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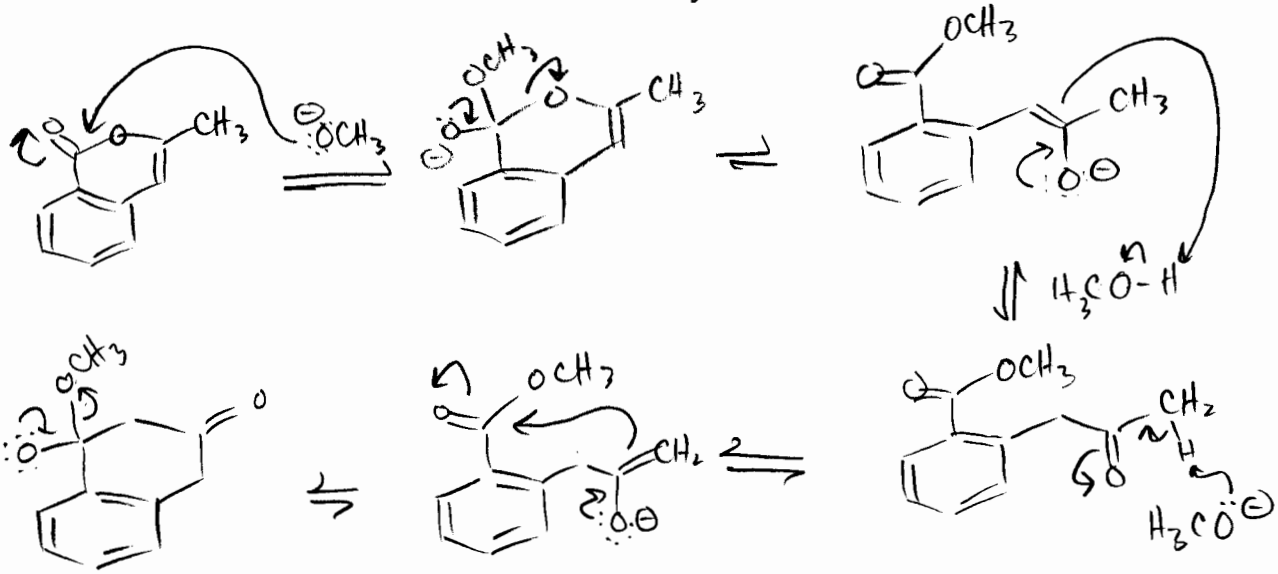
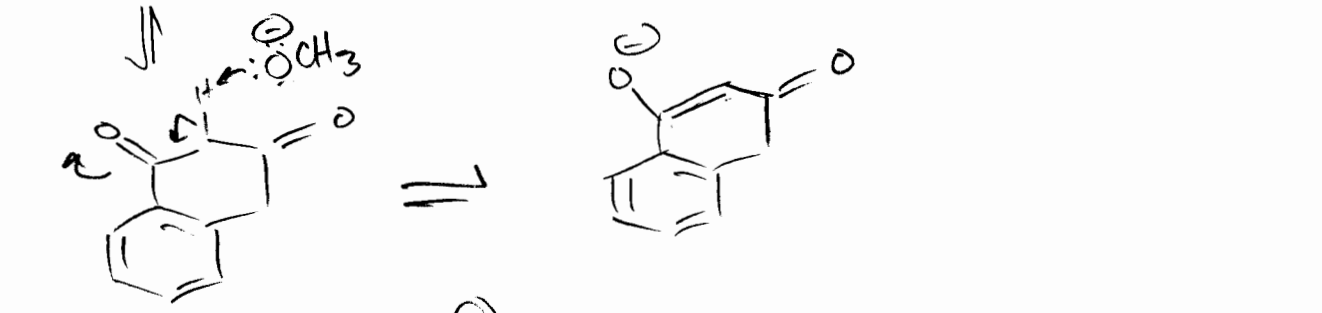
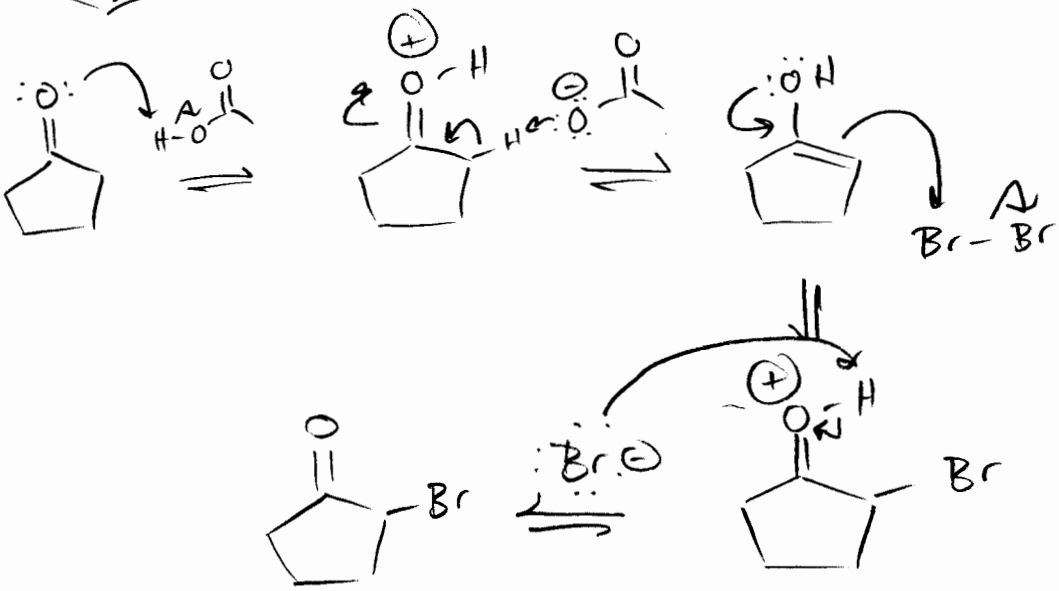
Problem Set 6 Answer Key

