Course Chem 343 Lecturer Gellman (11 am)

Day Monday Date 10/17/2011

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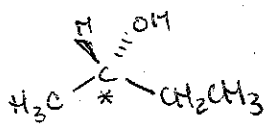
Review session on Thurs - 4-5 PM, Here

Sp^3 Carbon Stereochemistry

Ex.



$[\alpha]_D^{20} = +13.9°$

(S)-(+)-2-butanol

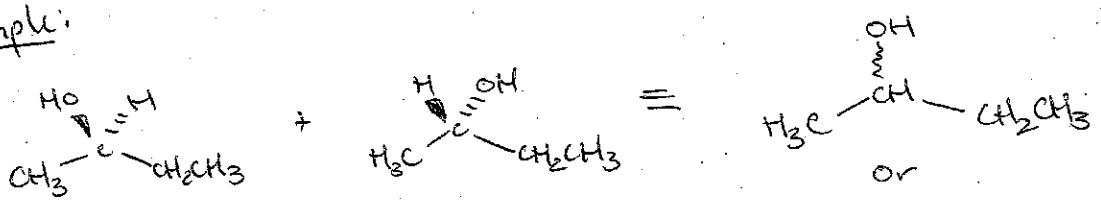
(+) — optical activity - derived from measurement of optical rotation

(S) — configuration of carbon as drawn in space

Racemic Mixture (Racemate)

↳ 1:1 Mixture of enantiomers (mixture is not optically active)

Example:



1:1 (Racemic)

[(±)-2-butanol]

→ Reactions that create chiral centers typically produce racemic mixtures (assuming that the reagents are not chiral).

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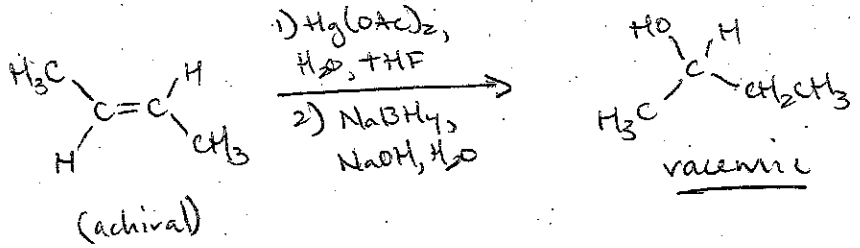
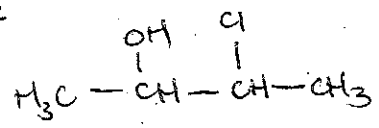
Example



Why do we care? - Our bodies & many organisms are chiral, thus chirality becomes important in developing drugs & other molecules that interact with the biosphere.

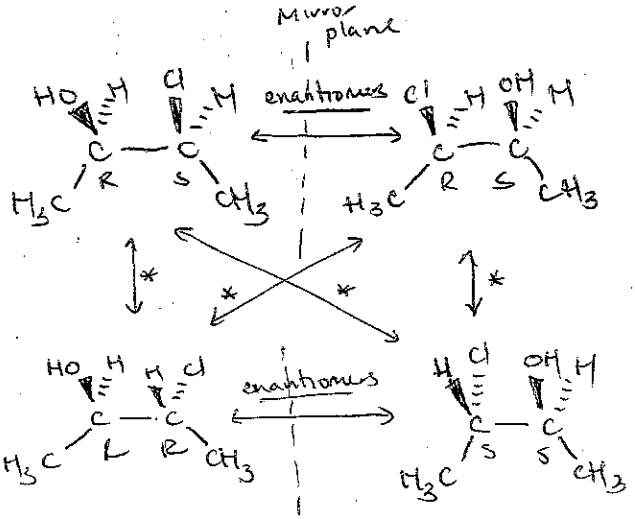
Molecules that contain 2 stereogenic centers

ex:



→ 4 possible stereoisomers (2x stereogenic centers

(2-chloro-3-butanol)



* Diastereomers

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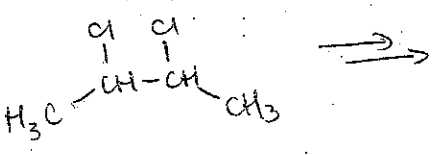
Stereoisomers (sp^3 Carbons) - Isomers differing only in the spacial arrangement of their components (not connectivity)

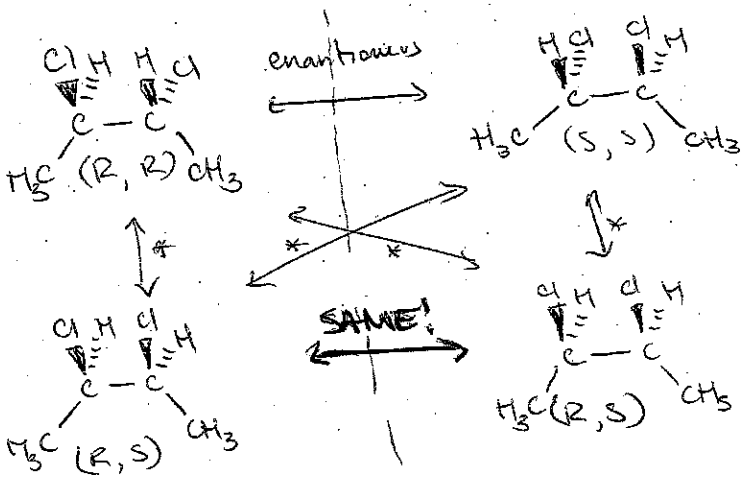
Enantiomers - Non-superimposable, (non-identical) mirror images

Diastereomers - Everything else (stereoisomers not related as a molecule & it's mirror image).

Another Example:



* Diastereomers



NOTE! MOLECULES THAT CONTAIN STEREOGENIC CENTERS CAN BE ACHIRAL

→ Arises from the presence of an internal plane of symmetry in the molecule

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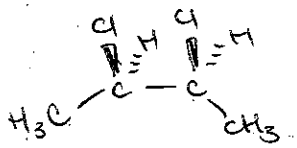
(R,S)-2,3-dichlorobutane

OR

(2R,3S)-dichlorobutane

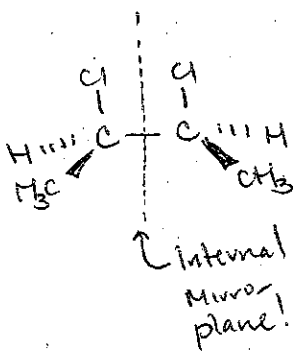


↳ is a MESO compound

MESO compound - an achiral molecule that contains stereogenic centers.

- Contain an internal mirror plane or a point of symmetry when drawn in a proper conformation

Meso-2,3-dichlorobutane



General Rule: A molecule with n x sp^3 stereocenters, will have a maximum number of stereocenters 2^n.

(fewer than 2^n if any are meso.)

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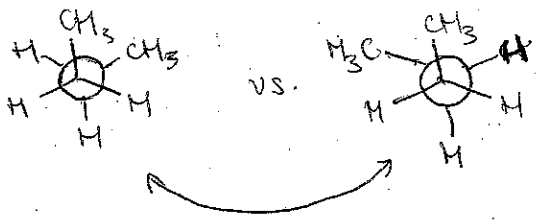
Molecules vs. Conformations - Typically we assign stereochemical designations to molecules (R or S, E or Z) to molecules rather than conformations

Consider: n-butane gauche conformation

$CH_3CH_2CH_2CH_3$



Non-superimposable mirror images

*However, on average it is an achiral compound ↳ will have no net optical rotation even though it can adopt chiral conformations

** NOTE: As long as a molecule can adopt an achiral conformation, then the molecule is achiral (consider: anti-butane).

In Addition: In rarer cases, a molecule can be chiral without containing sp^3 ~~sp~~ stereocenters (see section 6.9 in txt).

