California State Polytechnic University, Pomona

Chem 316
Midterm Exam
Fall, 2009
Beauchamp

Name:_____

Topic	Total Points Exam Points	Credit
1. Nomenclature (1)	30	
2. Arrow-pushing Mechanism	20	
3. Reactions page 10 x 3 lines of reactions studied so far in organic chemistry	30	
4. Synthesis using specific functional groups or reagents	30	
5. ^{14}C synthesis (methane, ethane, cyclopentane, propane, bromobenzene, NaCN, CO_2, ^{14}C compounds)	30	
6. Tautomers (acid or base)	30	
7. Bio-Organic Game	40	
Total	210	

This is a long exam. It has been designed so that no one question will make or break you. The best strategy is to work steadily throughout the period, starting with those problems you understand best. Make sure you **show all of your work**. In mechanism problems, draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement. If resonance is present in a mechanism problem, draw at least one additional resonance structure to show you recognize this feature (make sure the "best" resonance structure is included in your two resonance structures). On synthesis and reaction problems, do not write mechanisms (unless you need to prompt yourself). You are only given credit for the correct product and/or reagents. Only write answers on the front of each page. Do your best to show me what you know in the time available.

We learn only when it is too late that the marvel is the passing moment.

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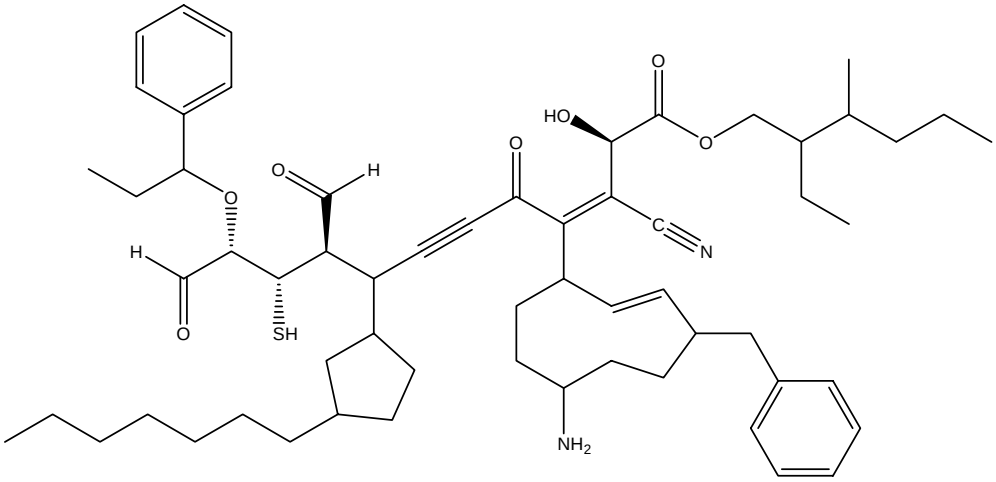
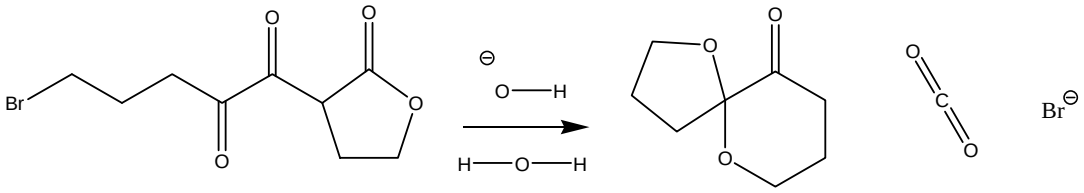
1. Provide an acceptable name for the following structure. Only identify stereochemistry where shown (30 pts)



2. Provide complete arrow-pushing mechanisms for the reaction below. Include curved arrows, lone pairs of electrons and formal charge. If resonance is important to your solution, draw the best resonance structure and one additional resonance structure to show you recognize this feature. Write out each discrete step of your mechanism (do not combine steps). (20 pts)



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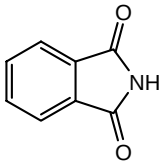
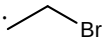
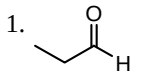
3. Provide the expected product for each of the following transformations. Show regiochemistry and stereochemistry clearly, if relevant. Do NOT show mechanisms. (30 pts)

a.

