MTW 2-8

2024年2月8日 13:15

Sp24HWSet3

Homework Problem Set 3 Iverson CH320N Due Monday February 3

NAME (Print): _____

SIGNATURE: _____

Chemistry 320N
Dr. Brent Iverson
3rd Homework
January 30, 2024

Please print the first three letters of your last name in the three boxes

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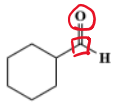
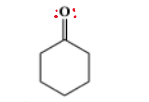
(4 pts) An important part of chemical understanding is being able to recognize the chemical reactivity of different functional groups. On the carbonyl group below, DRAW A BOX around the atom that will be attacked by nucleophiles and DRAW A CIRCLE around the atom that will be protonated in acid.

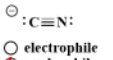


(12 pts) Being able to recognize the chemical personality of different species is one of the most important skills you can develop in Organic Chemistry. Fill in the correct circle under the structures to indicate whether that structure is considered an electrophile or nucleophile. Notice that some of the nucleophiles can also be considered bases, but we are not worrying about that for this questions.

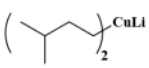


● electrophile
○ nucleophile

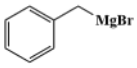
● electrophile
○ nucleophile



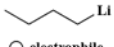
○ electrophile
● nucleophile



○ electrophile
● nucleophile



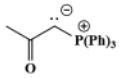
○ electrophile
● nucleophile



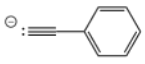
○ electrophile
● nucleophile

○ electrophile
● nucleophile

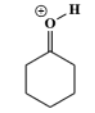
● electrophile
○ nucleophile



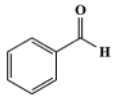
○ electrophile
● nucleophile



○ electrophile
● nucleophile



● electrophile
○ nucleophile



● electrophile
○ nucleophile

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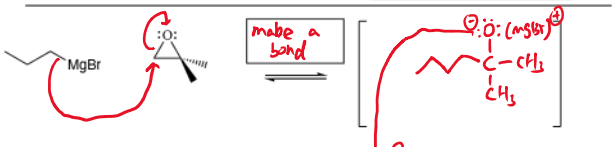
(20 pts. total) Complete the mechanism for the following two Grignard reactions. **Be sure to show arrows to indicate movement of all electrons, write all lone pairs, all formal charges, and all the products for each step.** Remember, I said all the products for each step. **IF A NEW CHIRAL CENTER IS CREATED MARK IT WITH AN ASTERISK AND WRITE "RACEMIC" IF APPROPRIATE.** I realize these directions are complex, so please read them again to make sure you know what we want.

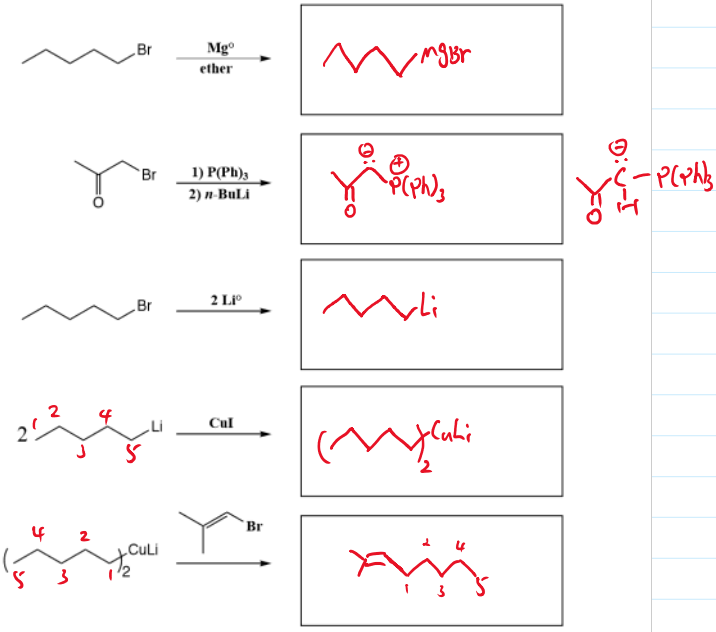


NOTICE THIS

⇓

In the boxes provided adjacent to the arrows, write which of the four basic mechanistic elements are involved (i.e. "Make a bond", "Add a proton", etc.)

