Wittig Reaction ← not on Exam 1

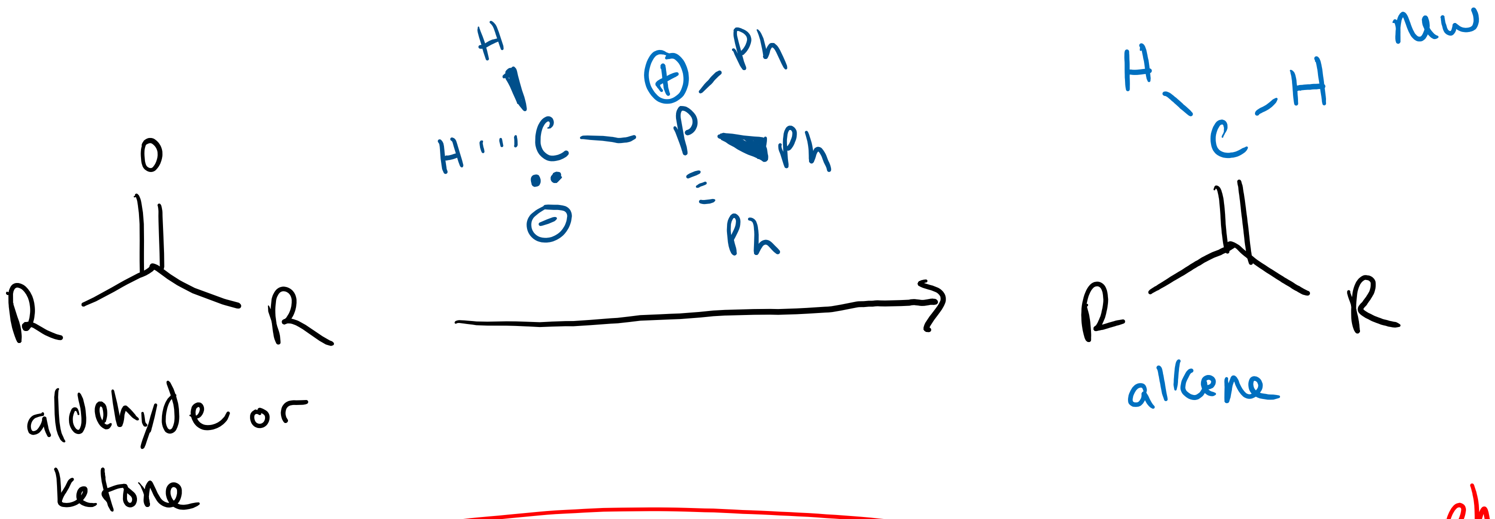
Exam 1 Review

2/15/2023

Wittig Reaction

(19.10)

(Not on Exam 1)



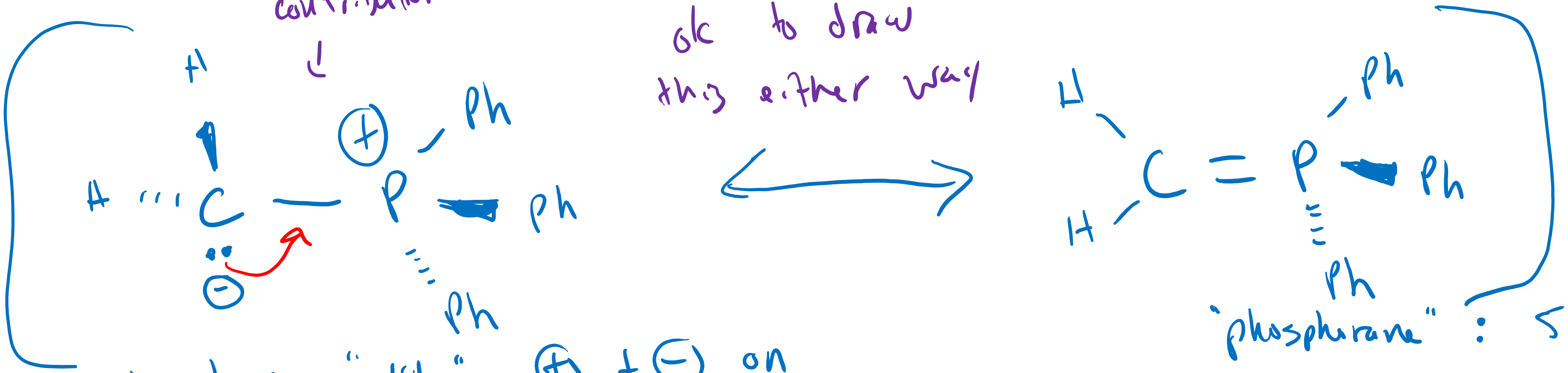
$O=PPh_3$

triphenylphosphine oxide

phosphine: $:PR_3$

larger resonance contributor !