Course 108 Lecturer Larson

Day Friday Date 10/14/11

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Ozone hole - thinning of ozone layer in a specific location (large area of < 220 ppb O_3)

- global average of O_3 ~300 ppb.
- hole is over Antarctica
- Concentration of Ozone has a seasonal dependence.
- since 1979, ozone "hole" has become larger in area and lower in concentration of O_3
- lowest in southern hemisphere spring (~October)
- south pole is coldest, has least light, specific wind patterns
- polar stratospheric clouds (PSC)
  - need extreme cold & extreme dark to make
  - storage bins for chemicals responsible for ozone hole.
  - conditions are best in Antarctica
- need ~108 F for formation of PSC ⇒ much more likely to form over south pole than other poles.
- PSCs contain Cl.
  - PSCs break down when the atmosphere warms up

- CFC = chloro fluoro carbon
- know methane, ethane, propane, butane
- CFCs contain no hydrogen
- contain at least 1 chlorine and 1 fluorine
- name groups alphabetically => CCl_3F = tri chloro fluoro methane.

Course _____ Lecturer _____

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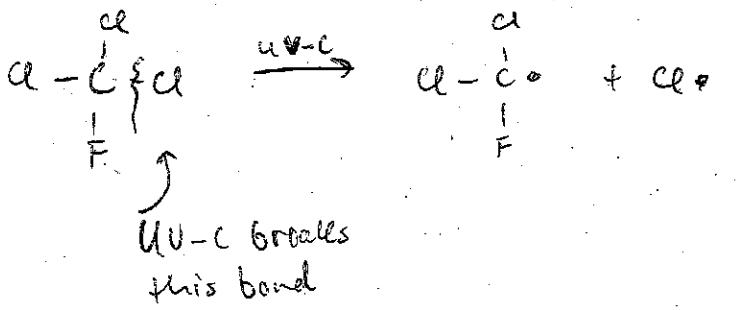

$Cl\cdot + O_3 \longrightarrow Cl\text{-}O\cdot + O_2$

$Cl\cdot$ destroys ozone.

} more on monday

Course Chem 345 Lecturer Yoon

Day Monday Date 10-17-11

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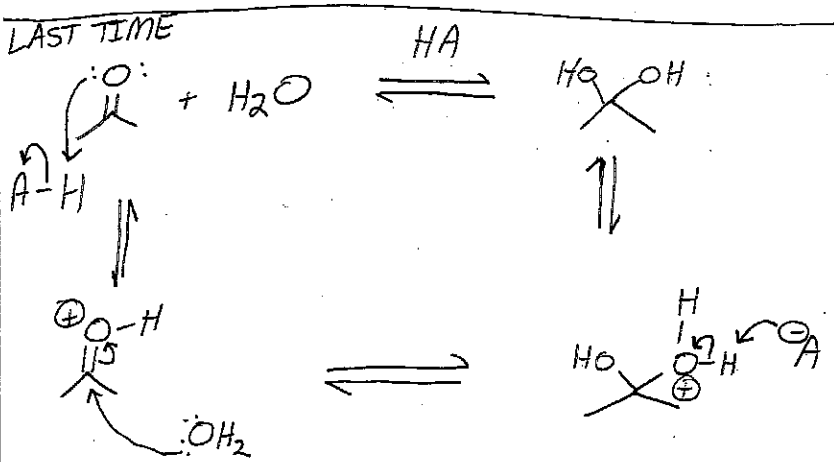
Today: ① Carbonyl Hydration - Base Catalysis
② Reversibility of carbonyl additions (hydrocyanation)
③ Addition of alcohols to carbonyls
- Base catalysis
- Acid catalysis

PS #2 back today

Exam #2 (Monday) covers through 19.9 (inclusive)

↳ extra office hour Wed @ 4:30 in chem B371

LAST TIME



Gem-diol
or
Ketone hydrate

Acid-catalyzed addition

Acid catalyst makes carbonyl a better electrophile! Then it's activated for nucleophilic attack.

Equilibrium controlled by stability of SM & pdts. Equilibrium lies far to the left-hand side due to strong stability of $\rangle C=O$.

Another way to increase rxn is to ↑ nucleophicity of nucleophile... that's what base-catalyzed does.

Course Chem 345 Lecturer Yoon

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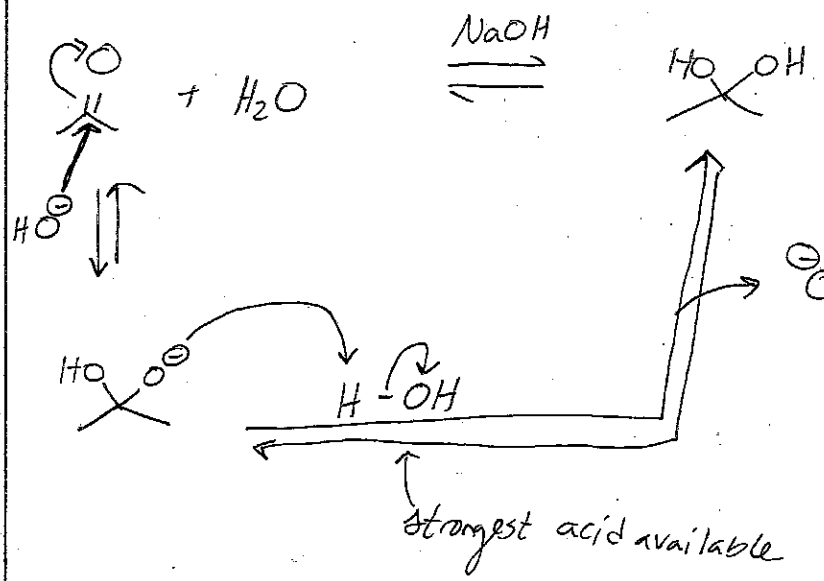
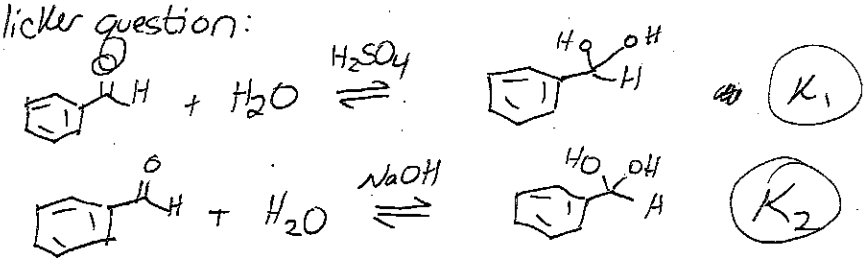
Base-catalyzed hydration



lowest energy pathway in forward direction = lowest energy pathway in backwards direction

Backwards direction:

Clicker question:



A. $K_1 > K_2$

B. $K_1 = K_2$

C. $K_1 < K_2$

They are the same! Why?

Equilibrium: compare SM + pdts ⇒ it does NOT matter what the catalyst is!

$K_{eq} = \frac{[sm]}{[pdts]}$ No catalyst in this eqn!