(3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (▬) and dashes (·····) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.**



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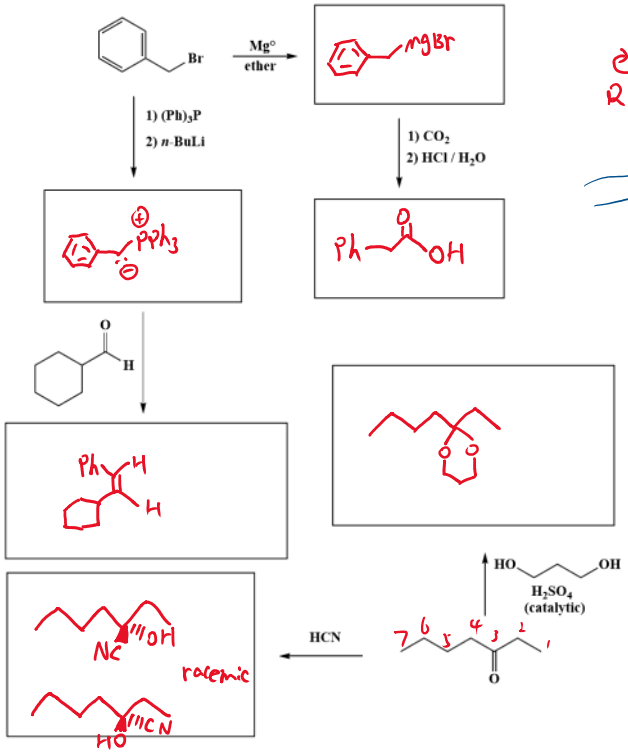
(3 or 5 pts each) Fill in the box with the product or products that are missing from the following chemical reaction equations. When a racemic mixture is formed, **you must write "racemic" under both structures EVEN THOUGH YOU DREW BOTH STRUCTURES**. For these draw all carbon containing products.



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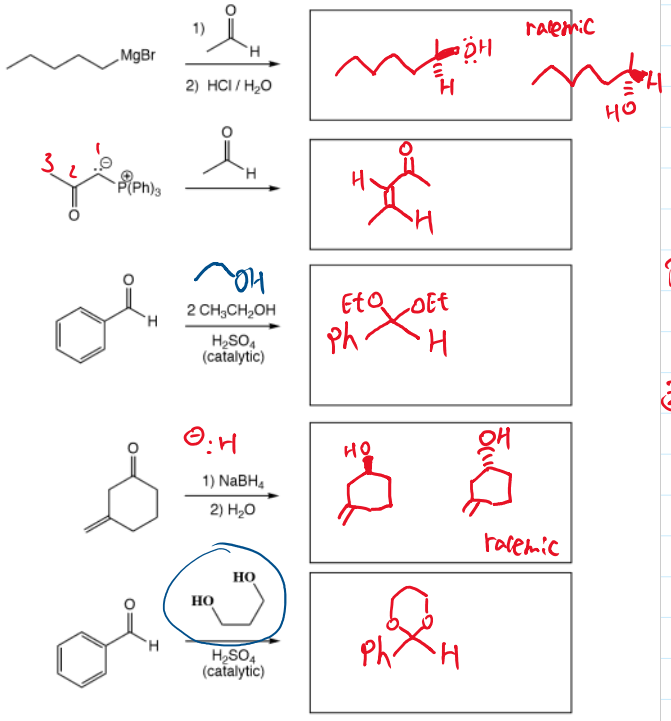
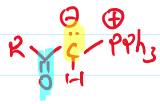
(3 or 5 pts.) Write the predominant product or products that will occur for each transformation. **If a new chiral center is created and a racemic mixture is formed, you must draw both enantiomers and write "racemic" under the structure. Use wedges (▬) and dashes (·····) to indicate stereochemistry. To get full credit, you only need to write the the major organic product for these. You do not have to worry about the other products.**



E/Z preference: determined by ylide:

① Z: alkyl ylide

② E:



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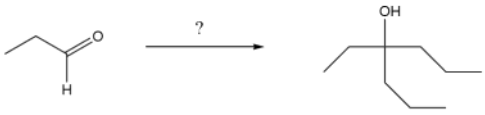
These are synthesis questions. You need to show how the starting material can be converted into the product(s) shown. You may use any reactions we have learned. Show all the reagents you need. Show each molecule synthesized along the way and be sure to pay attention to the regiochemistry and stereochemistry preferences for each reaction. If a racemic molecule is made along the way, you need to draw both enantiomers and label the mixture as "racemic".