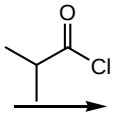


1. NaOH
2. 
3. NaOH

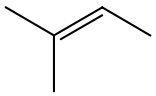
→

1. 
TsOH (-H_2O)
2. NaH_3BCN
3. WK

→



b.

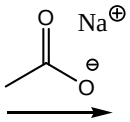


1. BH_3
2. H_2O_2, $HO^{\ominus}$

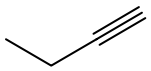
→

1. TsCl, py
2. NaBr

→



c.



1. $NaNR_2$
2. 
3. WK

→

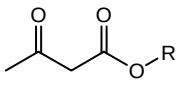
1. excess $NaNR_2$
2. WK

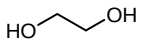
→

1. R_2BH
2. H_2O_2, HO

→

d.

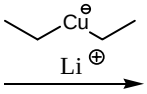



TsOH (-H_2O)

→

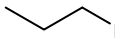
1. 2 eqs. CH_3MgBr
2. H_2SO_4/Δ (-H_2O)

→



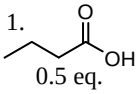
→

e.

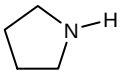


Li

→

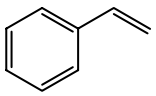
1. 
0.5 eq.
2. WK

→


TsOH (-H_2O)

→

f.

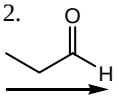


1. BH_3
2. Br_2, $CH_3O^{\ominus}$

→

Ph_3P

→

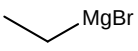
1. nBuLi
2. 

→

g.

NaCN

→

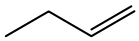
1. 
2. WK

→

1. $LiAlH_4$
2. WK

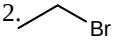
→

h.



Br_2

→

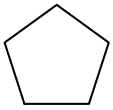
1. excess $NaNR_2$
2. 

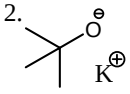
→

Na/NH_3

→

i.



1. $Br_2/h\nu$
2. 

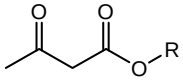
→

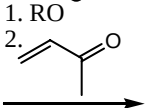
mCPBA

→

CH_3OH
$CH_3OH_2^+$

→



1. $RO^{\ominus}$
2. 

(forms ring, -H_2O)

→

$H_3O^+/H_2O/\Delta$ (-CO_2)

→

1. $Ph_3P{=}CH_2$
2. WK

→

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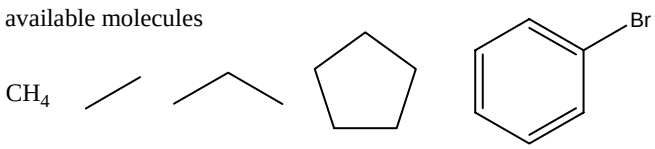
4. Propose a synthesis for the following compound using methane, ethane, propane, cyclopentane, sodium cyanide and carbon dioxide. Your only source of radioactive ^{14}C carbon is ^{14}C methane, $*CH_4$, carbon dioxide, $*CO_2$ and sodium cyanide, $Na*CN$. You may also use any typical organic reagents. Often the best strategy is to work backwards from the target molecule. The last step of the synthesis should be your first step. Show the reagents and reactant for each backwards step until you reach allowable starting molecules. Do not show mechanisms. (30 pts)