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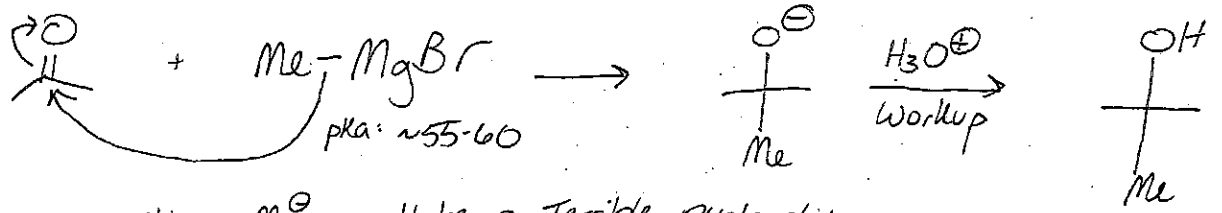
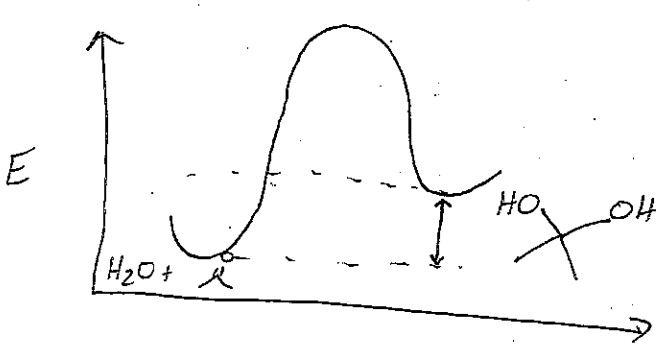
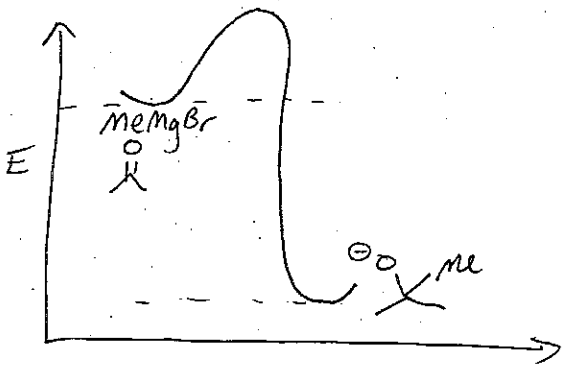


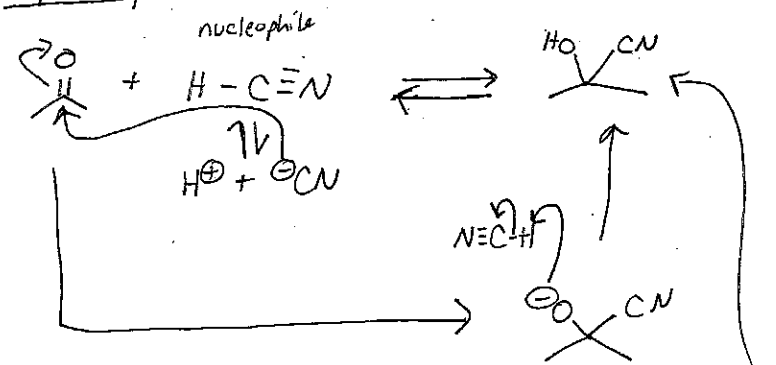
Not reversible... $Me^{\ominus}$ would be a Terrible nucleophile.
pka tells you how stable neg charge is
pka of Me-MgBr so high - that tells you it cannot be a good LG.





Huge energy barrier to go backwards

Cyanohydrin formation



autocatalytic: one of the SM's IS the catalyst of the rxn

pKa(HCN) ~9.4
↳ low ⇒ good LG ⇒ rxn is reversible

Can isolate under neutral or acidic conditions — not under basic conditions

MATERIAL FOR EXAM #2 ENDS HERE

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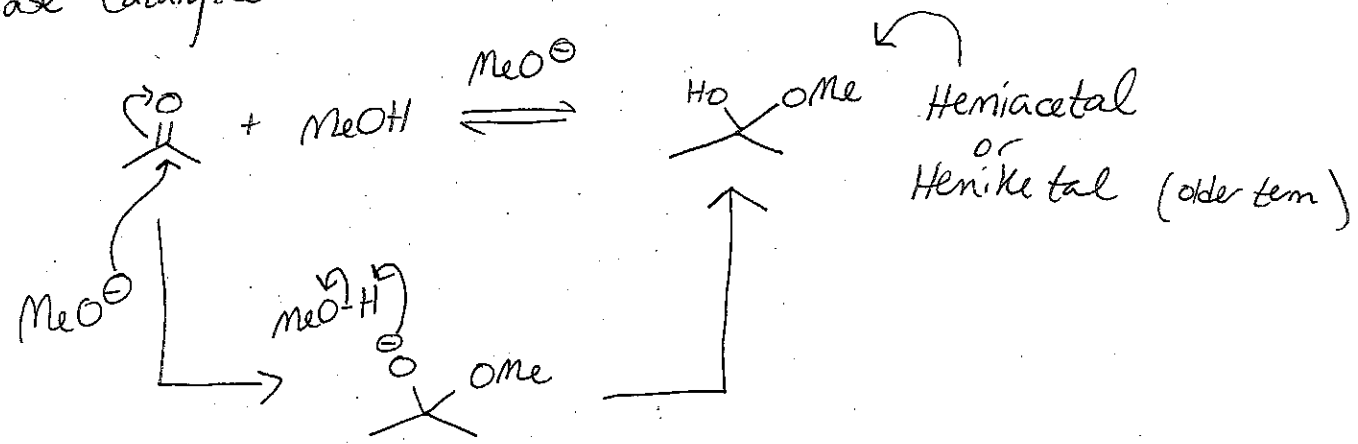
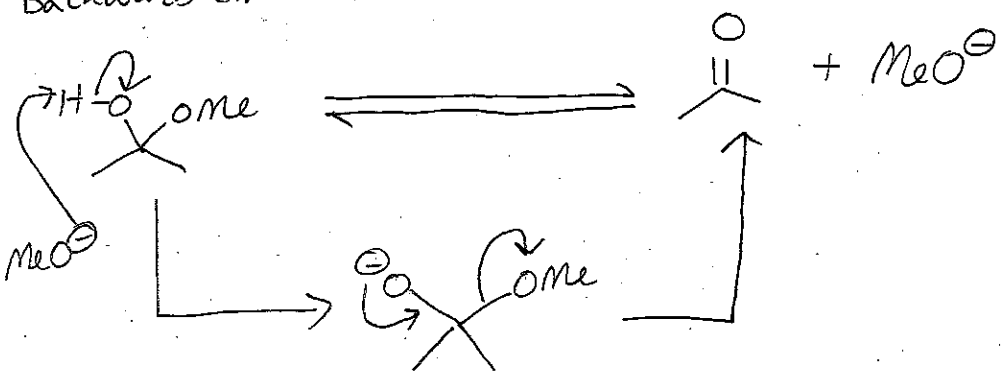
Addition of Alcohols to Carboxyls

Base catalyzed:



Backwards direction:



Favor ketone b/c C=O bond more stable. Hemiacetals usually ~2-5% in soln.

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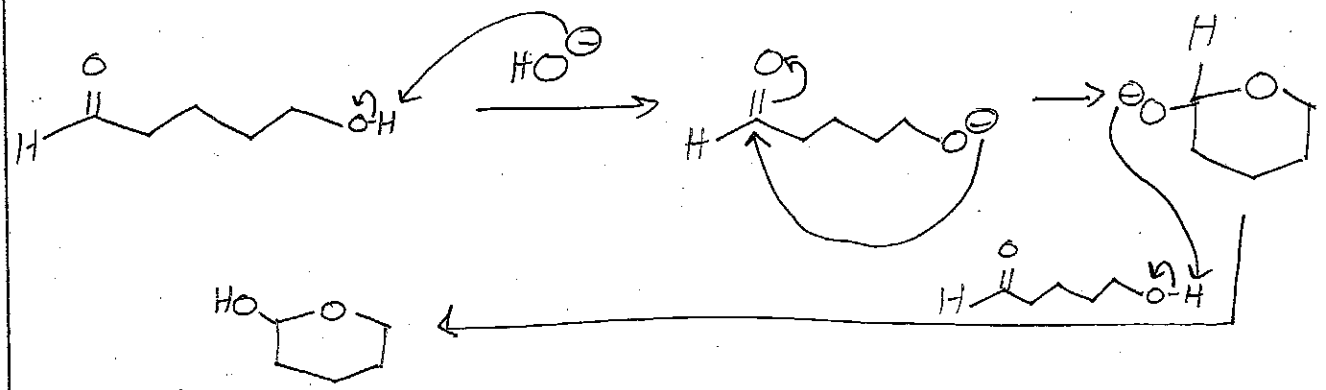

Cyclic hemiacetal
-stable!