(1) a)





b)



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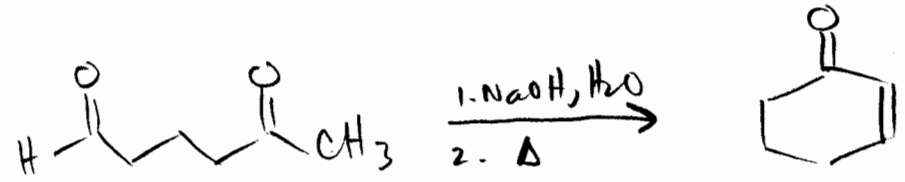
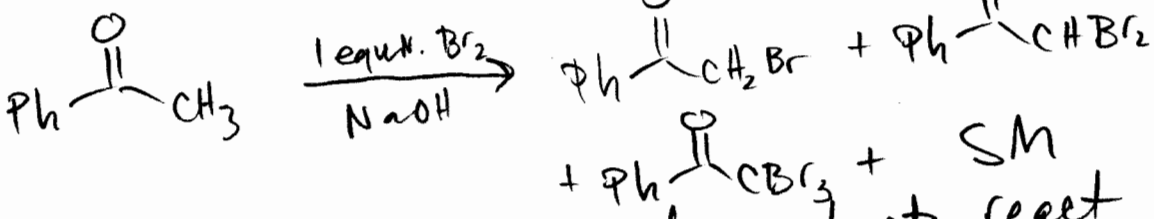
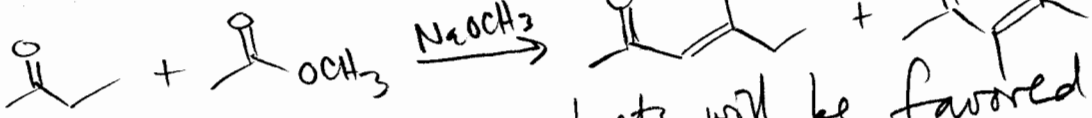
(2) a) 

Selective: Only one of the three possible enolate will react to give a six-membered ring. The other two would give four-membered rings. (BAD)

b) 

Unselective: The brominated products react faster than the SM → get mixtures of mono-, di-, and tri-brominated products in addition to unreacted SM.

c) 

Unselective: Claisen products will be favored because of formation of the enolate of the β-dicarbonyl, but ketone is unsymmetrical. Both α-carbons have at least 2 enolizable protons.

