CHEM 222 section 01

LECTURE #04 Thurs., Sept.13, 2007

Lecture topics & readings

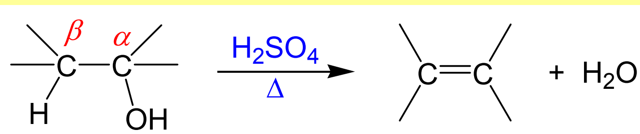
Today's class
- continue reactions of alcohols: elimination, oxidation

Before next class
- read all of Ch.10
- **practice** in-chapter examples
  end-of-chapter problems (#43a-h,44,49,52,57,61,71)

Next class
- finish Ch.10 rxns
- on your own: work on <u>rest</u> of problems listed in syllabus

(1)

ROH rxn type 3: Elimination rxns of alcohols (Bruice 10.4)



Reagents:
- H_2SO_4 or H_3PO_4 (conc. strong acid with non-Nu anion) *OR*
- $POCl_3$ / amine *(special: for acid-sensitive compounds)*

Trends:
- Substitution rxns compete: yielding ether products…
  1. avoid good Nu's in rxn mixture (*e.g.,* H~~Br~~)
- To drive elimination rxn forward:
  1. HEAT IT UP: entropy-favoured reaction!
  2. REMOVE PRODUCT: $bp_{alkenes} < bp_{ROH}$ ⇨ distill
- Rxn involves converting OH to good LG
- More highly substituted ROH dehydrate more easily: 3° > 2° > 1°

General mechanism: **Activation (make good LG)** + **Elimination (E1 or E2…) (B: takes β-H⁺, LG leaves)**

General mechanism: **Activation** **+** **Elimination (E1 or E2…)**
(make good LG) **(B: takes β-H$^+$, LG leaves)**

3a) for 2°& 3° ROH: E1 pathway

Review 221; on board…

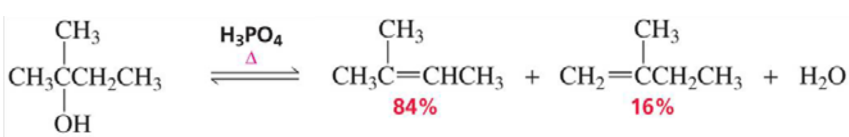
(3)

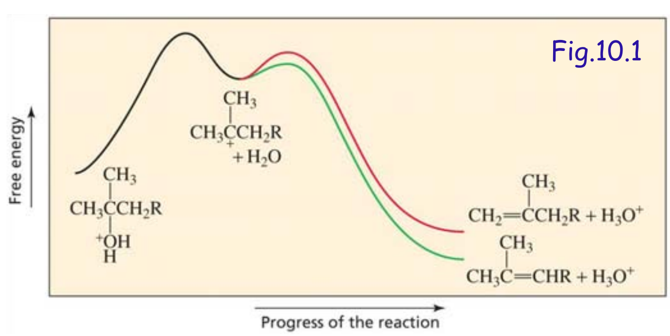
Regiochemistry for alcohol dehydration

Review 221: Ch.9

Zaitsev's rule: more highly substituted alkene product dominates

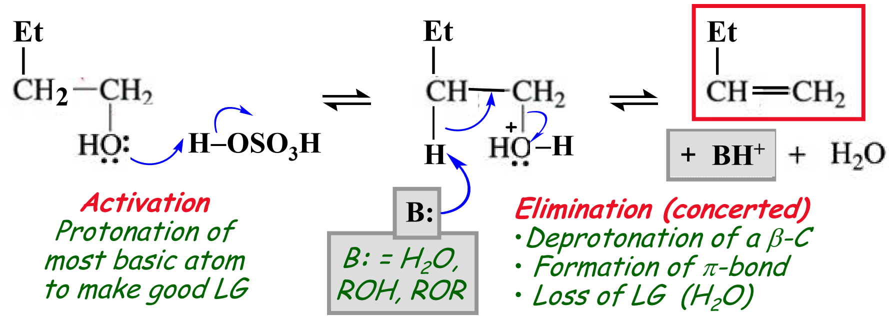
- When >1 alkene could form: major product = most stable alkene
- Recall:
  - more stable alkene ⇨ ‡ leading to it is more stable *(resembles it…)*



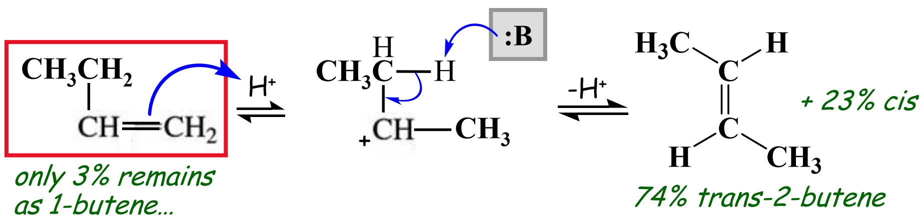


(4)

3b) for 1° ROH: starts via E2 pathway (1° C+ too unstable)

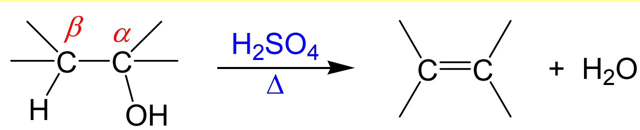


BUT THEN, because acid present ⇨ subsequent H⁺'n & re-H⁺'n …



OVERALL: obtain same regio- & stereo-chemistry as E1 pathway!