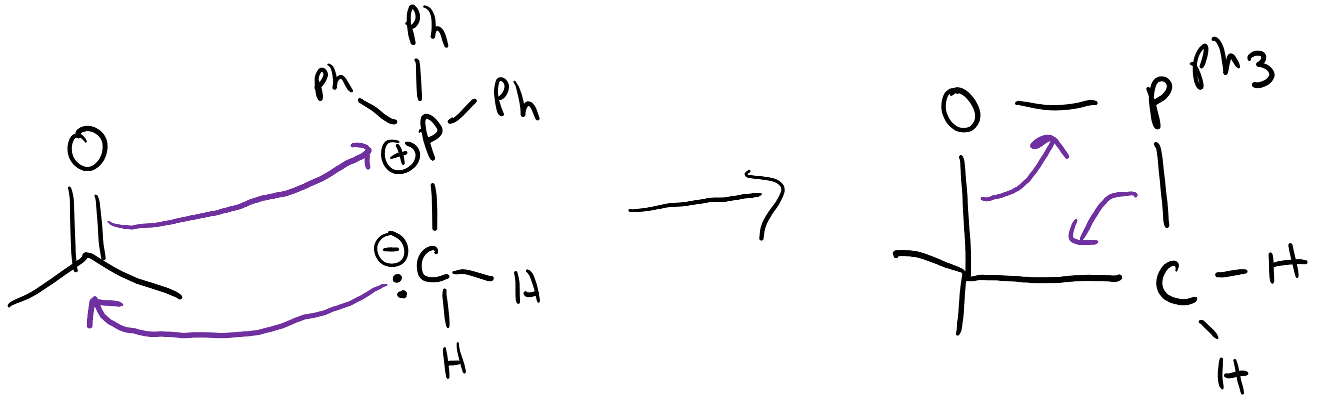
ok to draw this either way



phosphorus "ylide" - ⊕ & ⊖ on adjacent atoms, but neutral overall

"phosphorane": 5 bonds to P

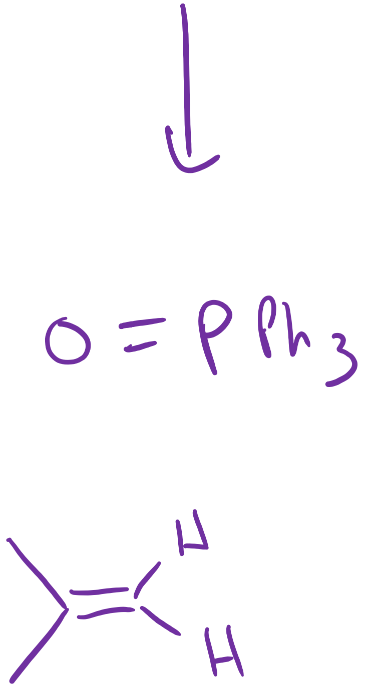
Wittig Reaction: Mechanism



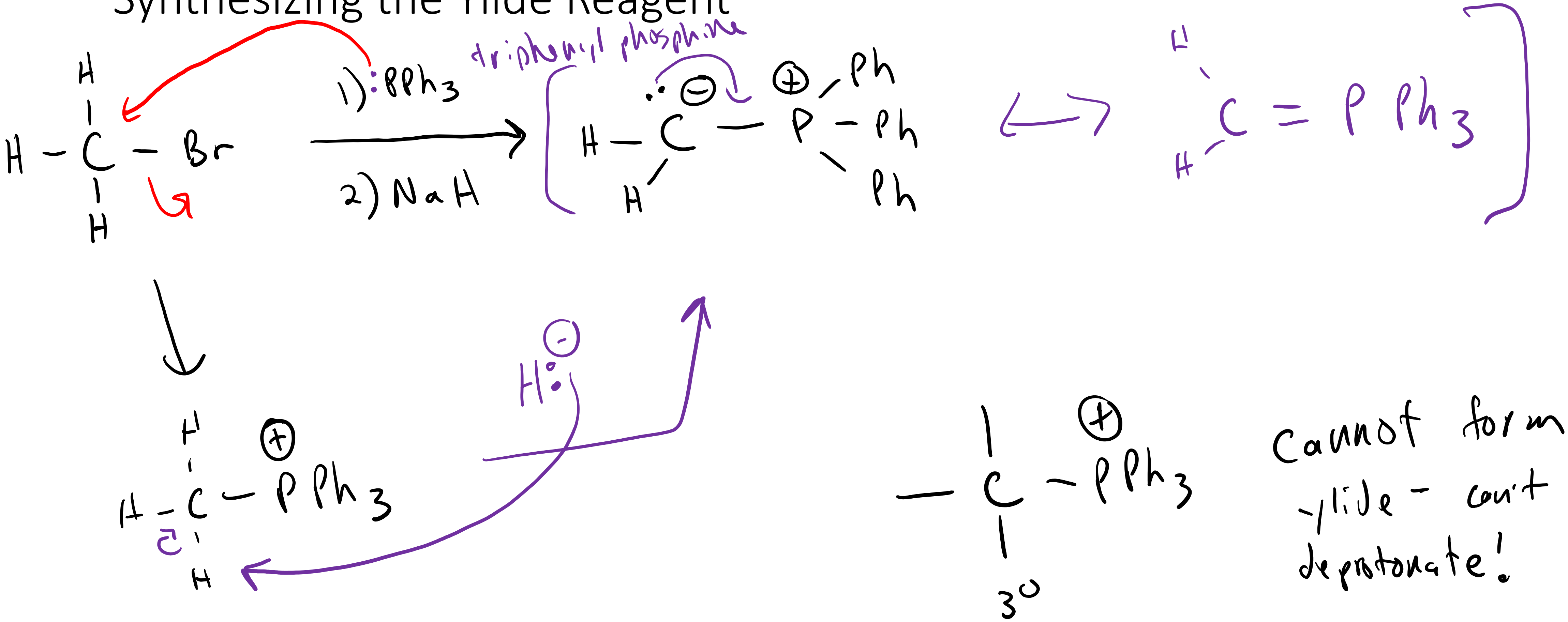
oxaphosphetane

mech. geometry is more complicated when reactants are assymmetrical.