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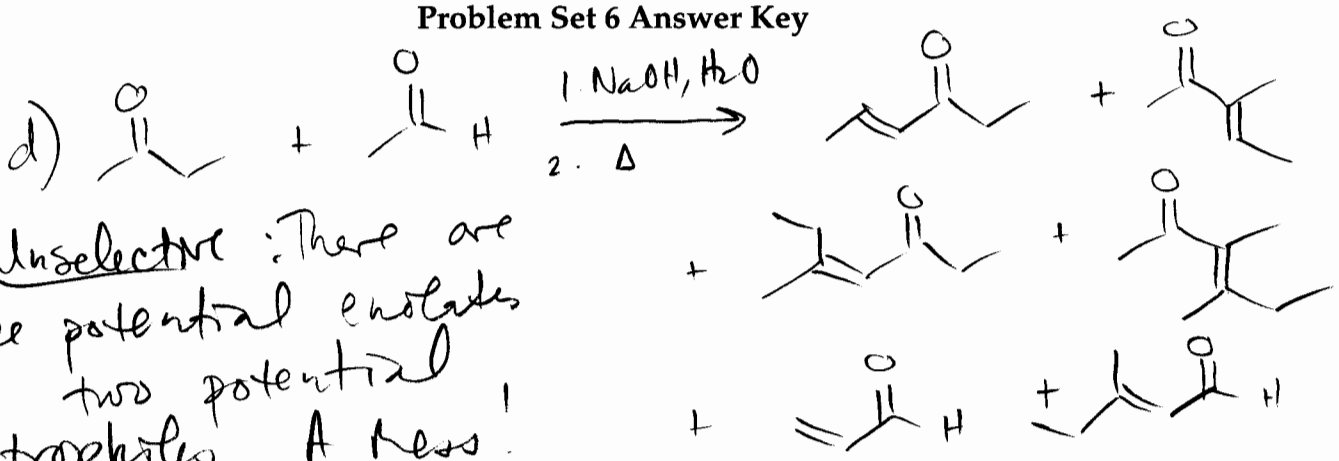
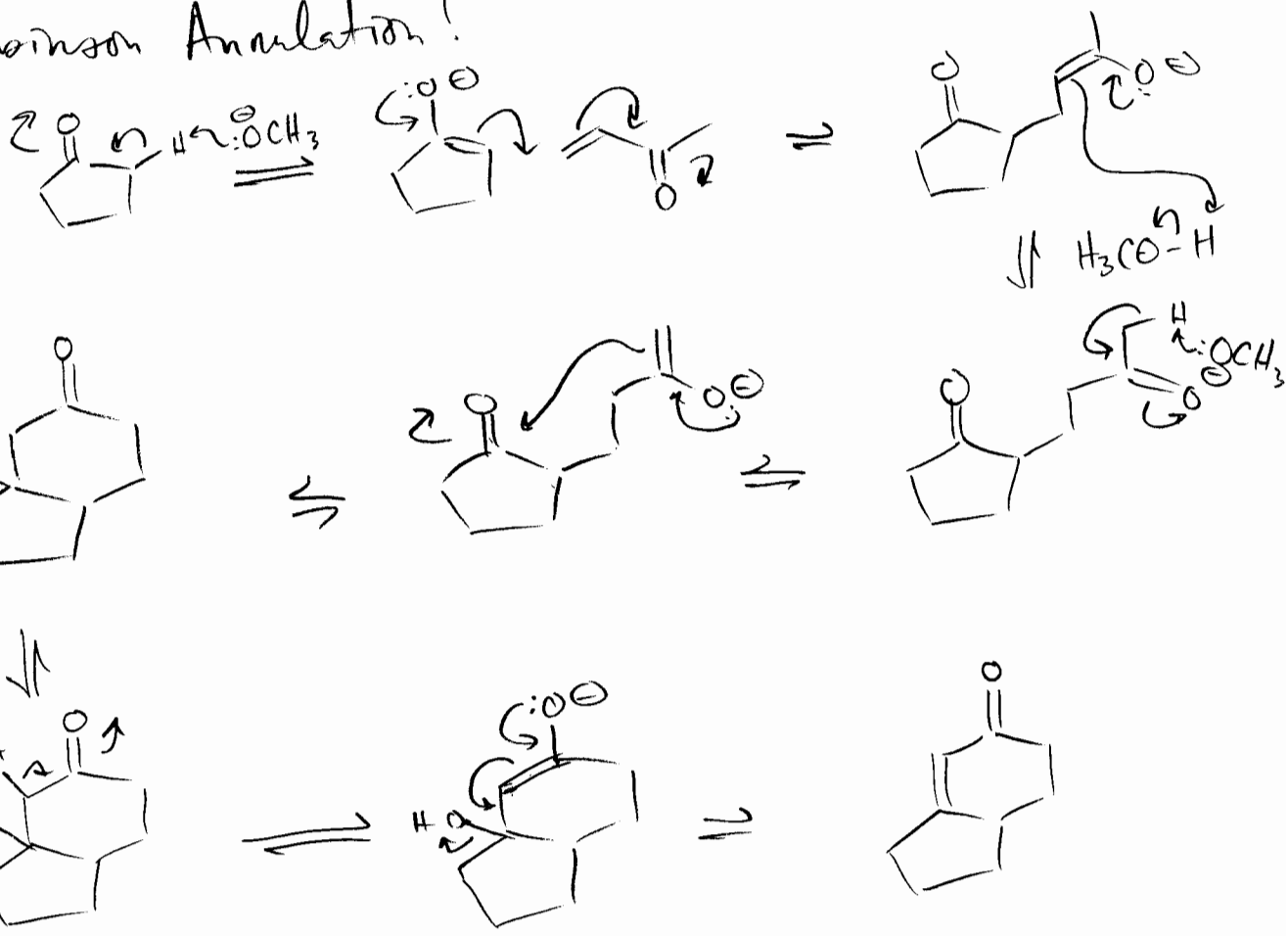
d) 