(16 pts) **All of the carbon atoms of the products must come from the starting material for this one!**



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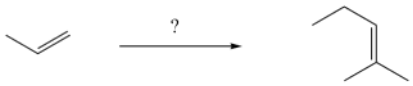
(15 pts) **All of the carbon atoms of the products must come from the starting material for this one!**
You have seen this before, try not to look at the answer before attempting it.



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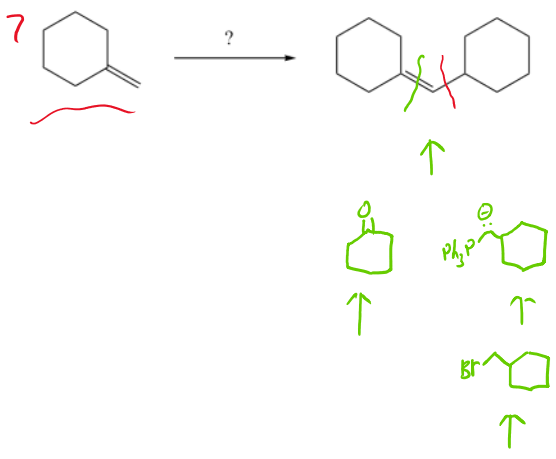
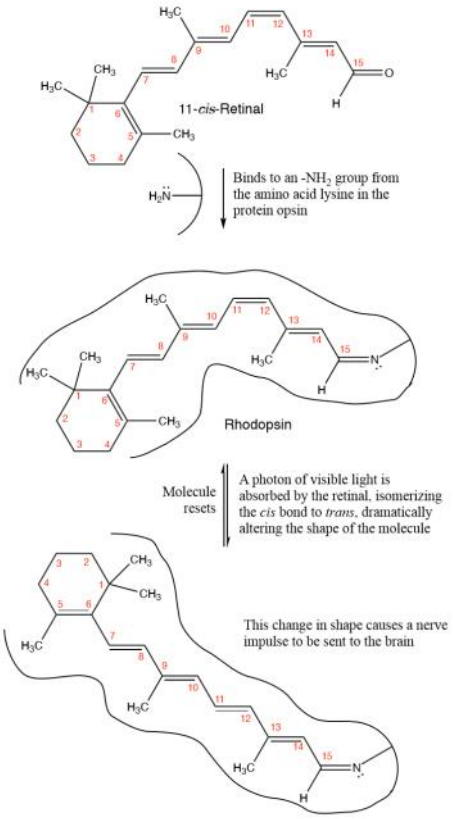
(13 pts) **All of the carbon atoms of the products must come from the starting material for this one!**

#0
① backwards
② looking for KRE in final pdf.
③

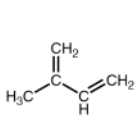


Week 4
Handouts

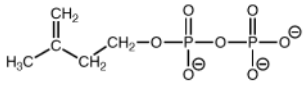
How vision works



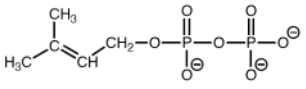
Terpenes



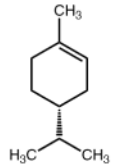
Isoprene



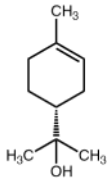
Isopentanyl diphosphate



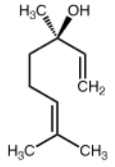
Dimethylallyl diphosphate



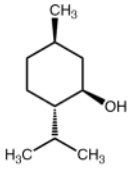
Limonene (citrus flavor)



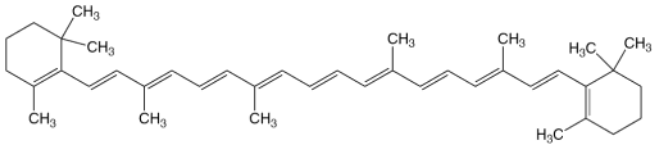
α-Terpineol (from lilacs, used in perfume)



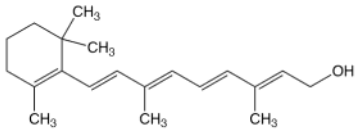
(*R*)-(-)-Linalool (from lavender, used in perfume)



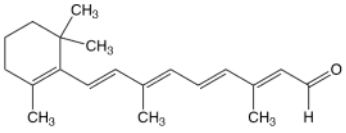
(-)-Menthol (common flavoring from peppermint)