Glucose, fructose, etc are all cyclic hemiacetals.

Course 343-4 Lecturer Burke

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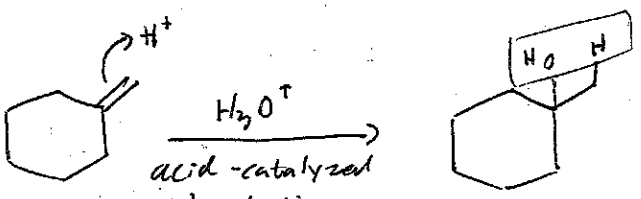
Minitest on Friday

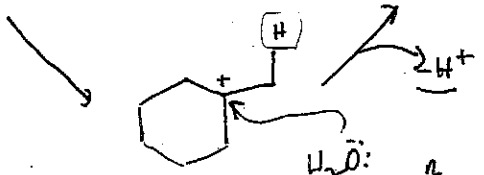
Chapters 4, 5 & Spectroscopy.

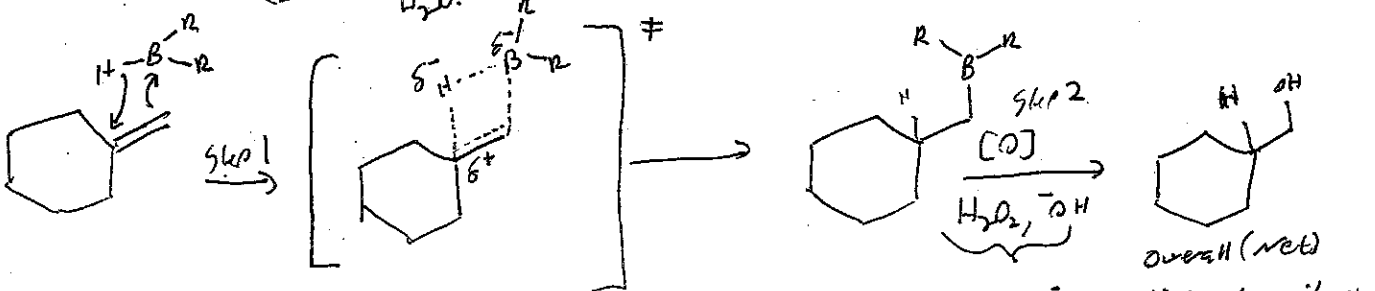
Hydroboration - Oxidation

↑
Ignored by
Text book author
(Stereochemistry, P. 312, Chapt 7)



Markovnikov addition of H_2O across alkene (Hydration)





(Boron is electrophile)
Regiochemistry Controlled by Electronics and Sterics.

Overall (Net) anti-Markovnikov hydration.

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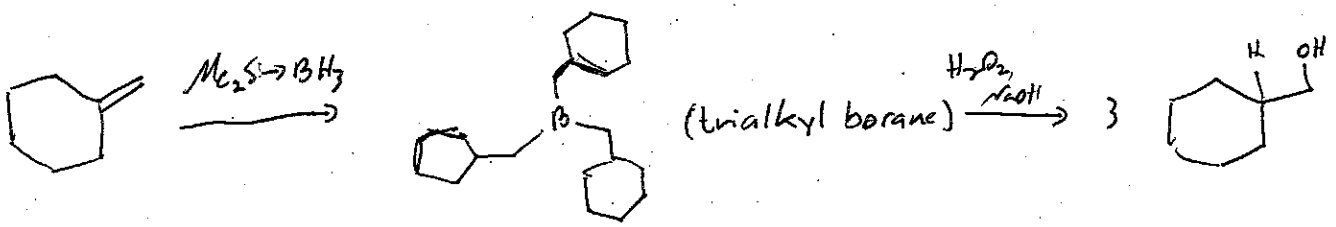
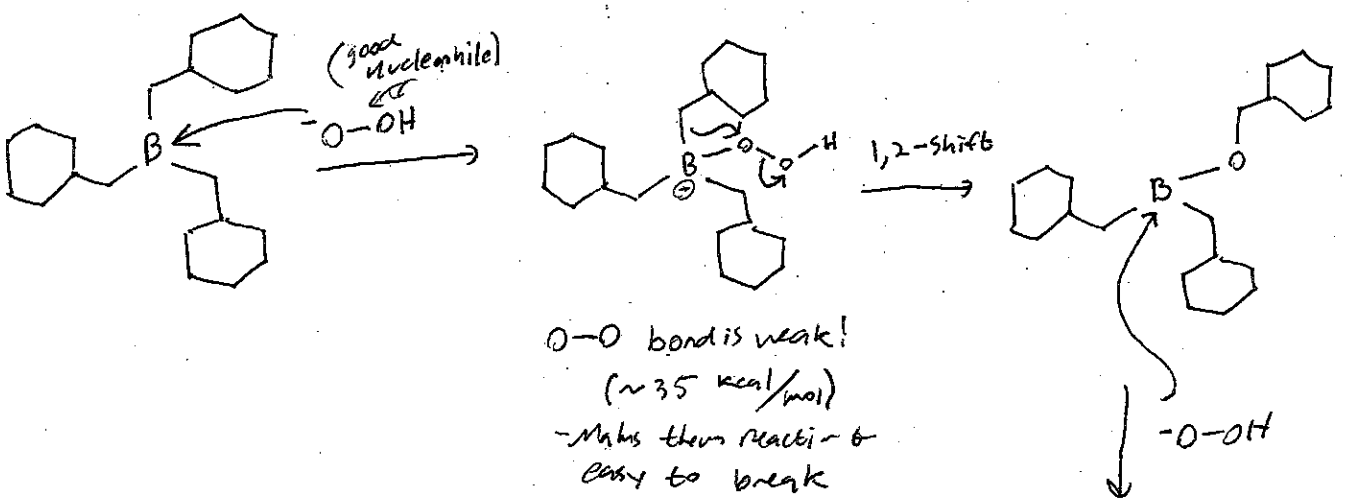
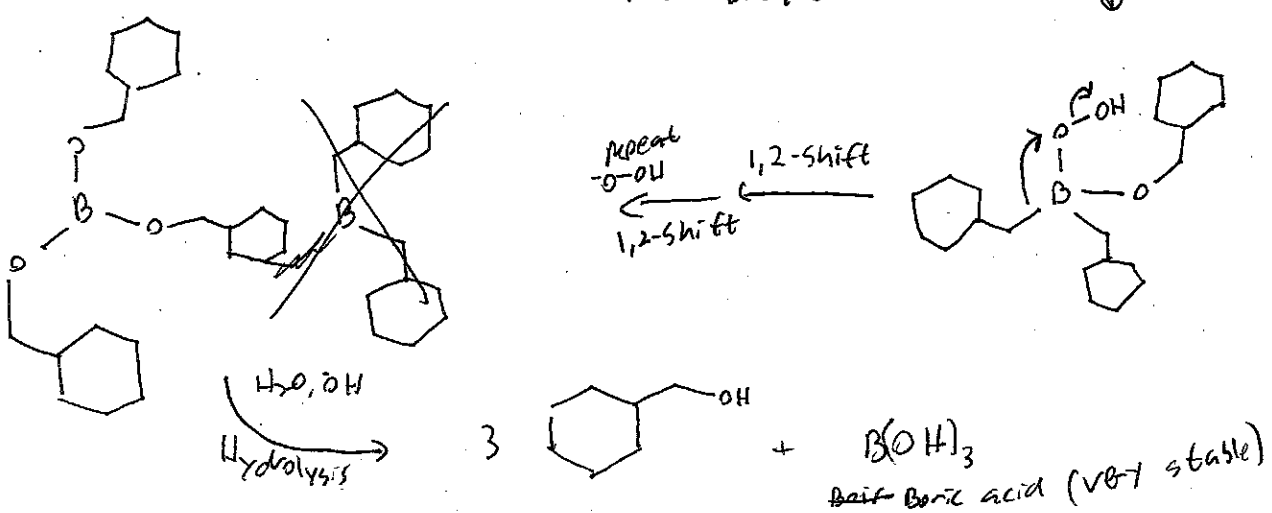
Typically reaction is done w/ $Me_2S \rightarrow BH_3$
lewis base lewis acid



