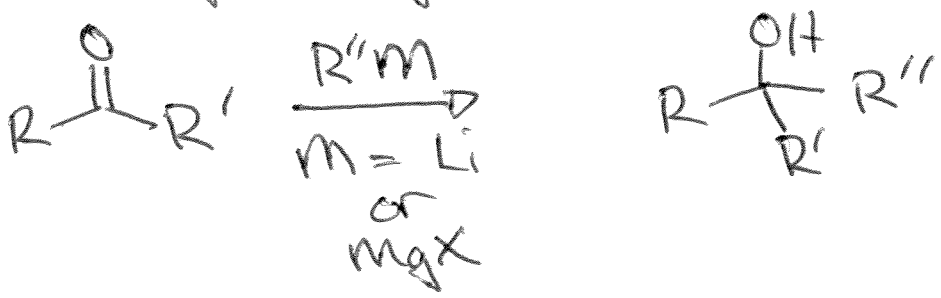
Functional group transformations of EAS products.







Addn of strong nuc to C=O

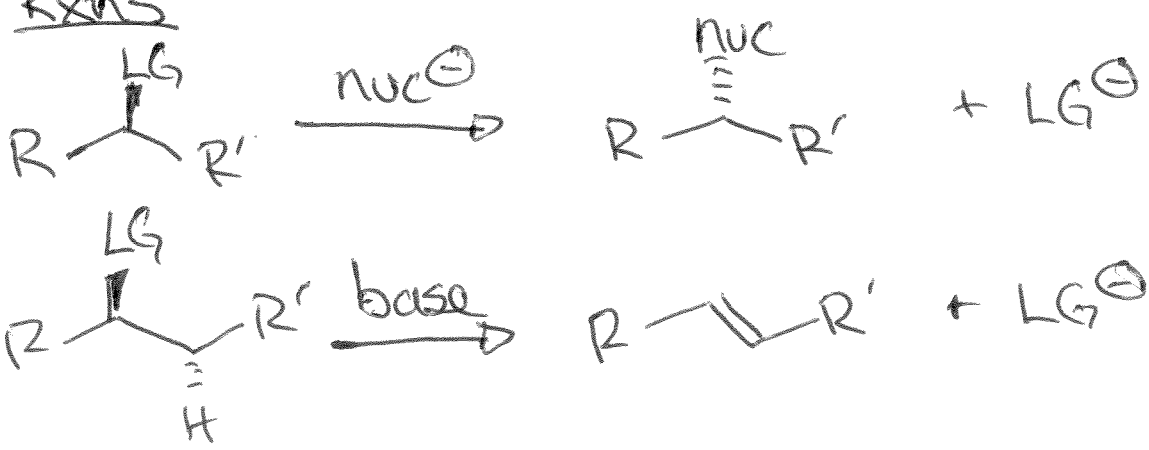


2120 up to Midterm 1

Mechanisms: S_N1, S_N2, E_1, E_2

Concepts: reaction coordinates, transition states, rate determining step, Leaving group. IR.

Rxns



IR - vibrational spectroscopy - ID functional groups.

FG	cm^{-1}
C=O	1600 - 1800
C-H sp^3	2900 - 3000
C-H sp^2	3000 - 3100
OH	3300 - 3600
COOH	2700 - 3300