Unselective: There are three potential enolates and two potential electrophiles. A mess!

(3) Robinson Annulation!



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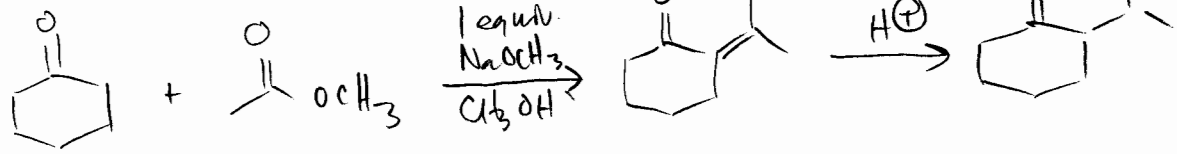
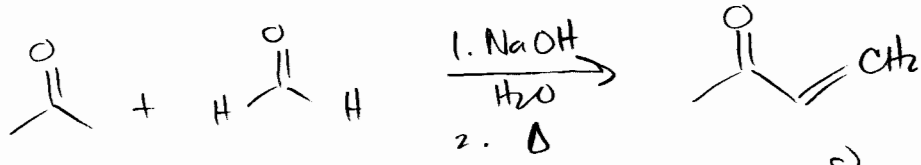
Problem Set 6 Answer Key

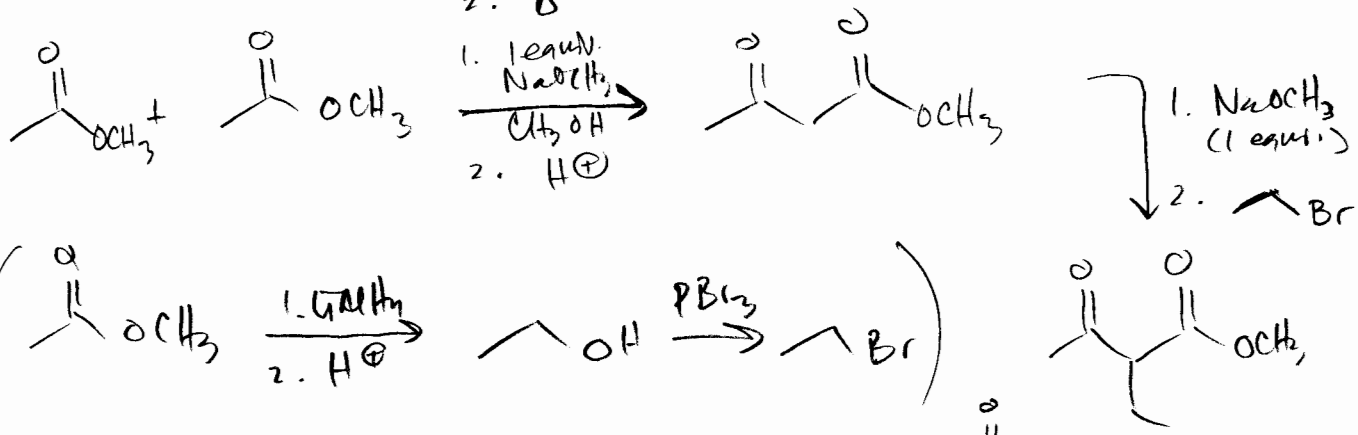
(4) a)