available molecules

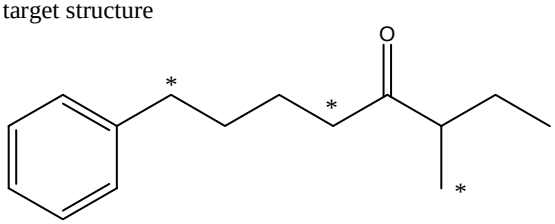


NaCN

CO_2

$^{*}CH_4$ $Na^{*}CN$ $^{*}CO_2$

target structure



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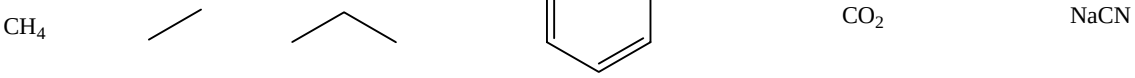
5. Propose an acceptable synthetic approach to each of the target molecules below, including the given requirements. Work backwards (retrosynthetic thinking) and show each intermediate structure and each reagent until you reach an acceptable starting point. Acceptable starting points are the following structures and any routine reagents we have discussed in the course. Mechanisms are NOT required. (30 pts)

Allowed sources of carbon



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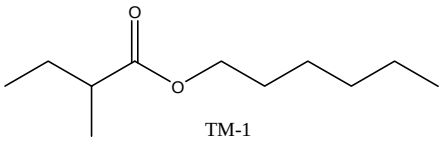
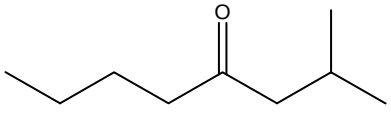
a. use an alkyne and an acid chloride



TM-1

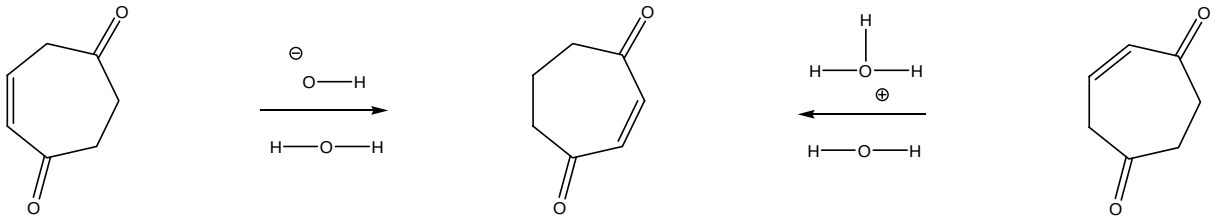
synthesis last step
= your first step

b. use ethyl acetoacetate (make it too, for full credit)



synthesis last step
= your first step

6. Propose a mechanism for the following tautomeric transformation in **acid or base**. (30 pts)



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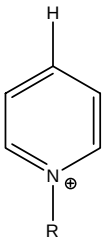
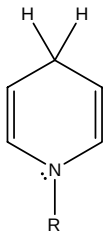
7. From the given bio-organic structure, use our simplistic mechanisms to show how each transformation could occur. If any structures are missing, use the descriptive term to fill in the necessary structures and details. Draw in any additional atoms or structures needed to demonstrate the transformations (e.g. a hydrogen atom or a water molecule, any co-factors, etc.). Use **B:** if you need a base and **B-H⊕** if you need an acid. Acceptable representations of possible co-factors are provided at the bottom of the last page. (40 pts)

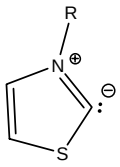
Simplified co-factors for the bio-organic game problems, if needed.