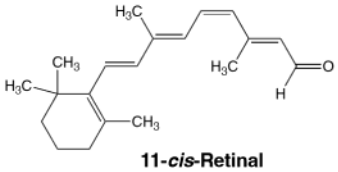
β-Carotene



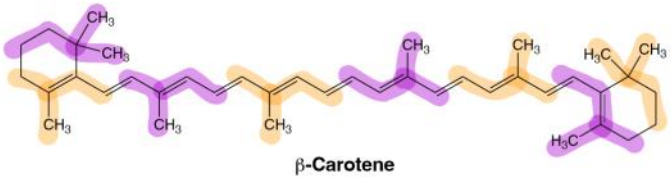
Vitamin A



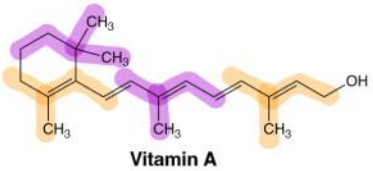
All *trans* Retinal



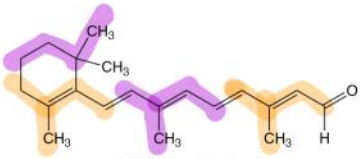
11-*cis*-Retinal



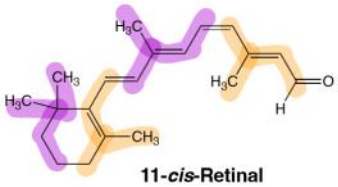
β-Carotene



Vitamin A



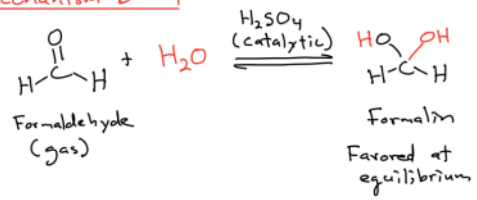
All *trans* Retinal

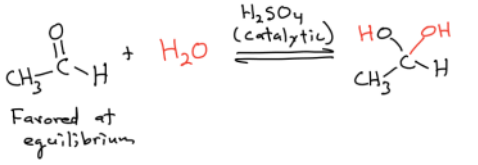


11-*cis*-Retinal

Geminal Diols: H_2O instead of ROH

Same mechanism as hemiacetal formation: Mechanism D



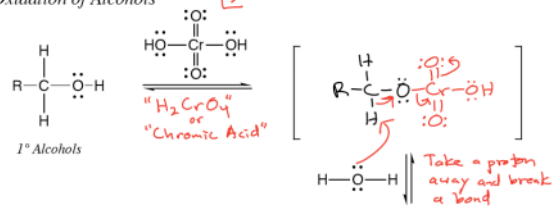


The geminal diol is in equilibrium with aldehydes and ketones, but it is only favored for the case of formaldehyde/formalin

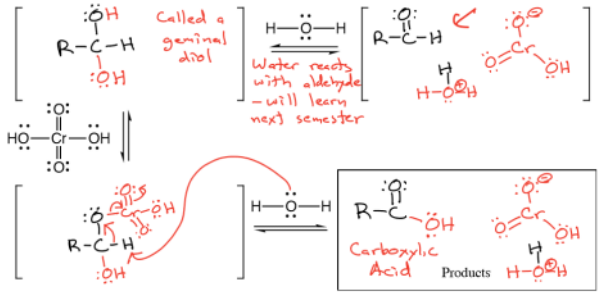
Chromic Acid Oxidation of Alcohols

Called "Jones Reagent" ($CrO_3 + H_2O$ or K_2CrO_7) + H_2SO_4

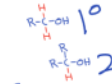
Not responsible for first step



Not responsible for this step

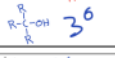


Summary:



1° alcohols ⇒ Carboxylic Acid

2° alcohols ⇒ Ketone

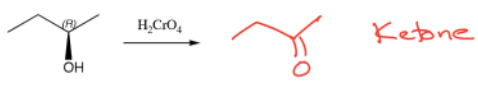


3° alcohols ⇒ NO REACTION

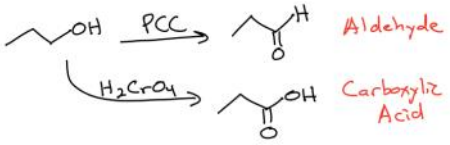
Regiochemistry: N/A

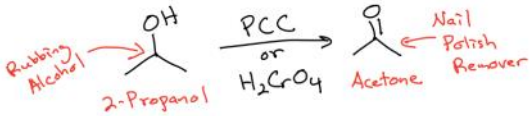
Stereochemistry: N/A

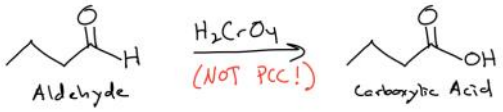
Example:



