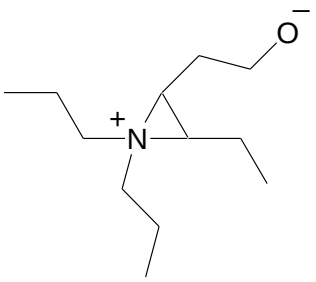
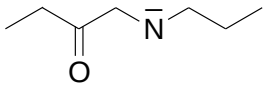
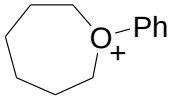
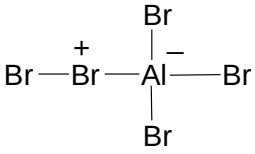
Mechanisms Midterm **100 points** NAME:_____

1) (12pts) Draw all the lone pairs on the following chemical species

a) 

b) 

c) 

d) 

2) (8pts) What is the hybridization of:

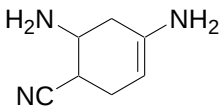
the Nitrogen in (a)

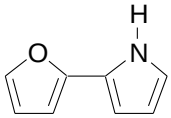
the Nitrogen in (b)

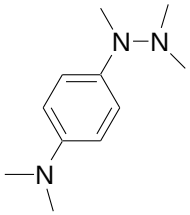
the oxygen in (c)

the positive Bromine in (d)

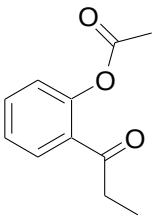
3) (6pts) Circle the most basic atom in these molecules.

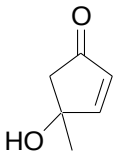


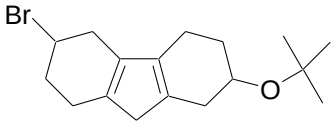


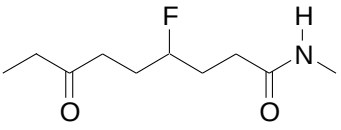


4) (8pts) Circle the most acidic hydrogen in these molecules.

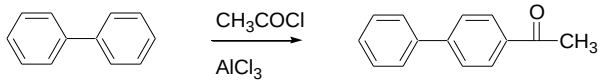


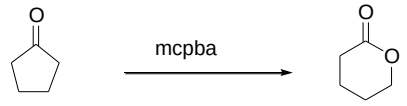


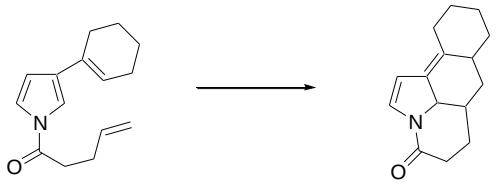


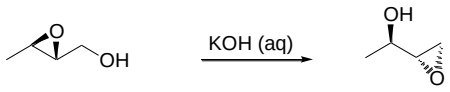


5) (12pts) Match these 8 transformations up with their correct name.