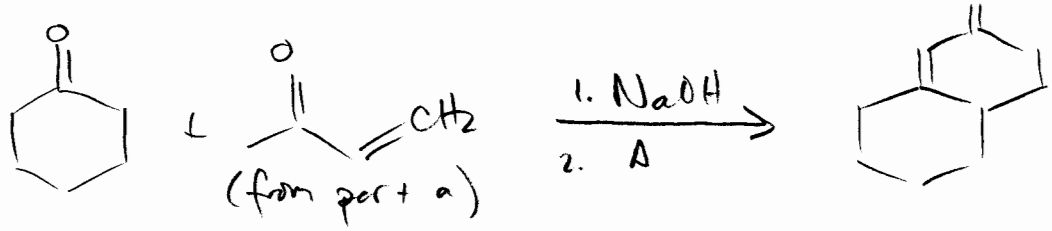
b)



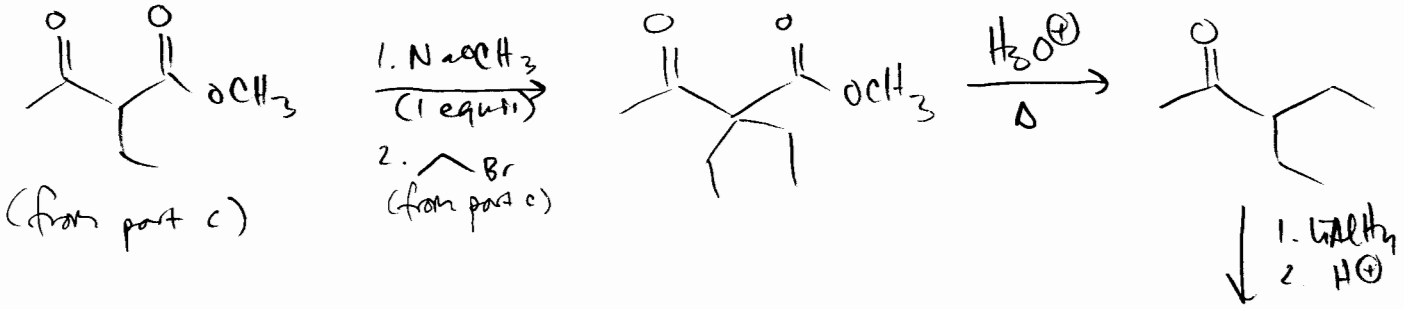
c)



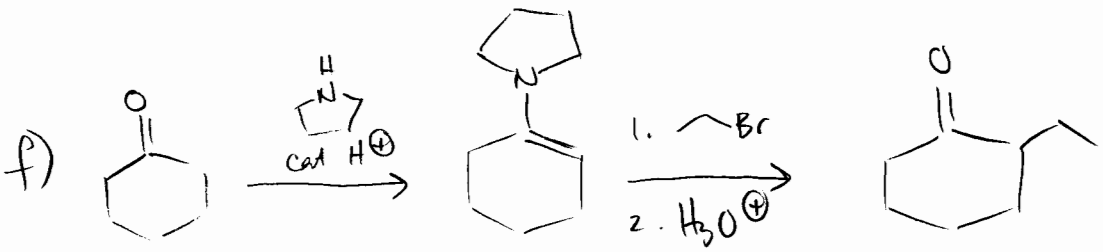
d)



e)



f)



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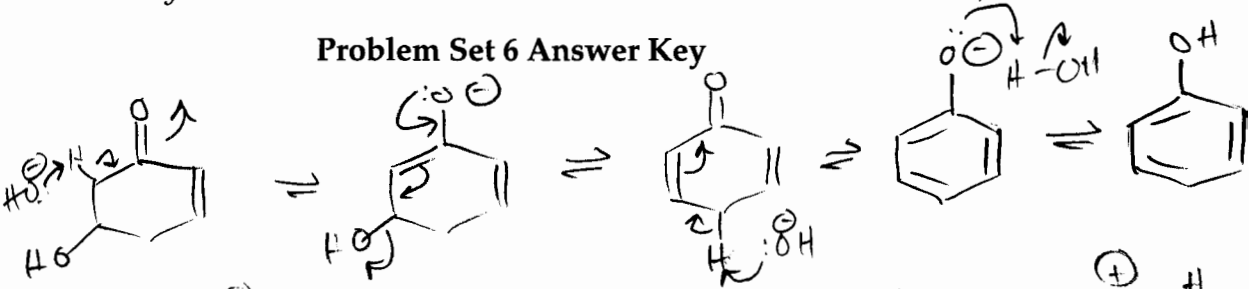
Problem Set 6 Answer Key