- there are 3 B-H bonds that can add to the alkene





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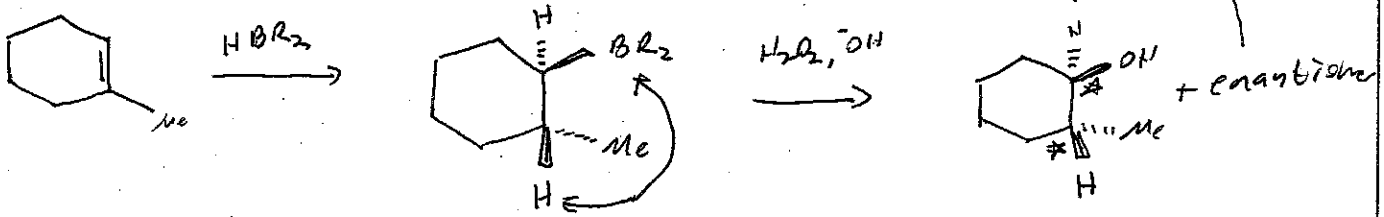
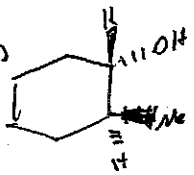
Stereochemical Retention



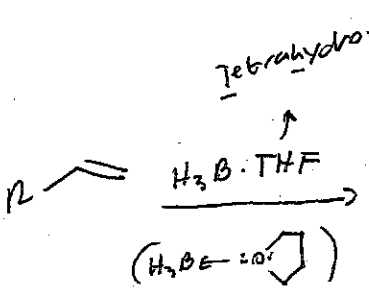
Hydroboration (from backside) gives enantiomer

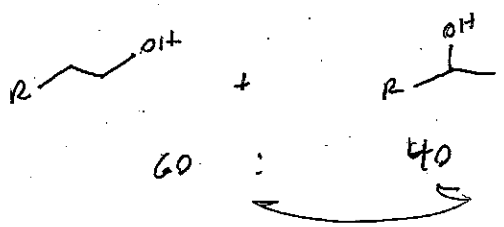


- Stereochemistry of C–B bond is Retained in C–O bond.

Transition state for front and Back hydroboration are enantiomeric.

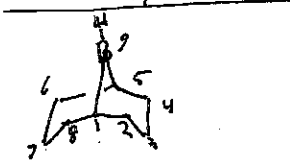
Product here is a Chiral Molecule w/ 2 asymmetric carbons
- Product must be formed as Racemate.



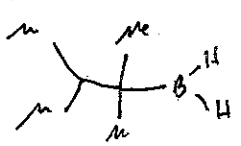


not enough electronic/steric difference @ 2 ends of alkene.

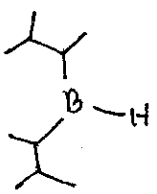
Oth hydroborating agents:



- 9-borabicyclononane (9-BBN)



thexylborane



disiamylborane

(All sterically demanding)

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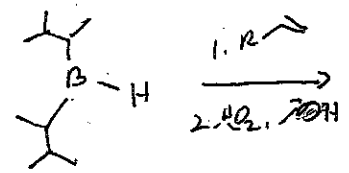
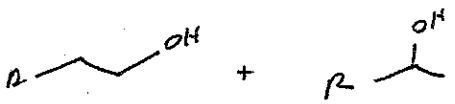
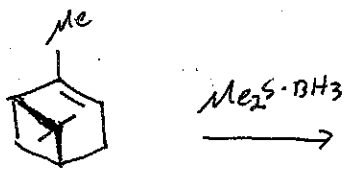
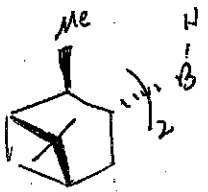




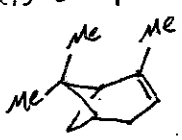
> 99 : 1 ratio! (excellent regioselectivity)



(+)-α-pinene



(-)-diisopinocamphylborane



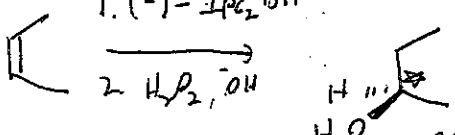
Chiral alkene

Both faces are different!

Chiral! → $(Ipc)_2B-H$

- Chiral Hydroborating agent!!!

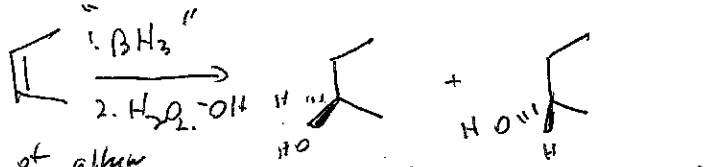
Can differentiate between alkene faces.



→ Chiral hydroborating agent.

↳ Transition states are diastereomic!
- Different energies

98.4% ee ⇒ $\frac{99.2}{.8}$ enantiomeric ratio



faces of alkene are enantiotopic

1:1 ratio (Racemic)

= enantiomeric transition states
- same energy

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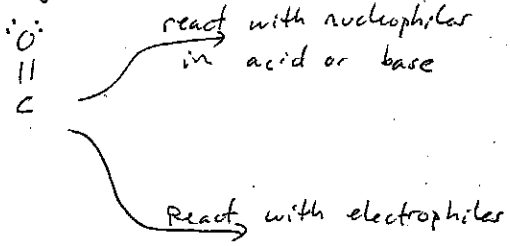
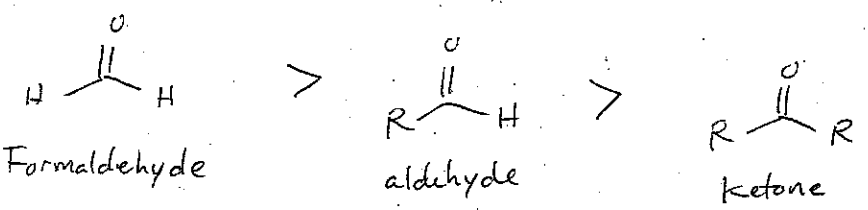
Carbonyl chemistry

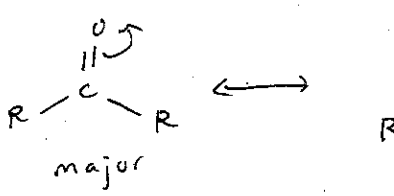


Simplest carbonyls are Ketones and aldehydes



R = any carbon

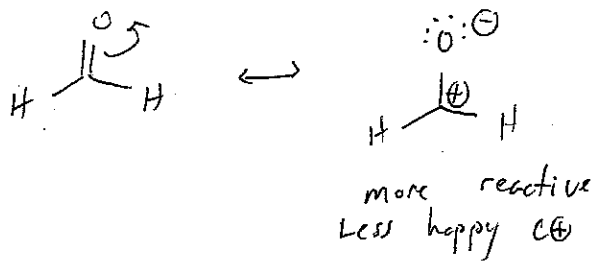
← Reactivity increases

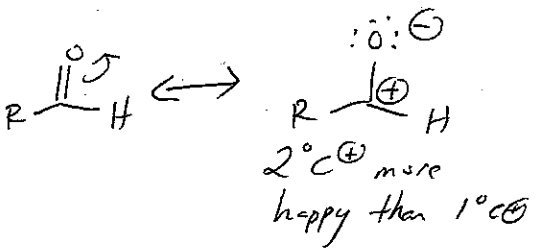


Resonance governs carbonyl chemistry.

nucleophiles react here.