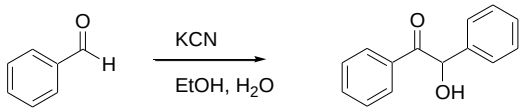


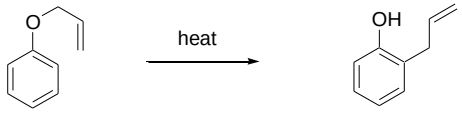


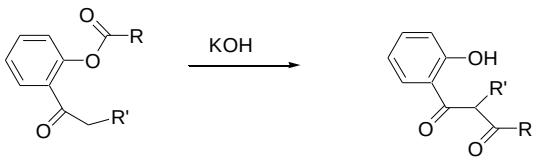


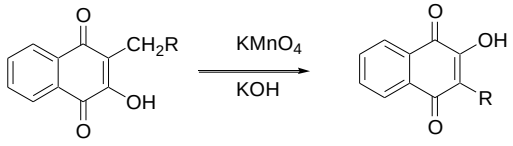


2









Hoffman Rearrangement

Diels Alder Reaction

Claisen Reaction

Baker-Venkataraman Rearrangement

Michael Addition

Bayer-Villiger Oxidation

Payne Rearrangement

Dieckmann reaction

Benzoin Condensation

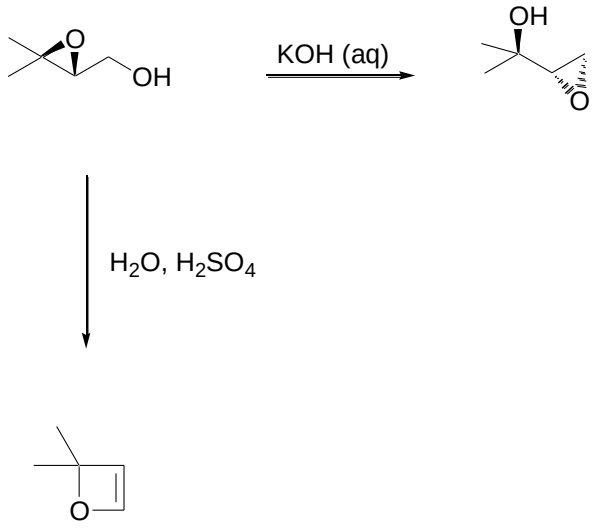
Friedal Crafts Acylation

Hooker Reaction

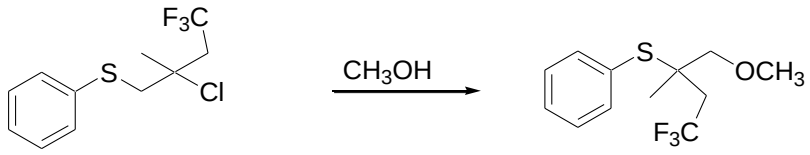
Danishevsky diene reaction

6) (14pts) For the starting material shown below, ring closure is media dependant – meaning in basic solution, a three membered ring is formed – but in acid a 4 membered ring is formed.

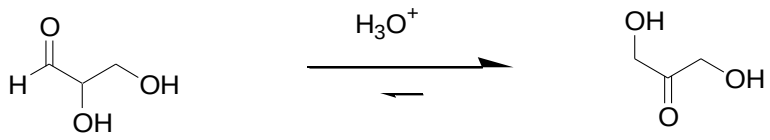
For BOTH reactions, write correct mechanisms AND also write short justifications explaining:
(1) the stereochemistry of the product epoxide
(2) why acid prefers to yield a 4 membered ring.



7) (9pts) Write the mechanism for this substitution process that obviously involves a rearrangement.



8) (17pts) The following transformation was first reported in 1895, where glyceraldeyhde rapidly converts to dihydroxyacetone.



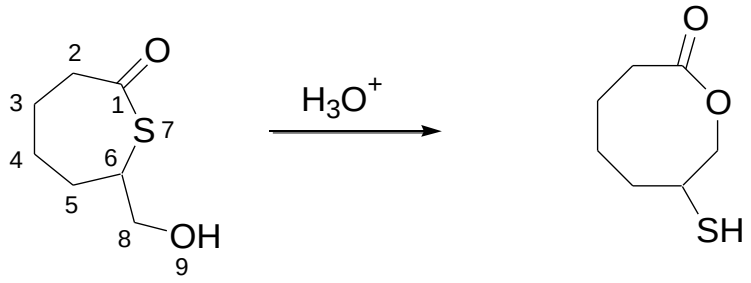
a) are these compounds isomers of one another?

b) are these compounds correctly described as *tautomers*?

c) justify briefly why the dihydroxyacetone is more stable than the glyceraldehyde.

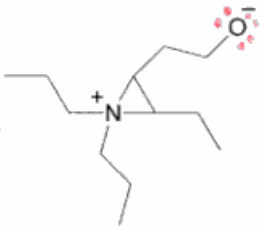
d) Write the acid catalyzed process for this rearrangement.

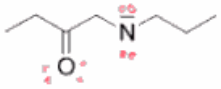
9) (14pts) For the below transformation, number the atoms in the product, and then write the correct acid catalyzed mechanism for this rearrangement.

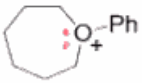


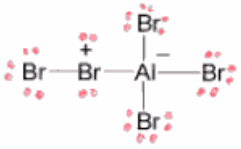
Mechanisms Midterm **100 points** NAME:_____

1) (12pts) Draw all the lone pairs on the following chemical species

a) 

b) 

c) 

d) 

2) (8pts) What is the hybridization of:

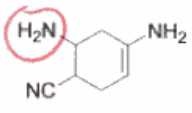
the Nitrogen in (a) sp^3

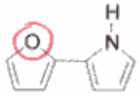
the Nitrogen in (b) sp^3

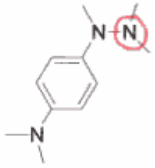
the oxygen in (c) sp^3

the positive Bromine in (d) sp^3

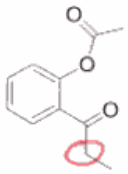
3) (6pts) Circle the most basic atom in these molecules.