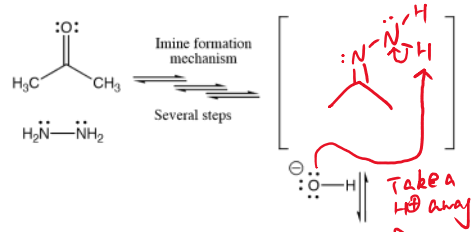
A chromic acid-like reagent WITHOUT WATER will stop at the aldehyde when using a primary alcohol as starting material

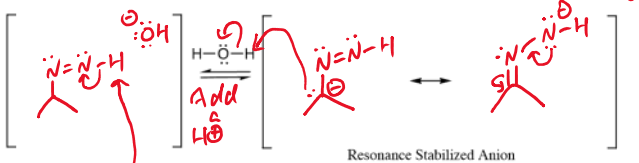


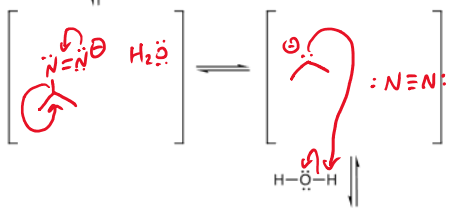




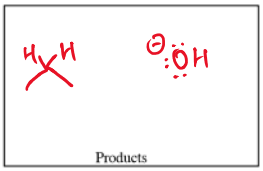
Wolff-Kishner Reduction of an Aldehyde or Ketone

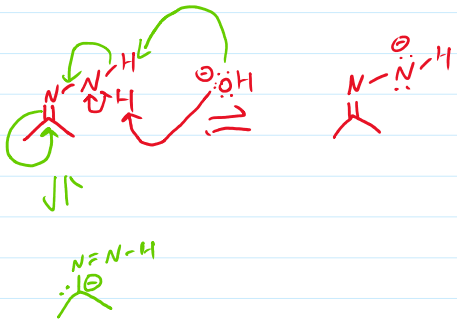




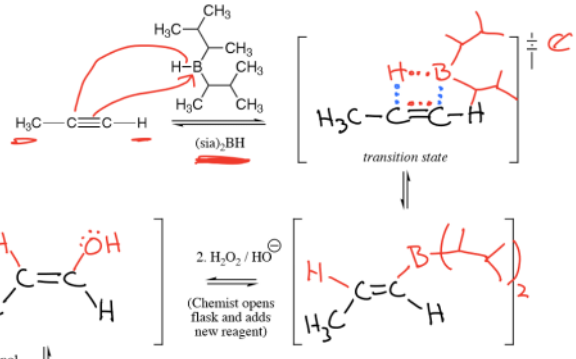


Key Recognition Element (KRE):





Terminal Alkyne Hydroboration



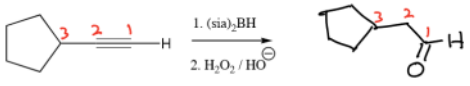
⇐ The C=O is on the C on the end → "non-Markovnikov"

Summary: The $(sia)_2BH$ reacts so the B atom attaches to the C atom on the end. The four-membered ring transition state makes both bonds simultaneously. 2. $H_2O_2/HO^{\ominus}$ → enol → keto

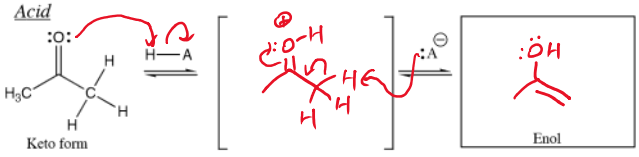
Regiochemistry: non-Markovnikov

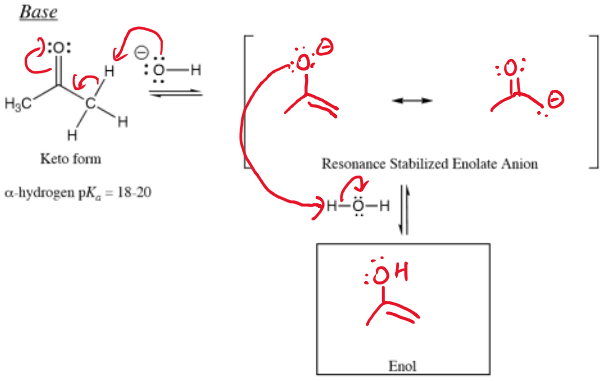
Stereochemistry: N/A

Example:



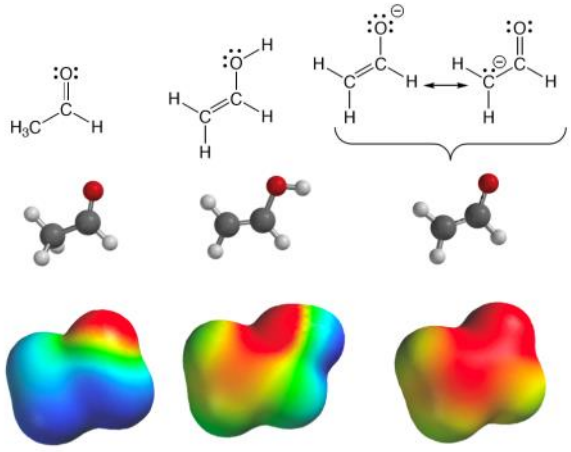
Keto-Enol Equilibrium Catalyzed by Acid or Base



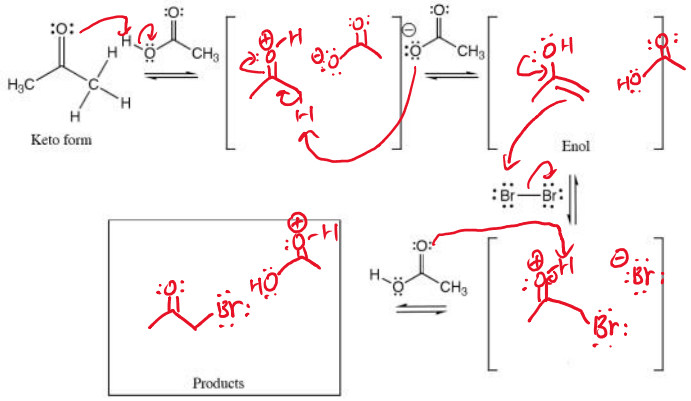


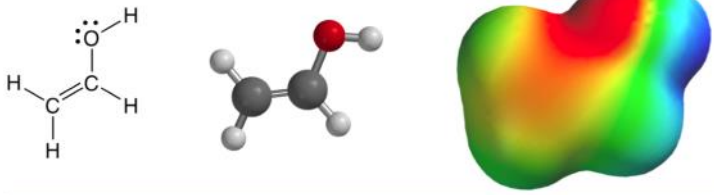
For both aldehydes and ketones, the keto form predominates at equilibrium, because C=O bonds are stronger than C=C bonds.

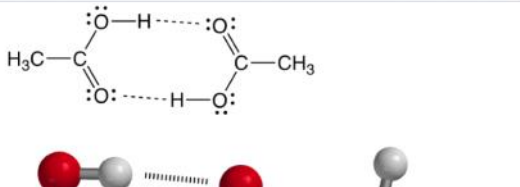
Enols are significant, however, because they react like _____, not carbonyls, and this is important in certain situations.