I will only ask for this mech. without stereochem



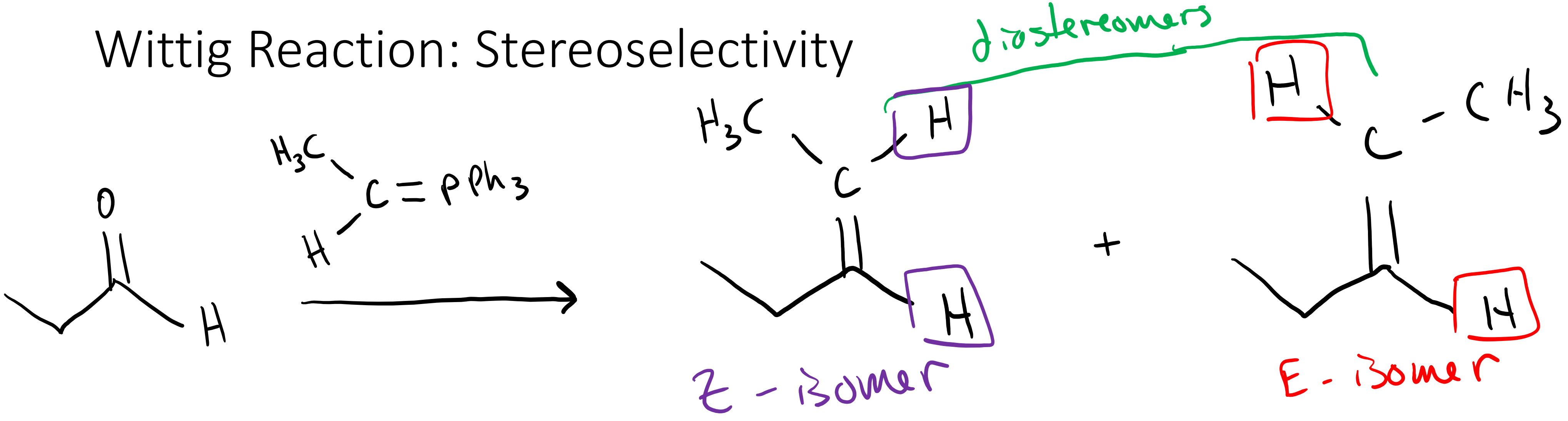
Synthesizing the Ylide Reagent



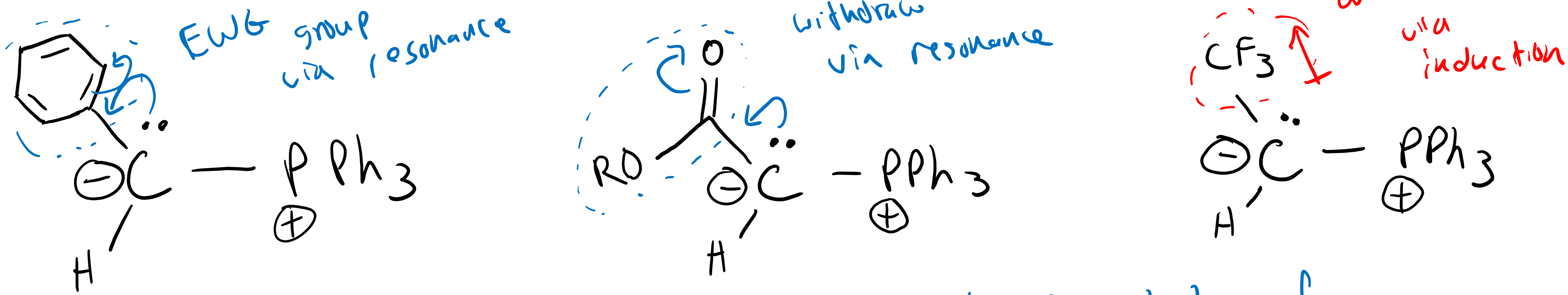
Cannot form ylide - can't deprotonate!

$-CH_3$ faster than 1° alkyl halide, faster than 2° alkyl halide

Wittig Reaction: Stereoselectivity



major product for "simple ylide"



ylides w/ EWG are "stabilized ylides", react more slowly, favor more stable E-isomer

Ch 18: EAS and S_NAr

Know….

- each group we can install and the reagents to do so.

H^+
$KMnO_4$

- how to transform those groups (ie $NO_2 \rightarrow NH_2$, $CH_3 \rightarrow COOH$, $CH_3 \rightarrow CBr_3$)

- the directing and activating/deactivating effects of each group we discussed + strengths (moderate vs strong)
  be able to explain the *origin* of those effects using resonance structures

- limitations of F-C reactions

- blocking/unblocking para position

- mechanisms we discussed in class (including generating electrophiles if we showed that in class)

- S_NAr reagents and restrictions

- There will be an EAS synthesis question.

Ch 12: Alcohols

Know…

★ new from last semester

- how to make an alcohol from an alkene (Markovnikov and anti-Mark. recipes)
- how to name (simple) alcohols
- how to calculate oxidation state of carbon in organic molecules
- how to determine whether a given atom has been oxidized or reduced in an overall reaction
- $\overset{6+}{\text{Cr}}$-based oxidation of alcohols: reagents and mechanisms (that we discussed in class)
  - You do NOT need to show arrows for generation of the chromate ester.
  - Aqueous vs nonaqueous → (PCC) CH_2Cl_2