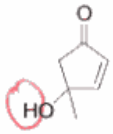


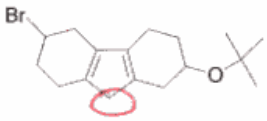


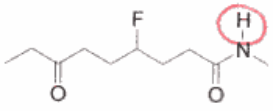


4) (8pts) Circle the most acidic hydrogen in these molecules.

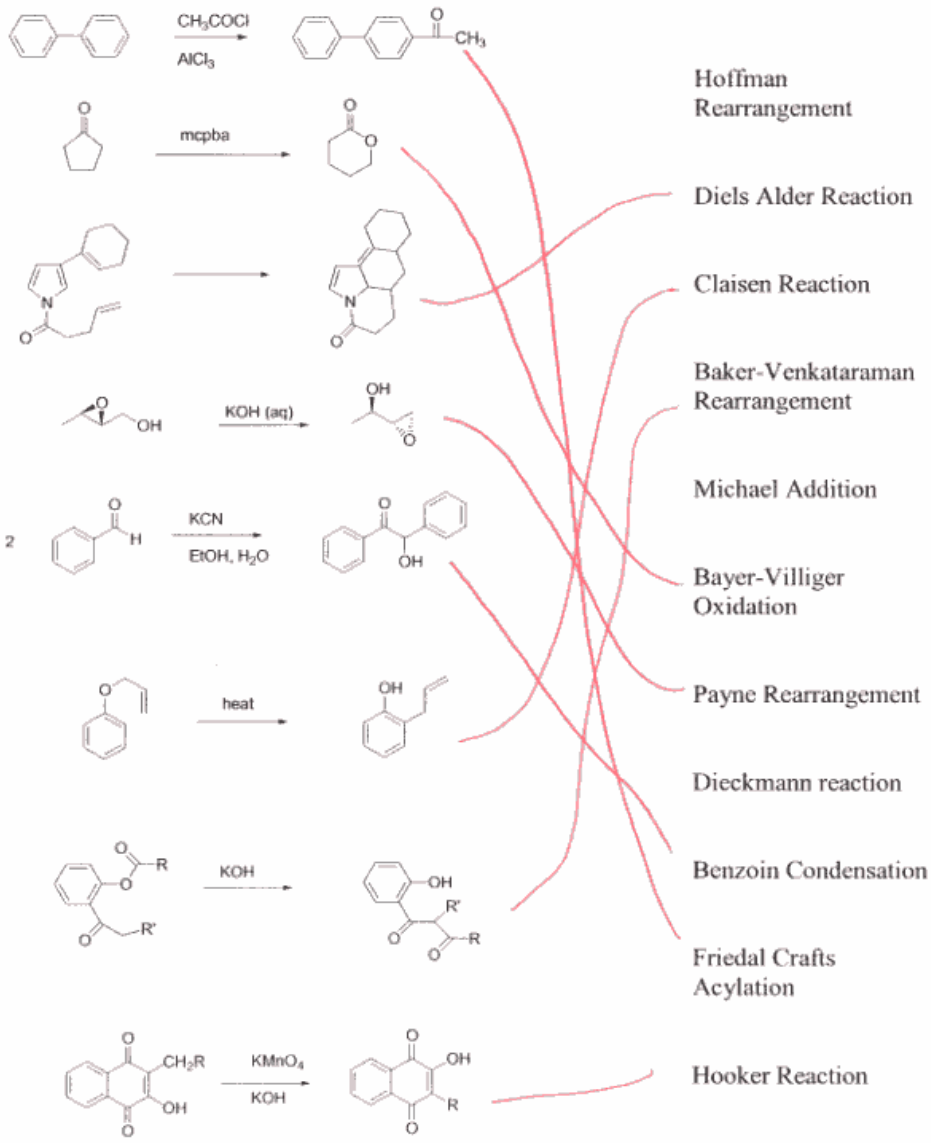








5) (12pts) Match these 8 transformations up with their correct name.