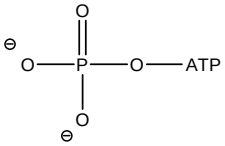
NAD^+ equivalent



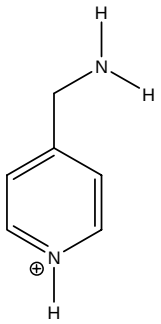
NADH equivalent



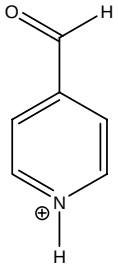
TPP ylid



ATP

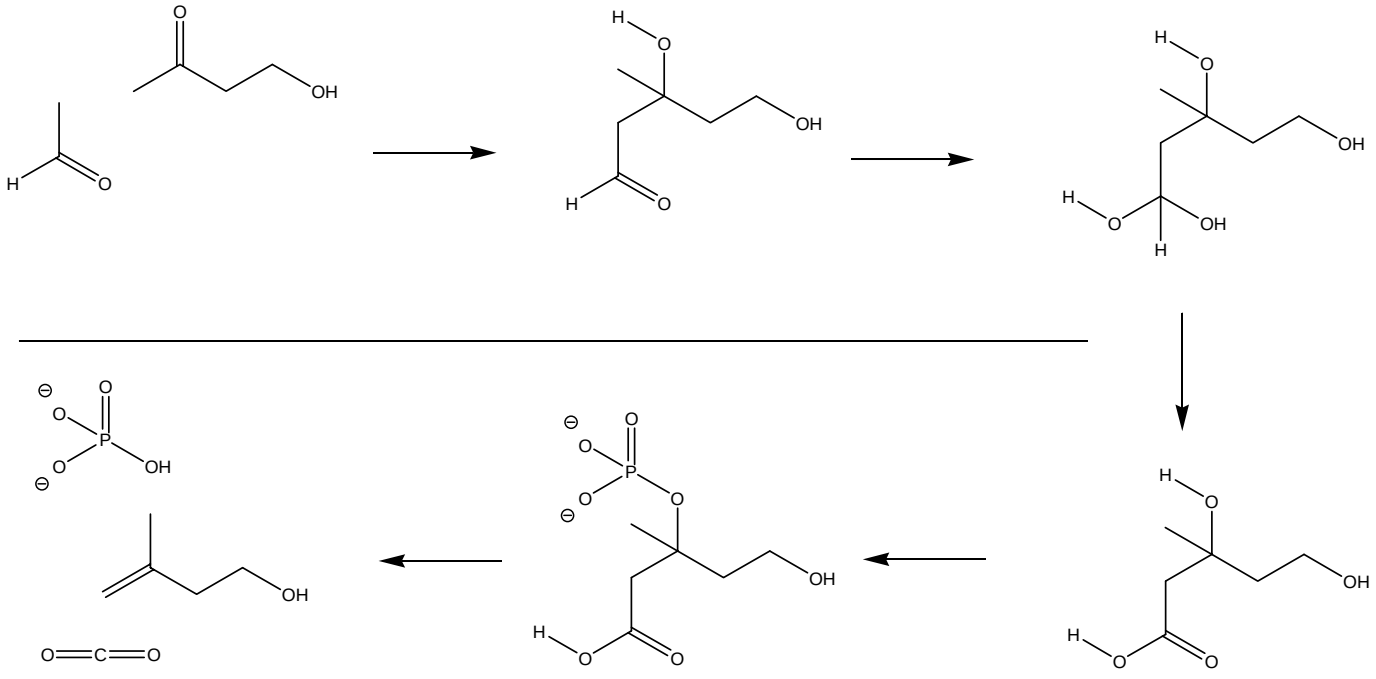


vitamin B-6 (1^o amine version)

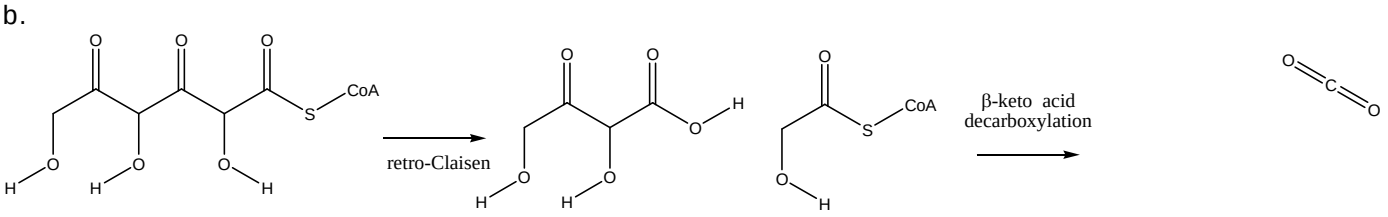


vitamin B-6 (aldehyde version)