(5) a)



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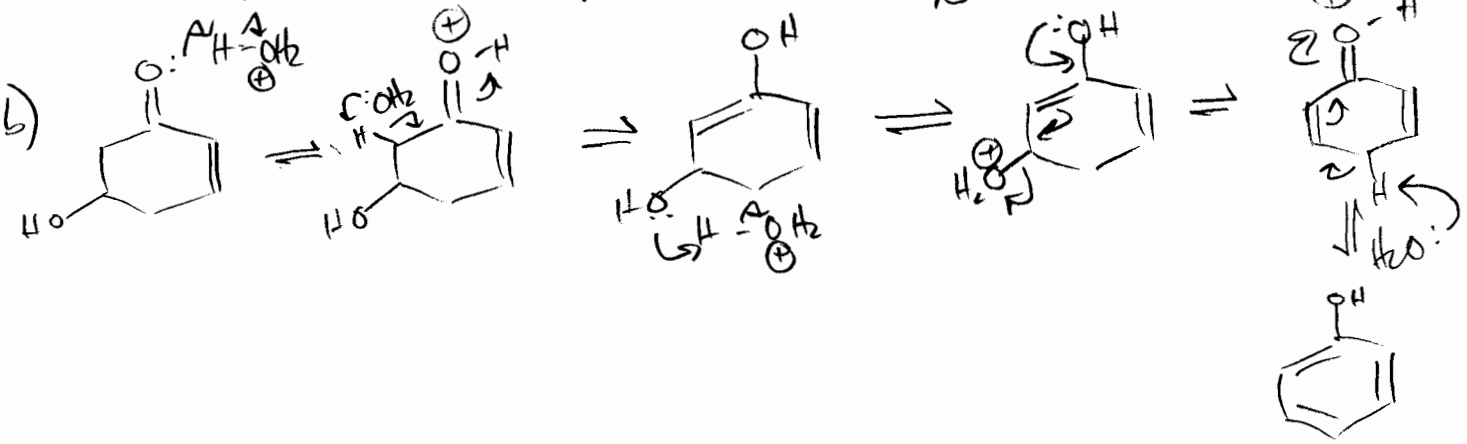
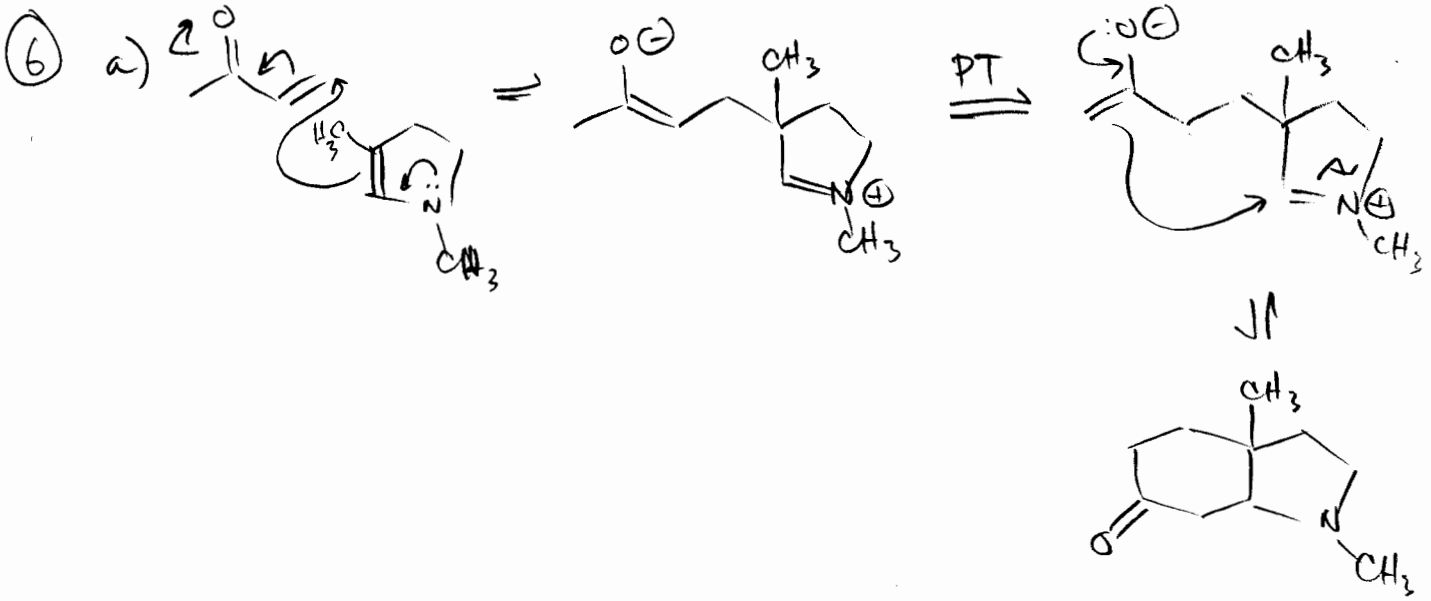