Midterm1 - midterm2

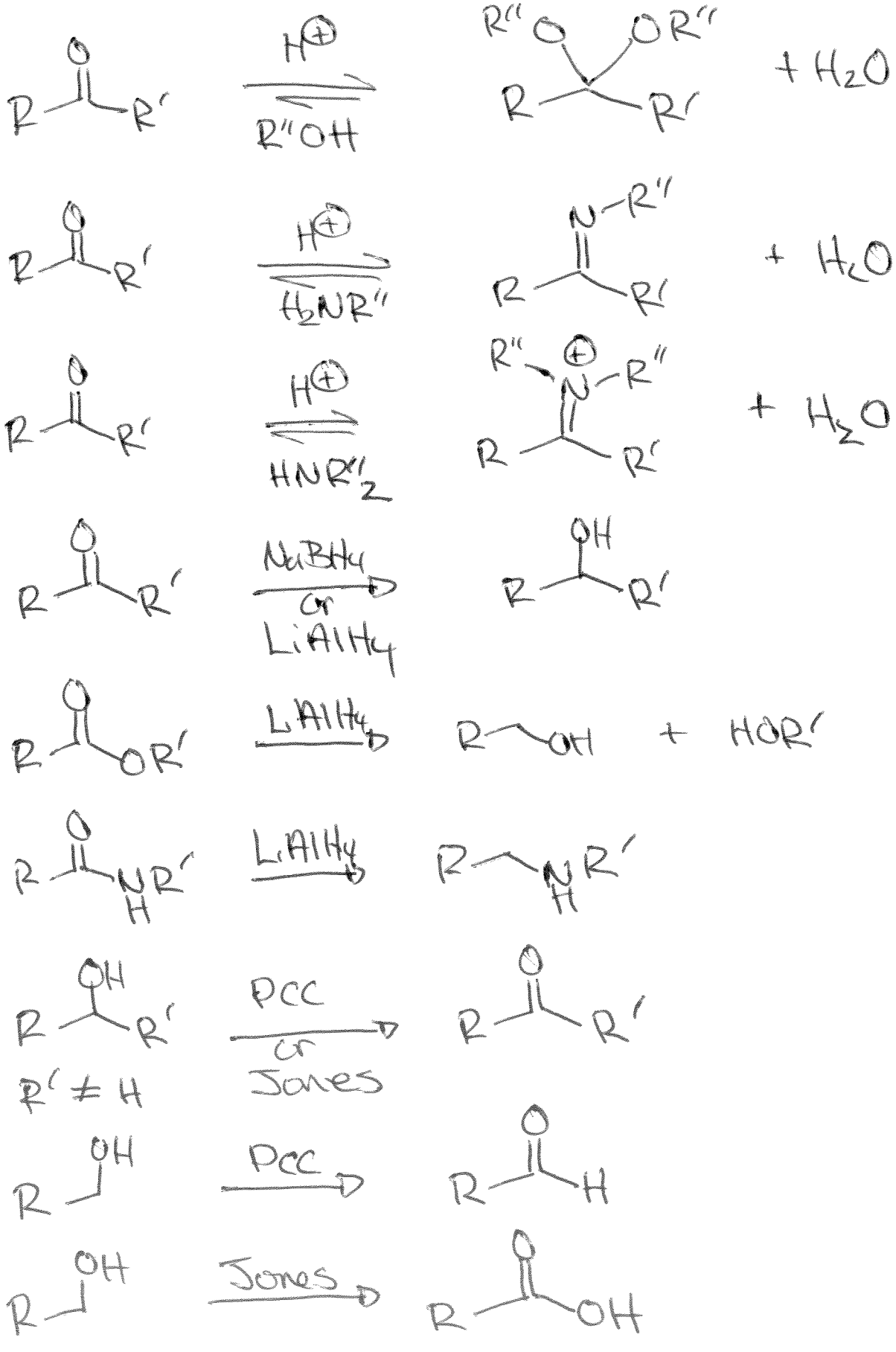
Mechanism: addition of weak nuc to carbonyls, addition of strong nuc to carbonyls, Reduction, Oxidation. Wittig, Baeyer Villager