If make carbocation less happy, makes them more reactive.





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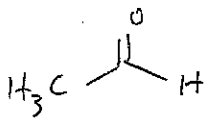
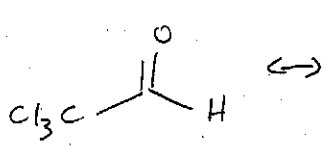
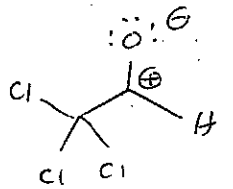


Acetaldehyde

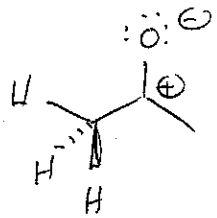
or



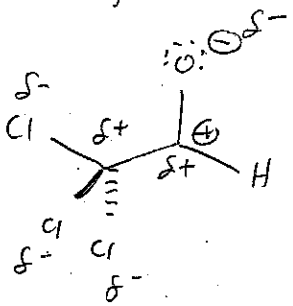
Chloral
major



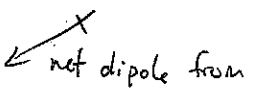
minor



Hyperconjugation
stabilizes carbocation

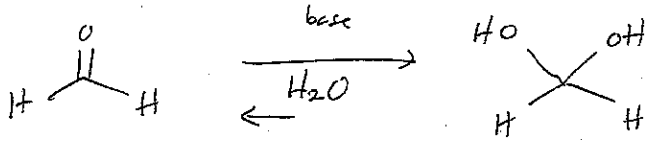


$\delta+$ $\delta-$ ↑ used to show dipole moment. Difference in electronegativity.

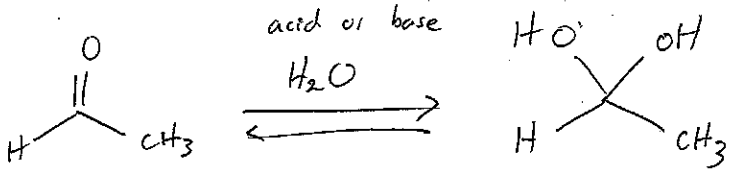


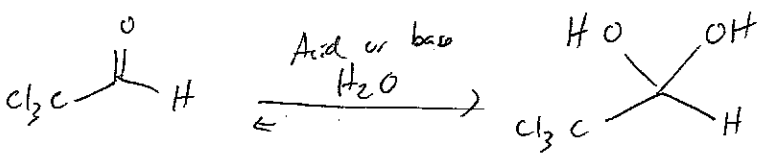
not dipole from Cl groups.

Instability of C⊕ makes chloral more reactive than acetaldehyde.



hydrate





chloral hydrate

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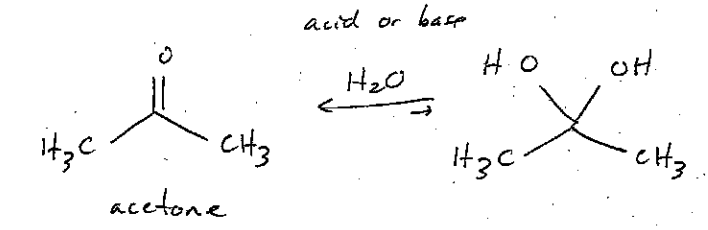
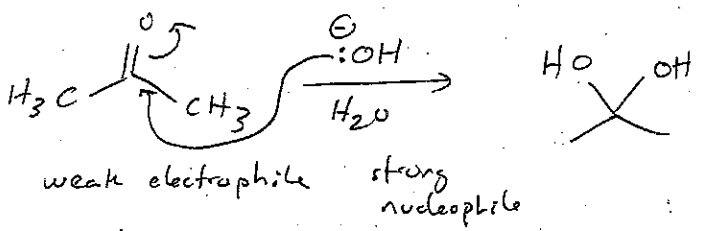
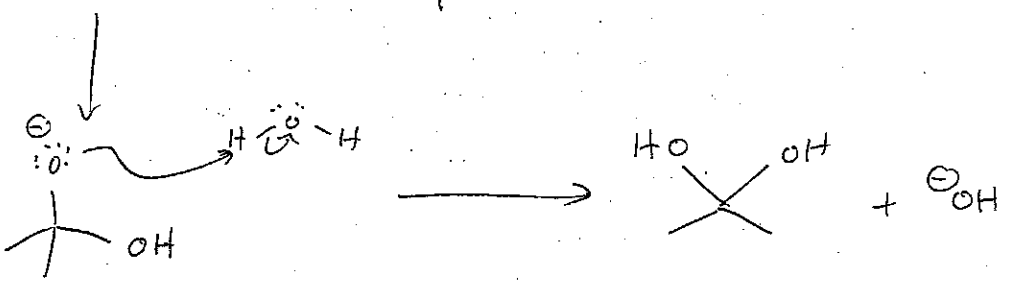
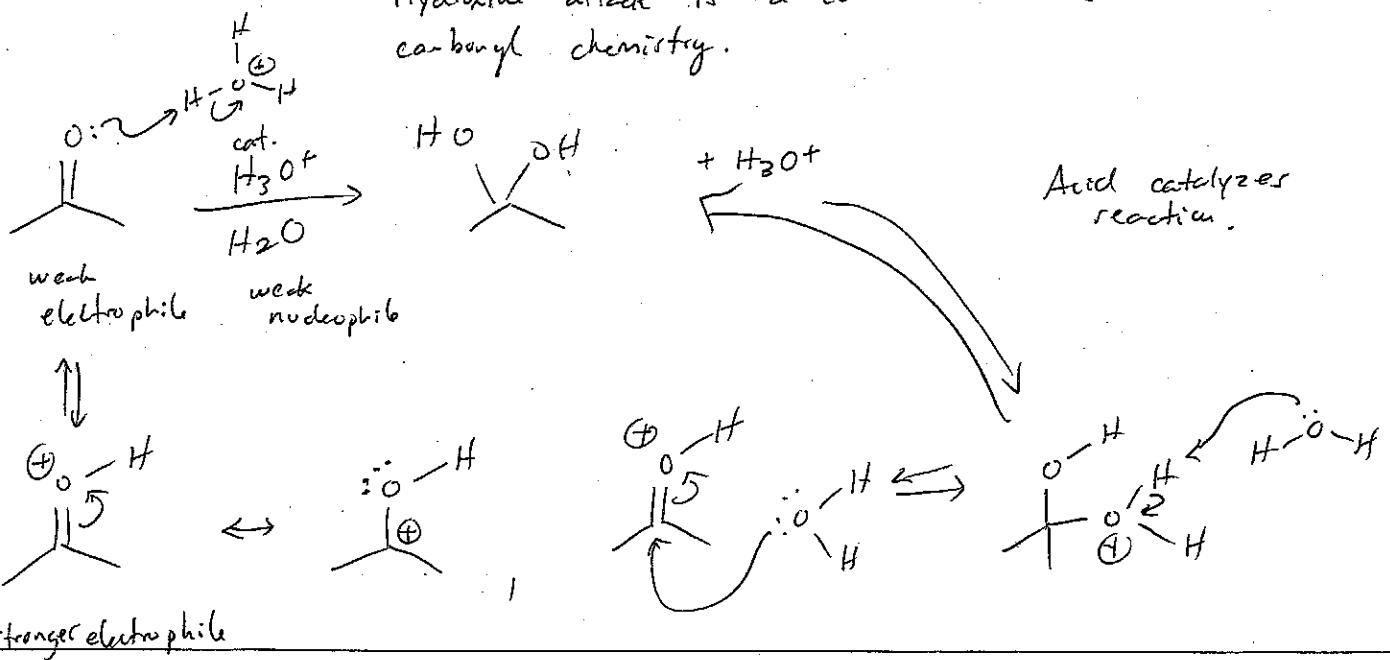