(6) a)



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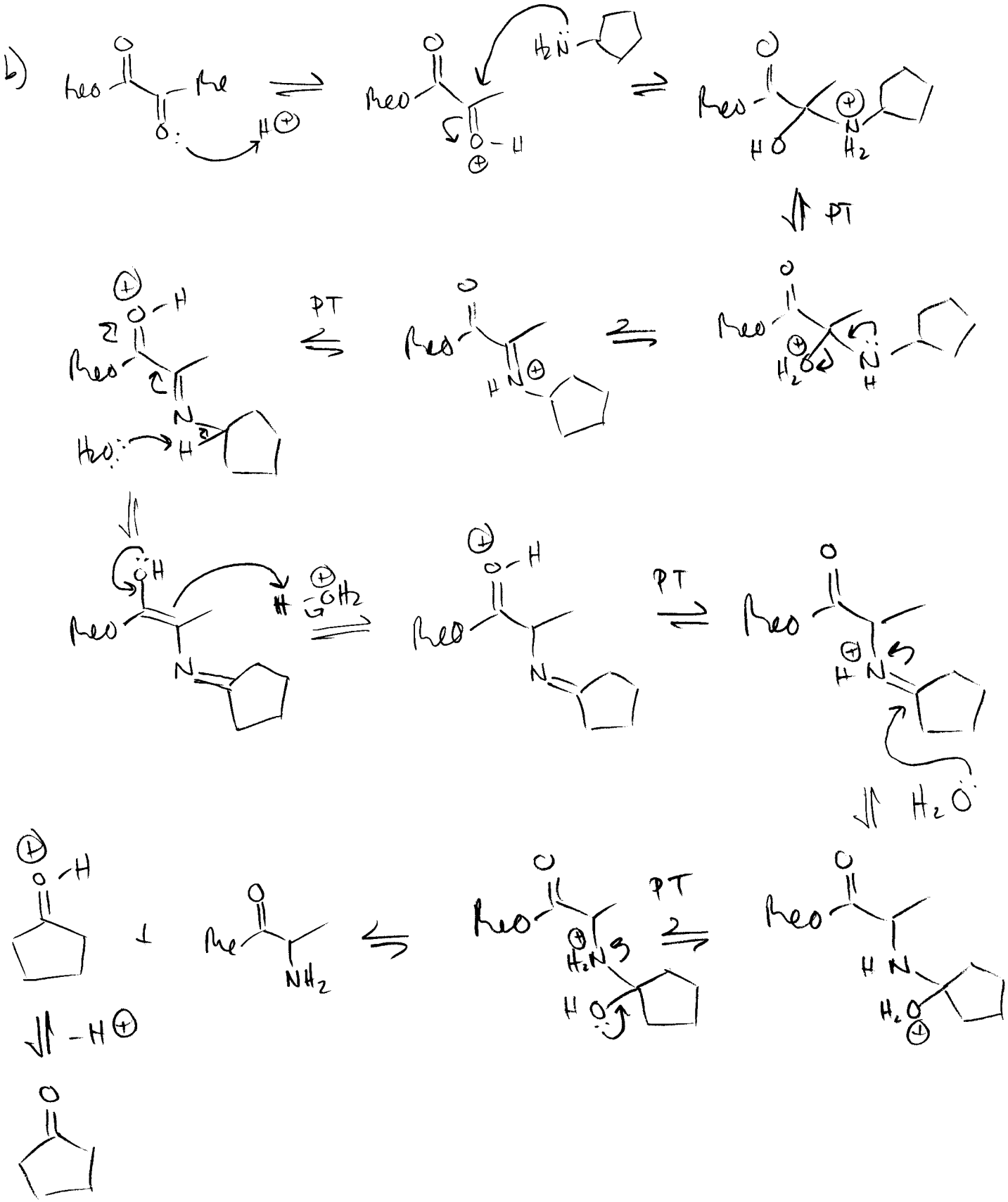
Problem Set 6 Answer Key

b)