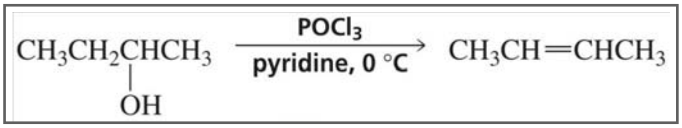
Summary: Elimination rxns of alcohols



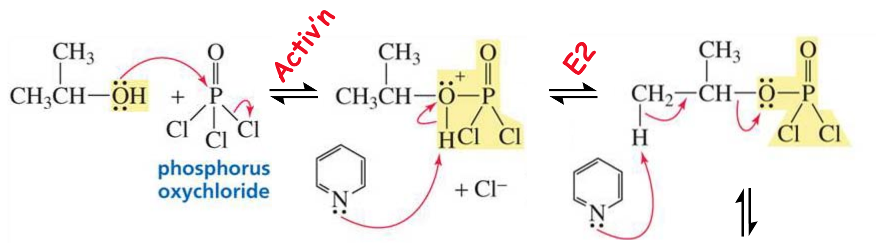
Most common reagents:
- H_2SO_4 or H_3PO_4 (conc. strong acid with non-Nu anion)

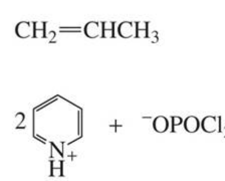
Summary of outcome:
- Substitution rxns compete: yielding ether products…
- More highly substituted ROH dehydrate more easily: 3° > 2° > 1°
- RXN UNDER THERMODYNAMIC CONTROL:
  - Rxn done at elevated temperature for long period of time
    - ⇨ Rearrangements, re-protonation/de-protonation, *etc…*
    - ⇨ System reaches equilibrium
    - ⇨ **Most stable alkene product dominates**

3c) Milder conditions alternative: using $POCl_3$ & pyridine



Mechanism:
Similar to PCl_3,
but yields E2…





Advantages:

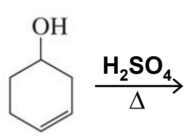
- Non-acidic conditions (& py removes "HCl")
- E2 pathway for elimination
- No danger of rearrangements

Disadvantages:

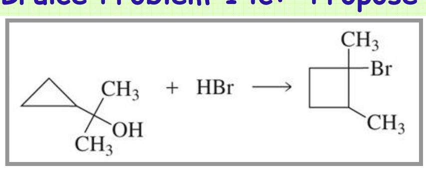
- More expensive
- $POCl_3$ requires dry conditions (*i.e.,* anhydrous)

(7)

Bruice Problem 15c: Give the major product for…



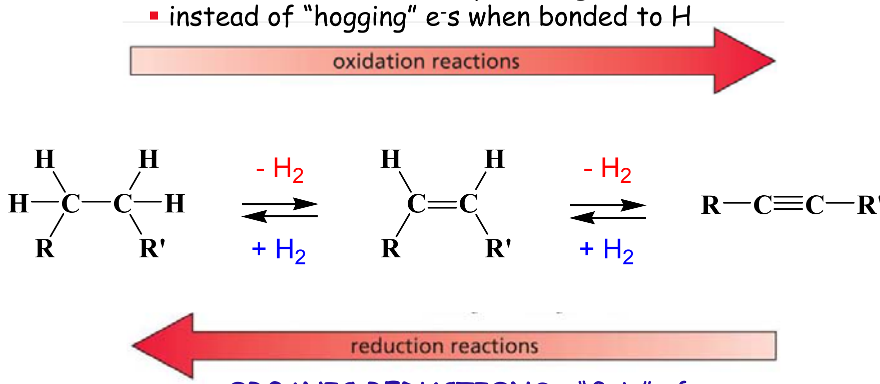
Bruice Problem 14c: Propose a mechanism for…



(8)

Organic Oxidation-Reduction reactions (Bruice 19.2)

ORGANIC OXIDATIONS: "Loss" of e^-s…
- C forced to share ~equally with other Cs or become δ^+ by bonding to heteroatoms
- instead of "hogging" e^-s when bonded to H

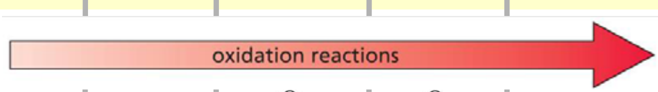


ORGANIC REDUCTIONS: "Gain" of e^-s…
- C permitted to "hog" e^-s by bonding to more Hs