$^{\ominus}OH$ recycled / catalyzes reaction.

Hydroxide attack is a common motif in carbonyl chemistry.



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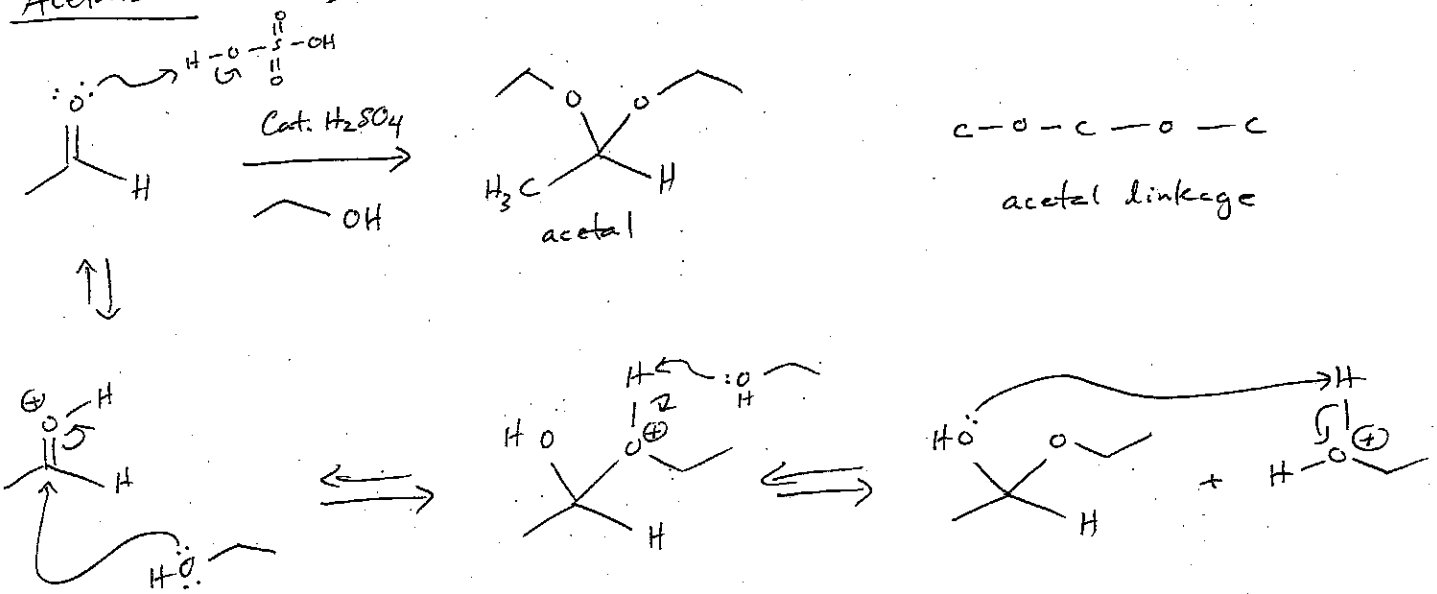
Acetals (Ketals)

Mechanism of acid catalyzed acetal formation.



C–O–C–O–C

acetal linkage

H–O–C–O–C

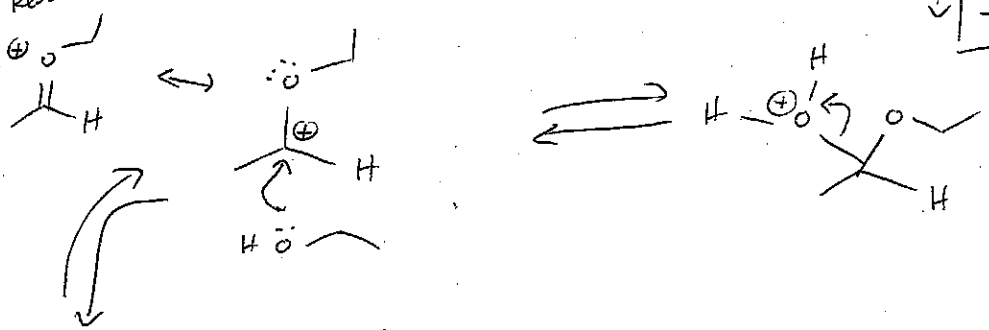
½ way there.

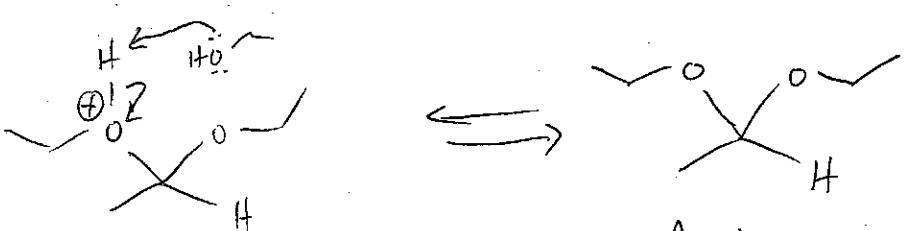
Hemiacetal

Typically unstable.