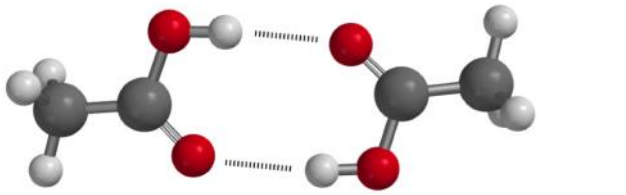


α-Halogenation of an Aldehyde or Ketone Catalyzed by Acid







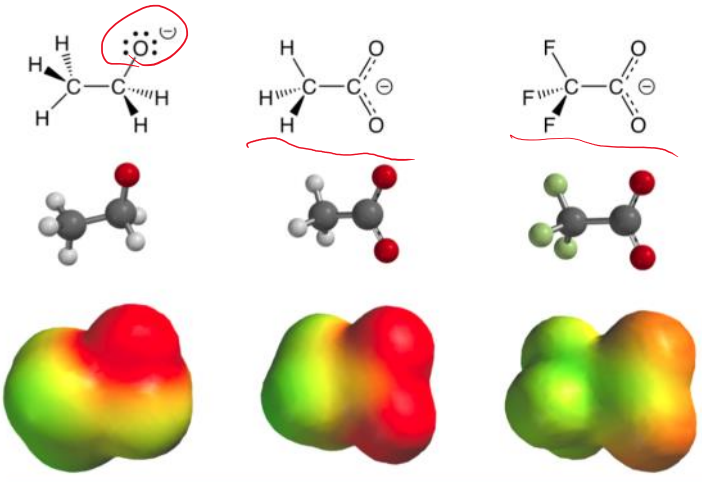


Acidity Revisited

$$H\text{-}A \rightleftharpoons H^{\oplus} + :A^{\ominus}$$

$$K_a = \frac{[A:^{\ominus}][H^{\oplus}]}{[HA]}$$

$$pK_a = -\log_{10} K_a$$



For an acid H-A

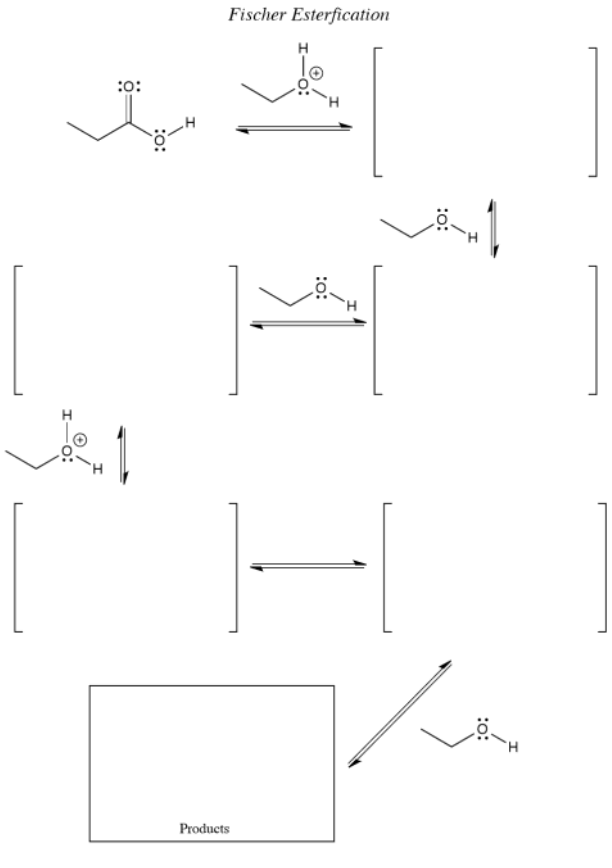
$$K_a = \frac{[A^{\ominus}][H^{\oplus}]}{[HA]} \qquad pK_a = -\log_{10} K_a$$

$$pH = -\log_{10}[H^{\oplus}]$$

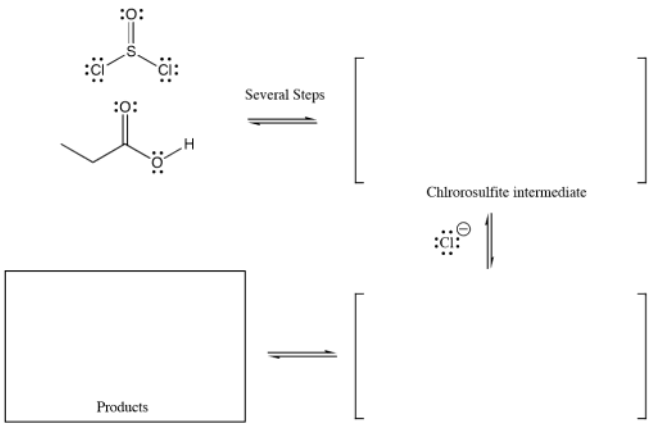
$$\frac{K_a}{[H^{\oplus}]} = \frac{[A^{\ominus}]}{[HA]} = 10^{(pH - pK_a)}$$

If $pH = 7$ and $pK_a = 3$

$$\frac{[A^{\ominus}]}{[HA]} = 10^{(pH - pK_a)} = 10^{(7-3)} = 10^4$$



Reaction with Thionyl Chloride



Decarboxylation of a β-Keto Acid