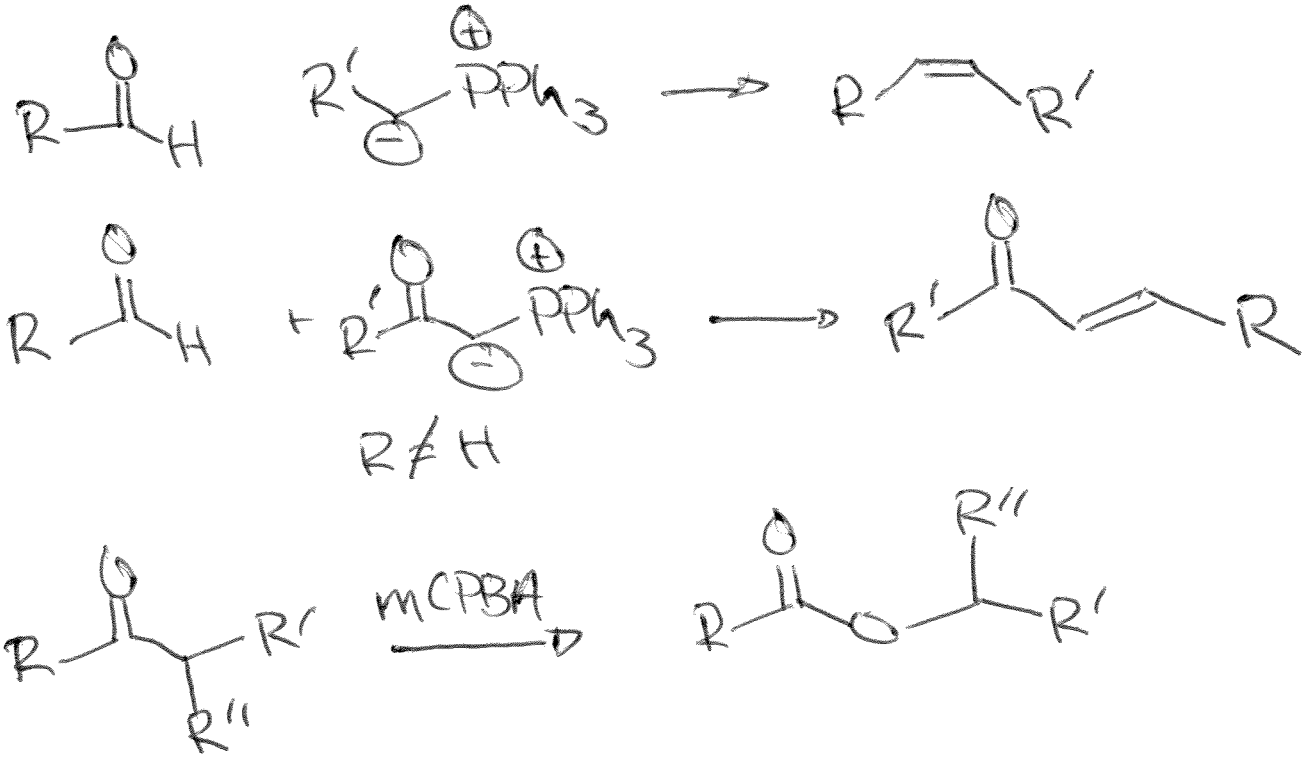
concepts: reversible vs irreversible addn to C=O, stereochem of wittig rxn, ^{1}H NMR.

^{1}H NMR - looks at chemical environment for <u>all</u> Hs in a molecule.

FG.	δ (ppm)
alkanes (no EWG).	0.5-1.8
C-H (weak EWG).	2-3
C-H-O (strong EWG).	3.5-5 ppm.
alkenes.	5-6.5
aromatics	6.8-8.5.

Key rxns.


H⊕
R''OH
+ H2O
H⊕
H2NR''
+ H2O
H⊕
HNR''2
+ H2O
NaBH4
or
LiAlH4
LiAlH4
+ HOR'
LiAlH4
PCC
or
Jones
R' ≠ H
PCC
Jones