SN1

Resonance stabilized





Acetal

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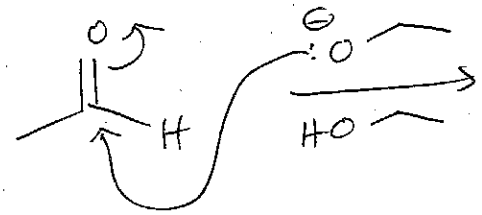
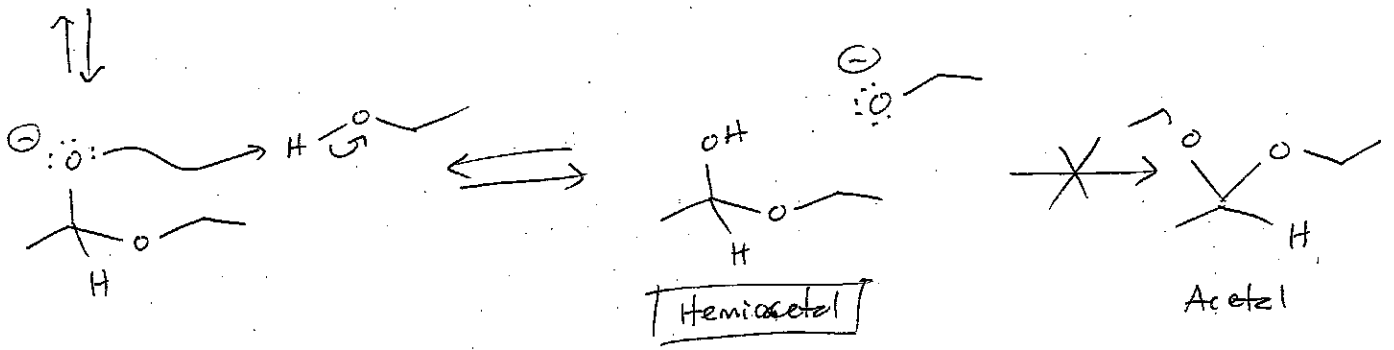
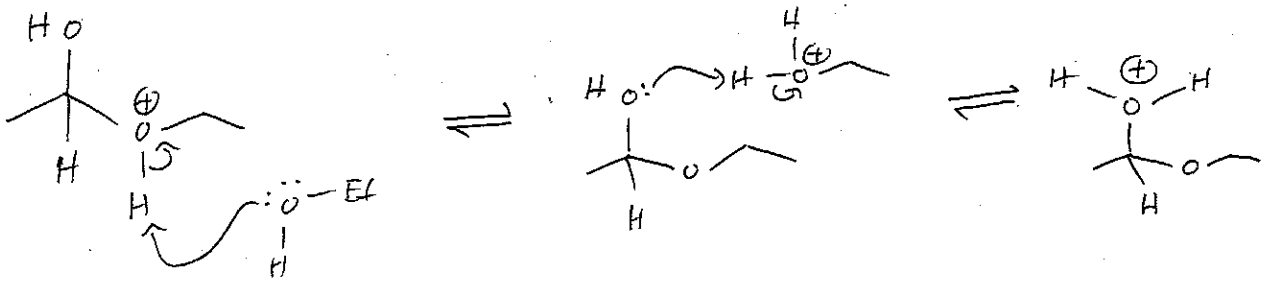
Base promoted acetal formation?

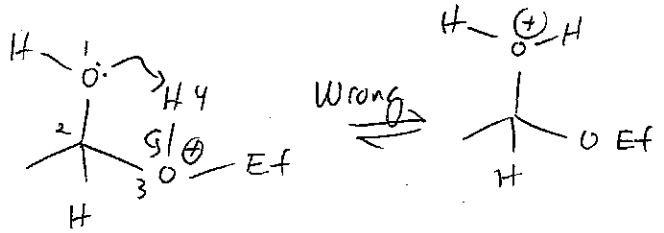




★ Basic conditions generate only the hemiacetal.

★ Acidic conditions generate either hemiacetal or acetal.





Needs to form 4-membered transition state... too difficult to form. Need to write out mechanism stepwise

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Exam will be turned in on Wed.

HW4 will be posted online this afternoon.

Save Mathcad file for future use.

Log-Log alpha plot. (asparcic acid)

$\log\alpha$ vs. $-pH$ $p = -\log$

β_0 is dominant in left side of the plot.

α_0 is dominant in right side of the plot

α_0 (H_3A) slope: +3, +2, +1, 0

$$\alpha_3 = \frac{K_1 K_2 K_3 [H^+]^{-3}}{1 + K_1[H^+]^{-1} + K_1K_2[H^+]^{-2} + K_1K_2K_3[H^+]^{-3}}$$

(dominant in basic region)

$[H^+]$ is very small in basic region, $[H^+]^{-3}$ is very very big.

$K_1K_2K_3[H^+]^{-3}$ is the dominant term.

Then $\alpha_3 = 1$. slope: 0

$[H^+]$ get bigger; $[H^+]^{-3}$ get smaller. $K_1K_2[H^+]^{-2}$ become dominant term

Then $\alpha_3 = \frac{K_1K_2K_3[H^+]^{-3}}{K_1K_2[H^+]^{-2}} = K_3[H^+]^{-1}$ slope: −1

Next region, $K_1[H^+]^{-1}$ become dominant term.

$\alpha_3 = \frac{K_1K_2K_3[H^+]^{-3}}{K_1[H^+]^{-1}}$ slope: −2

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At first region boundary, $K_1 K_2 [H^+]^{-2} = K_1 K_2 K_3 [H^+]^{-3}$

$\alpha_3 = \frac{1}{2}$. Point in the log-log plot will be log2 down at the boundary. ($\log 2 = 0.3$)

$\alpha_3 = \frac{[A^{3-}]}{C_A}$ C_A: analytical concentration of A

$[A^{3-}] = C_A \cdot \alpha_3$. $[HA^{2-}] = C_A \alpha_2$ $[H_2A^-] = C_A \alpha_1$ $[H_3A] = C_A \alpha_0$

$\log [A^{3-}] = \log C_A + \log \alpha_3$

$\log [HA^{2-}] = \log C_A + \log \alpha_2$

$\log [H_2A^-] = \log C_A + \log \alpha_1$

$\log [H_3A] = \log C_A + \log \alpha_0$

log (conc. of species) vs −pH.

$C_A = 0.1$ $\log C_A = -1$. Drag all curve down by 1 unit.

$H_2O \rightleftharpoons H^+ + OH^-$ $K_w = 1.0 \times 10^{-14}$ $pK_w = -\log K_w = 14.0$

neutral water $[H^+] = [OH^-]$
$\quad\quad\quad\quad\quad\quad x \quad\quad x$

$x^2 = K_w$ $x = \sqrt{K_w} = 1.0 \times 10^{-7}$ $pH = 7.0$.

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

$\log [H^+] = \log [H^+]$ slope $= +1$ intercept $= 0$

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$\log[OH^-] = \log\left(\frac{K_w}{[H^+]}\right) = \log K_w - \log[H^+]$ slope = -1 intercept = $\log K_w = -14.0$

Big X Diagram.

Vertical line represent the solution at a certain pH.

Balance equation for Acid-Base (Not charge balance equation)

H-OH Balance Equation.

example a triprotic weak acid system.

C_H analytical conc. of proton

C_{OH} ——— of OH^-

C_A ——— of the weak acid backbone

$$C_H - C_{OH} = [H^+] + [HA^{2-}] + 2[H_2A^-] + 3[H_3A] - [OH^-]$$

In pure water $C_H = 0$ $C_{OH} = 0$ $C_A = 0$

$$[H^+] - [OH^-] = 0 \qquad [H^+] = [OH^-]$$

50 mL 0.1 mol/L HCl 50 0.1M NaOH

$C_H = 0.1 \times \frac{50}{100} = 0.05\ M$ $C_{OH} = 0.05\ M$

Course Chem 108 Lecturer Dr. Teresa Larson

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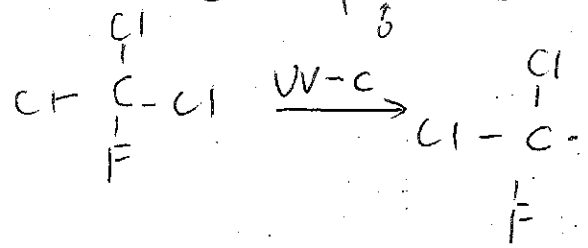
#1 Announcements

Sit according to your section in Exam 2 !

Back to CFCs ...

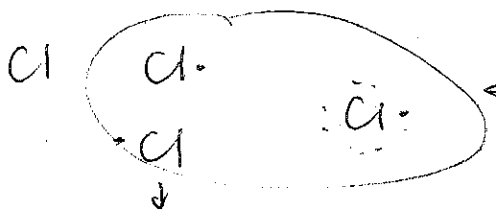
CFCs

chlorofluorocarbon

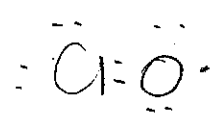


(produce 2 radicals)

Review: Cl atom



← All of them are fine as the lewis structure for chlorine atom doesn't matter where the dot is.



← unpaired electron is on oxygen atom

chlorine monoxide radical