Hoffman Rearrangement

Diels Alder Reaction

Claisen Reaction

Baker-Venkataraman Rearrangement

Michael Addition

Bayer-Villiger Oxidation

Payne Rearrangement

Dieckmann reaction

Benzoin Condensation

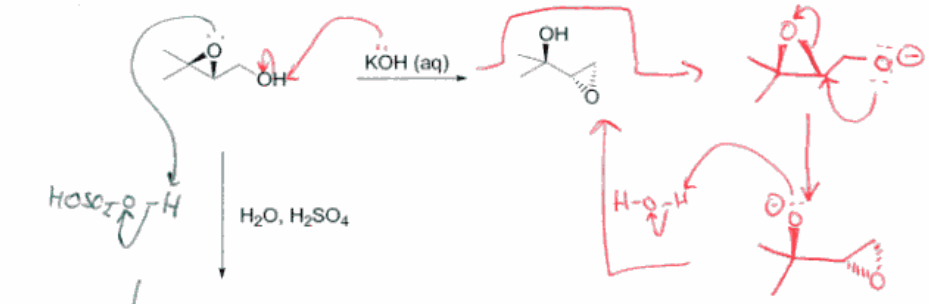
Friedal Crafts Acylation

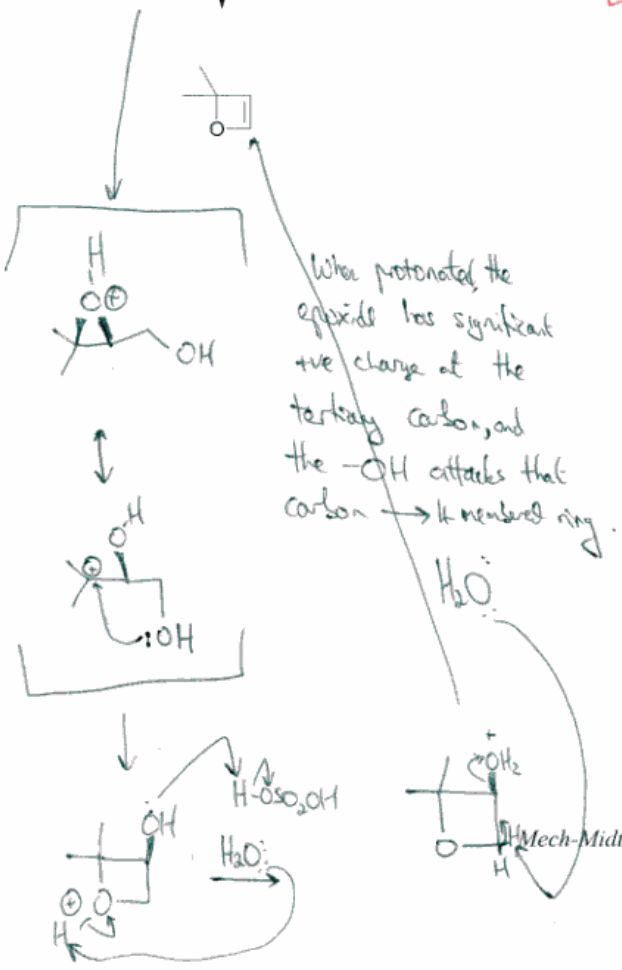
Hooker Reaction

Danishevsky diene reaction

6) (14pts) For the starting material shown below, ring closure is media dependant – meaning in basic solution, a three membered ring is formed – but in acid a 4 membered ring is formed.

For BOTH reactions, write correct mechanisms AND also write short justifications explaining:
(1) the stereochemistry of the product epoxide
(2) why acid prefers to yield a 4 membered ring.