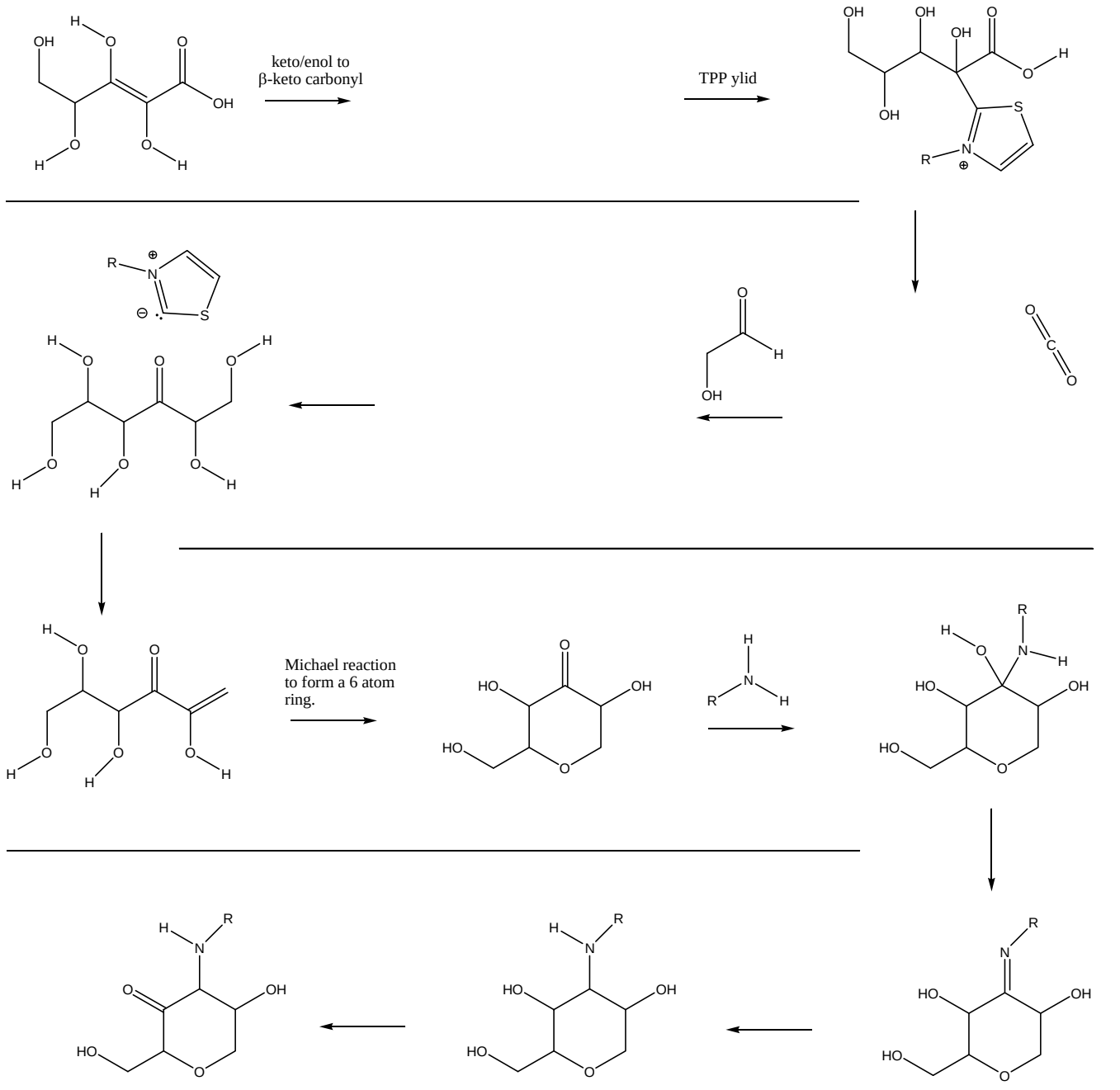
a.



b.



c.



d.