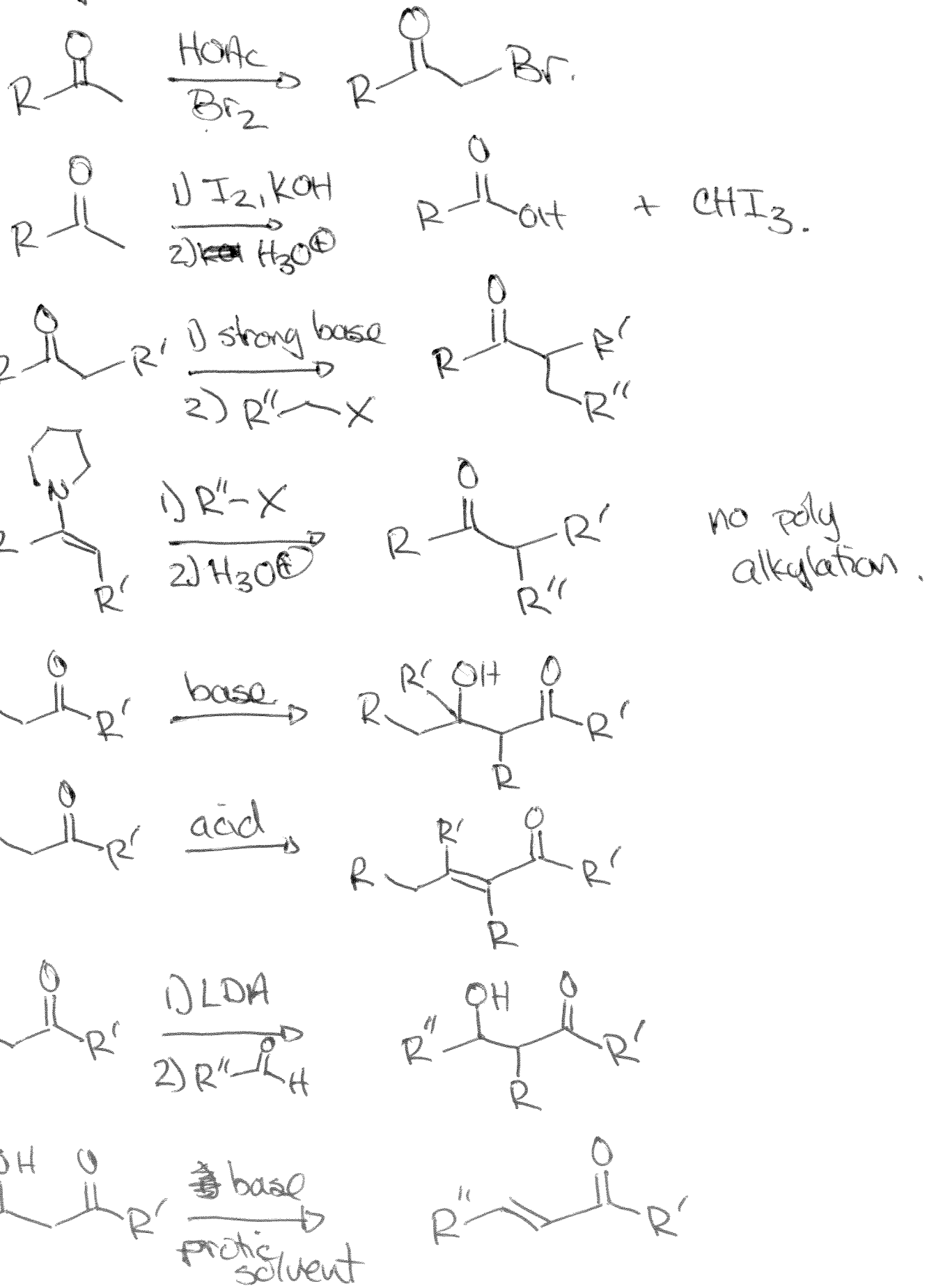


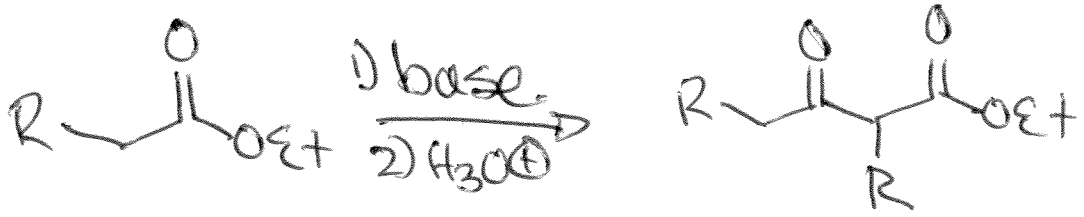
Midterm 2 - Final

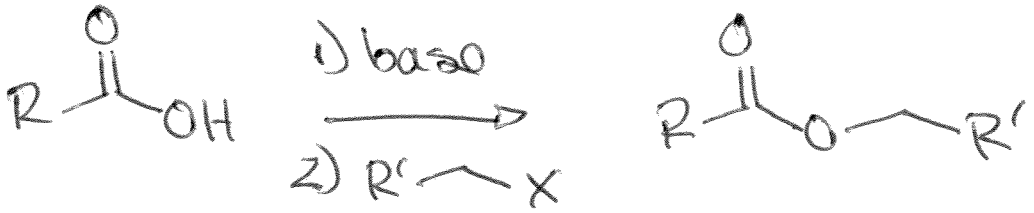
Mechanisms: carbonyls as nucleophiles (enolization, alkylation, Haloform, α-halogenation, Stork enamine synthesis, Aldol reaction, Claisen) nucleophilic ester formation, Fisher esterification, acid chloride formation saponification, Ecb, decarboxylation.