$HO-\overset{O}{\underset{}{\text{Cr}}}-OR$ with $=O$, $=O$

- "Green oxidation" reagents and why they are generally preferable to Cr^{6+}
- Reactions at the –OH group itself:
  - Making it a better leaving group (★TsCl, pyr; or ★$SOCl_2$; or PBr_3. Mechanisms for first 2)
  - Deprotonating (use NaH) to make an alkoxide nucleophile

Ch 19: Aldehyde and Ketones as electrophiles

Know…

- All the reactions on the Ch 19 recap of the last handout
  - And the reverse reactions for N and O nucleophiles (hydrolysis)
- Mechanisms that we discussed in class + enamine hydrolysis (which we did not fully draw, but I said some words about it, so that counts)
- Limitations of alkyllithium and Grignard reagents (no acidic FG's in substrate!)
- How to synthesi~~s~~ze alkyllithium and Grignard reagents from alkyl halides

  Li^0 (s) Mg^0 (s)

  R-Li R-MgBr R-Br
- Stereochemistry (* at new chiral centers) for H and C nucleophiles
- Relative electrophilicty of aldehyde and ketones and consequences for reactivity
- Protecting/deprotecting aldehydes using acetal formation/hydrolysis

cat. H_2SO_4

Probably some other things too

The last 3 slides are not a comprehensive list. These are just the most important things that came to mind for me from each chapter!

On the exam, you can expect:

- 1-2 mechanisms
- 1 EAS synthesis (open ended)
- Some fill-in-the-blank reaction schemes
- Some guided synthesis
- "Flawed" synthesis – identify and fix the mistake
- Naming
- Conceptual potpourri

(mixture

Approx 5 pages. Designed to be completed in about 1 hr 15 min total, so you should have plenty of time!