You cannot do a kindness too soon for you never know how soon it will be too late.
Ralph Waldo Emerson

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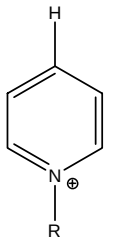
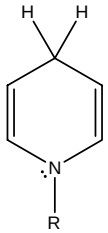
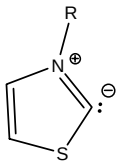
Simplified co-factors for the bio-organic game problems, if needed.



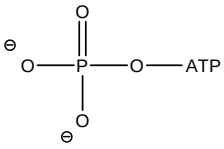
NAD^+ equivalent



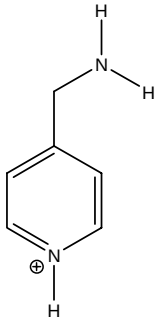
NADH equivalent



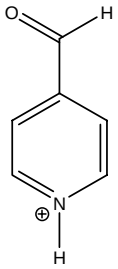
TPP ylid



ATP

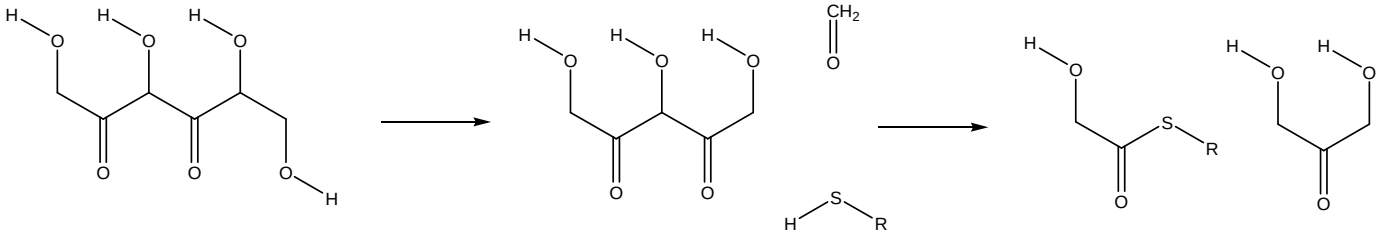


vitamin B-6 (1^o amine version)