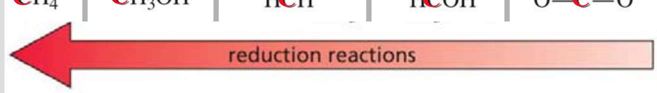
(9)

Organic Oxidation-Reduction reactions (Bruice 19.2)

OXIDATION STATE OF C	-4	-2	0	+2	+4
OXIDATION LEVEL =# BONDS to O,N,X	0	1	2	3	4



	CH_4	CH_3OH	HC(=O)H	HC(=O)OH	O=C=O



	CH_3OCH_3	$CH_3C(=O)CH_3$	$CH_3C(=O)OCH_3$	$CH_3OC(=O)OCH_3$
	CH_3NH_2	$CH_3C(=NCH_3)CH_3$	$CH_3C(=O)NH_2$	$CH_3OC(=O)NHCH_3$
	CH_3Cl	$CH_3C(OCH_3)_2CH_3(H)$	$CH_3C(=O)Cl$ $CH_3C\equiv N$	ClC(=O)Cl

TRENDS:

Oxidation rxns:

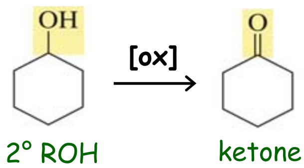
↓ # e^-s AND Hs via
- making bonds to heteroatoms "Z"
- making π-bonds

Reduction rxns:

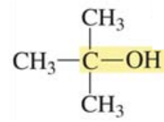
↑ # e-s AND Hs via
- losing bonds to heteroatoms
- saturating π-bonds

(10)

ROH rxn type 4: Oxidation of alcohols (Bruice 10.5)



Not 3° ROHs



1° ROHs ?

More details coming soon.

[ox] = Oxidizing agent

typical

Containing a reactive M-O bond:

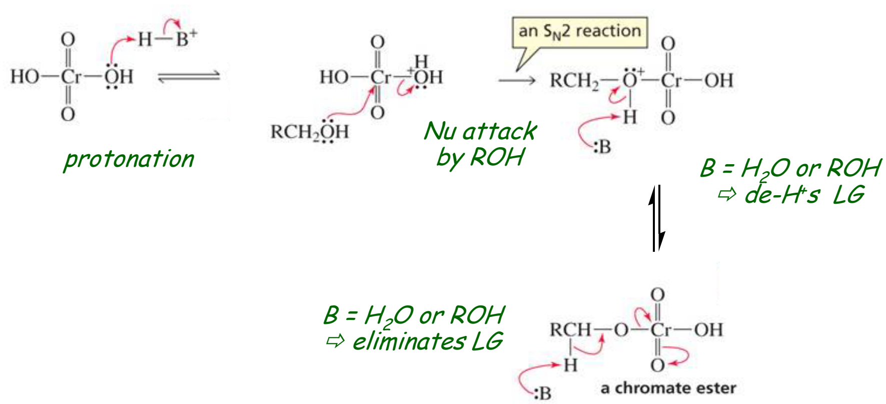
- Dichromates: $K_2Cr_2O_7$ / H_2SO_4
  $Na_2Cr_2O_7$ / H_2SO_4
- Chromic acid: H_2CrO_4
- Jones' reagent: CrO_3 / H_2SO_4
- Collins' reagent: "PCC" *(soon)*

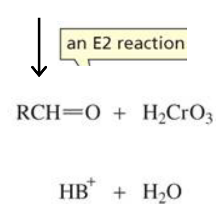
…Reactive O-O bond:

- Peroxyacids *(see later)*

(11)

Mechanism of oxidation by chromic acid



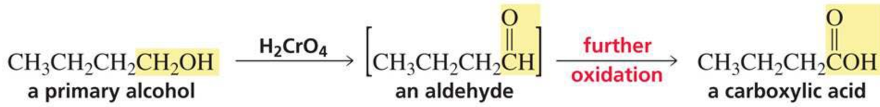


Comments: harsh acidic conditions

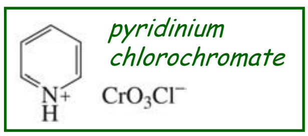
- Acid required to activate reagent
- Reaction occurs in aqueous media
- Strong oxidizing agent…

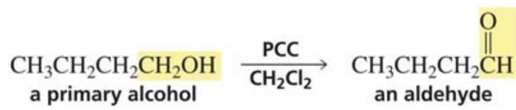
(12)

Primary alcohols are oxidized to aldehydes…



Milder oxidant stops at aldehyde level:
Collins' reagent, "PCC"

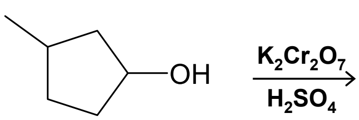


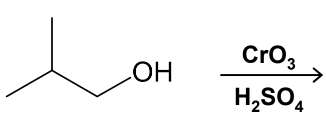


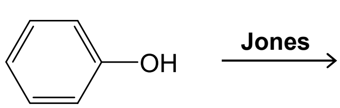
soluble in organic solvents
(cf: aqueous Cr reagents)

(13)

Give the major product for…







(14)