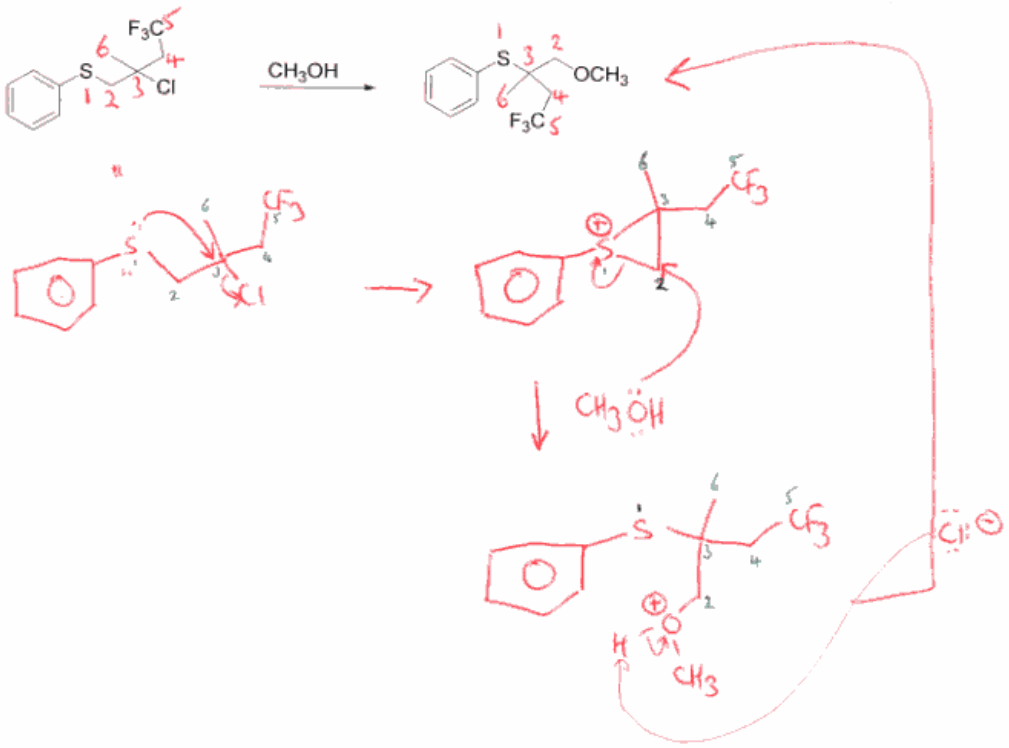




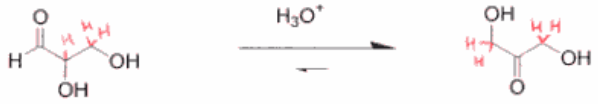
When protonated, the epoxide has significant +ve charge at the tertiary carbon, and the –OH attacks that carbon → 4 membered ring.

The epoxide ring opening occurs via SN2 back side attack, which requires the nucleophile to attack from the opposite face than the epoxide.

7) (9pts) Write the mechanism for this substitution process that obviously involves a rearrangement.



8) (17pts) The following transformation was first reported in 1895, where glyceraldeyhde rapidly converts to dihydroxyacetone.



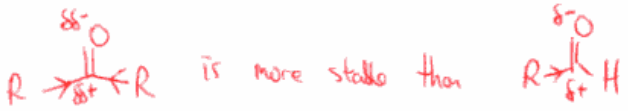
a) are these compounds isomers of one another? $C_3H_6O_3$ & $C_3H_6O_3$ so YES

b) are these compounds correctly described as *tautomers*? YES

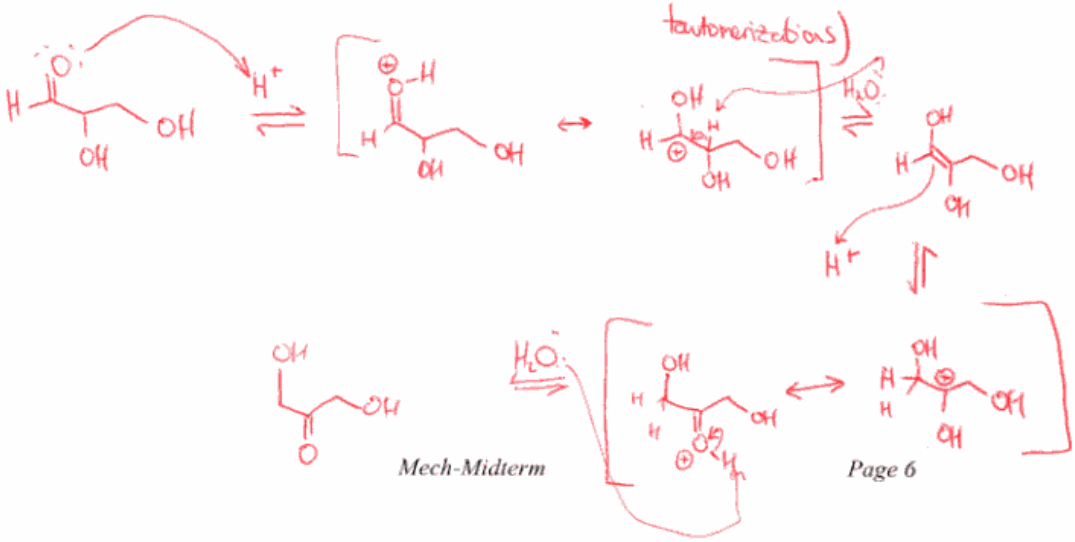
c) justify briefly why the dihydroxyacetone is more stable than the glyceraldehyde.

One is an aldehyde, the other is a ketone. Ketones are more stable than aldehydes.

The partial +ve charge on the carbonyl carbon is stabilized by higher alkyl substitution.



d) Write the acid catalyzed process for this rearrangement. (= 2 keto-enol tautomerizations)



9) (14pts) For the below transformation, number the atoms in the product, and then write the correct acid catalyzed mechanism for this rearrangement.