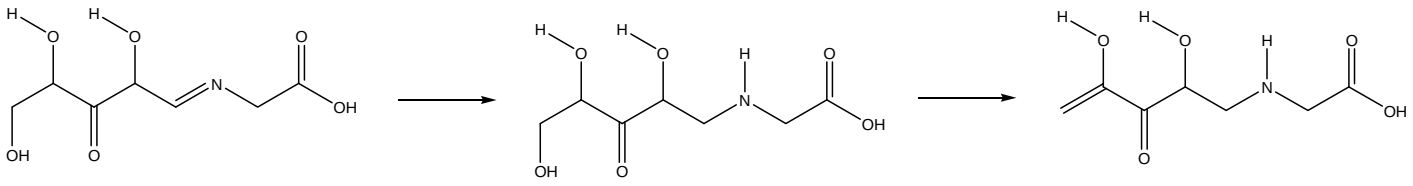


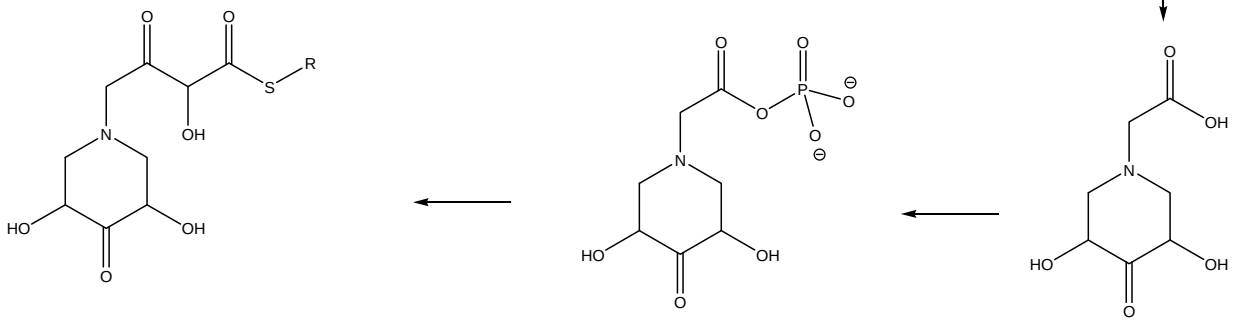
vitamin B-6 (aldehyde version)

d.

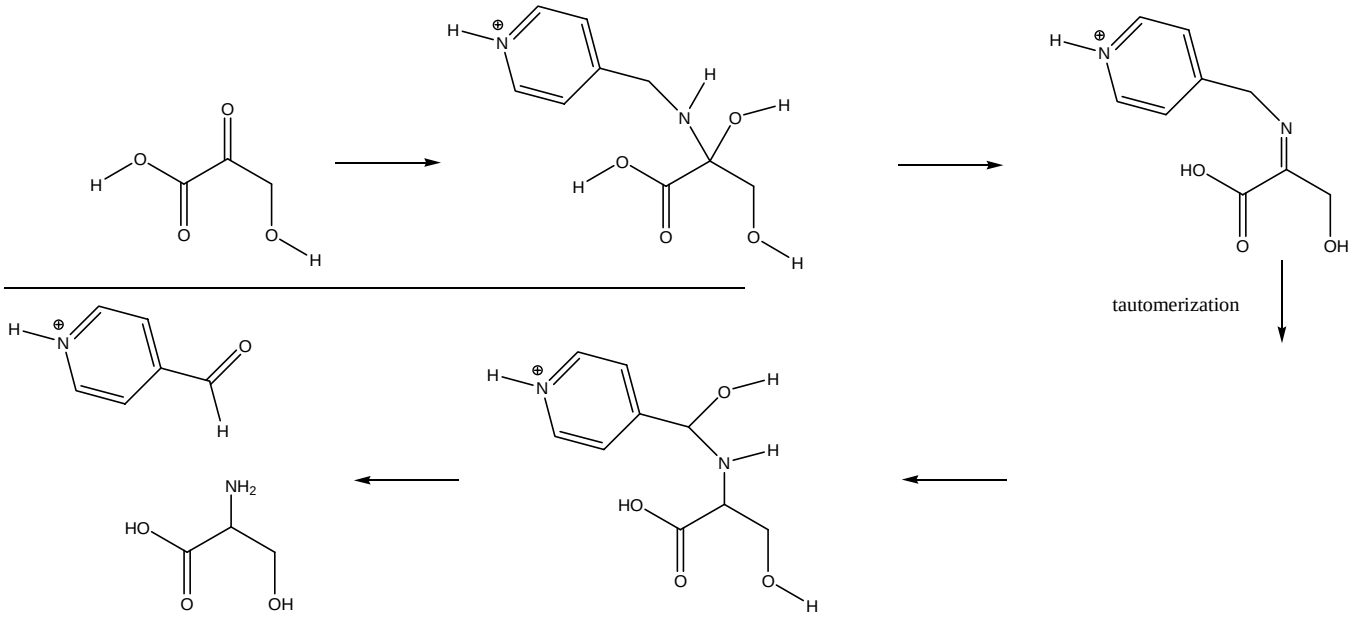


e.





f.



b.