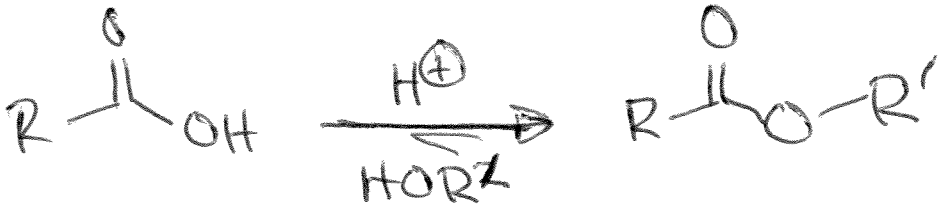
Concepts: tautomerization, kinetic / thermodynam enolates, electrophilicity of carbonyls. activated "esters"

Key rxns


HOAc
Br_2
Br
1) I_2, KOH
2) $H_3O^{\oplus}$
OH
+ CHI_3.
1) strong base
2) R''–X
1) R''–X
2) $H_3O^{\oplus}$
no poly alkylation.
base
OH
acid
1) LDA
2) R''–CHO
OH
base
protic solvent


1) base
2) H_3O^+

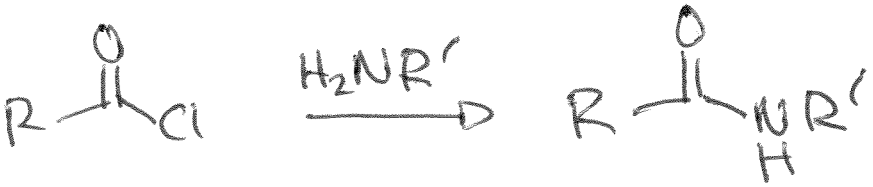

1) base
2) R'—X

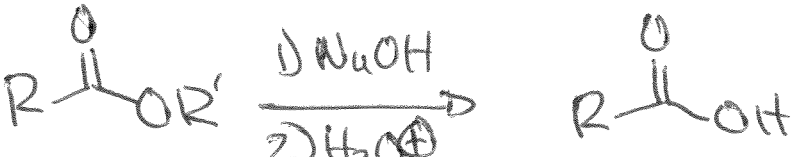

H^+
HOR'

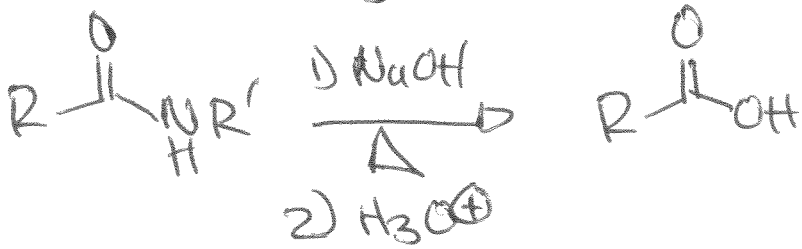
1° ; 2° alcohols.

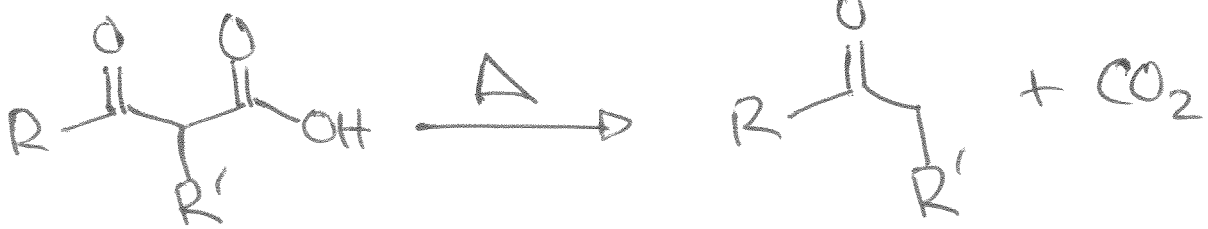

$SOCl_2$


R'OH


H_2NR'


1) NaOH
2) H_3O^+
+ HOR'


1) NaOH
Δ
2) H_3O^+
+ H_2NR'


Δ
+ CO_2