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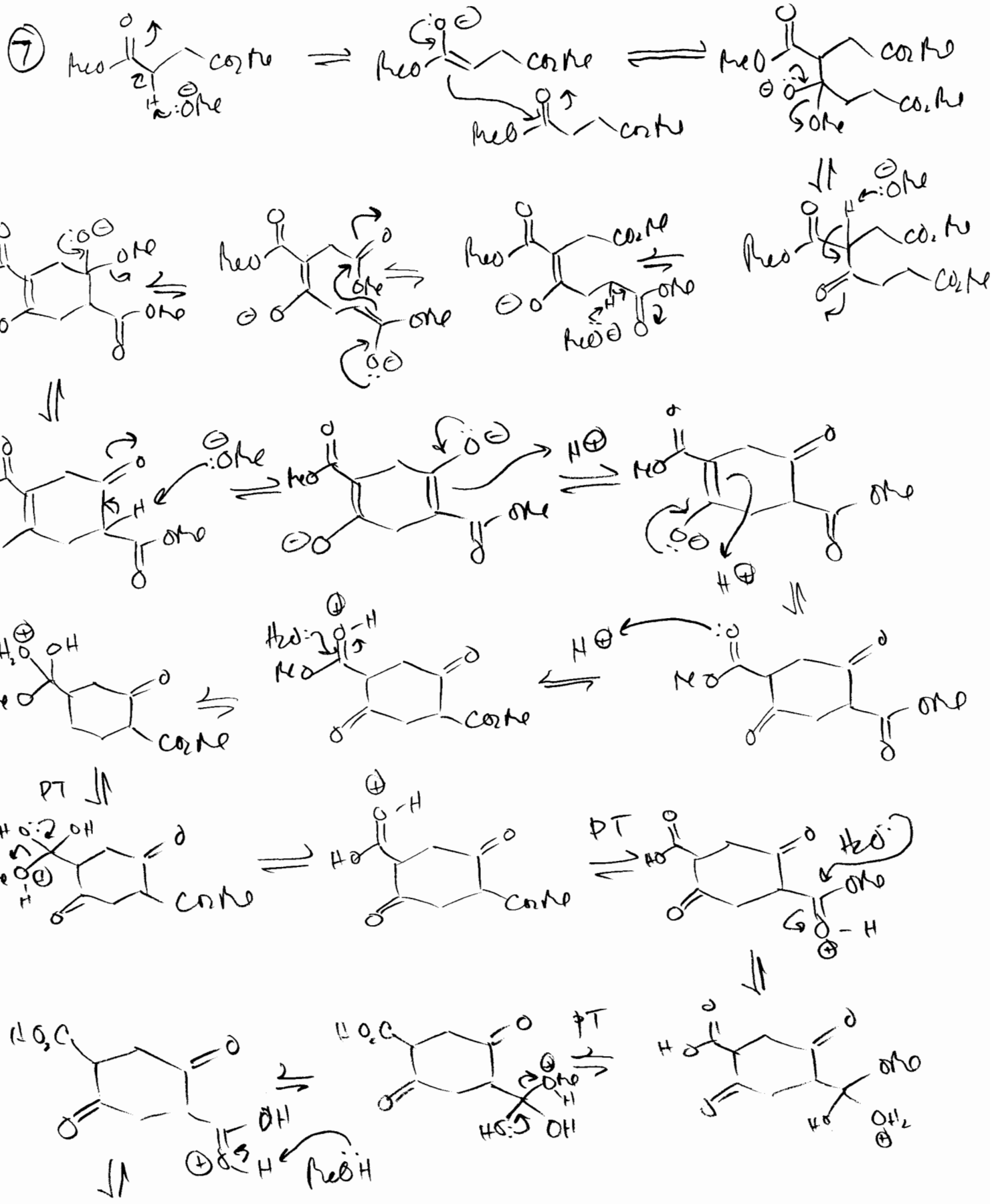
Problem Set 6 Answer Key



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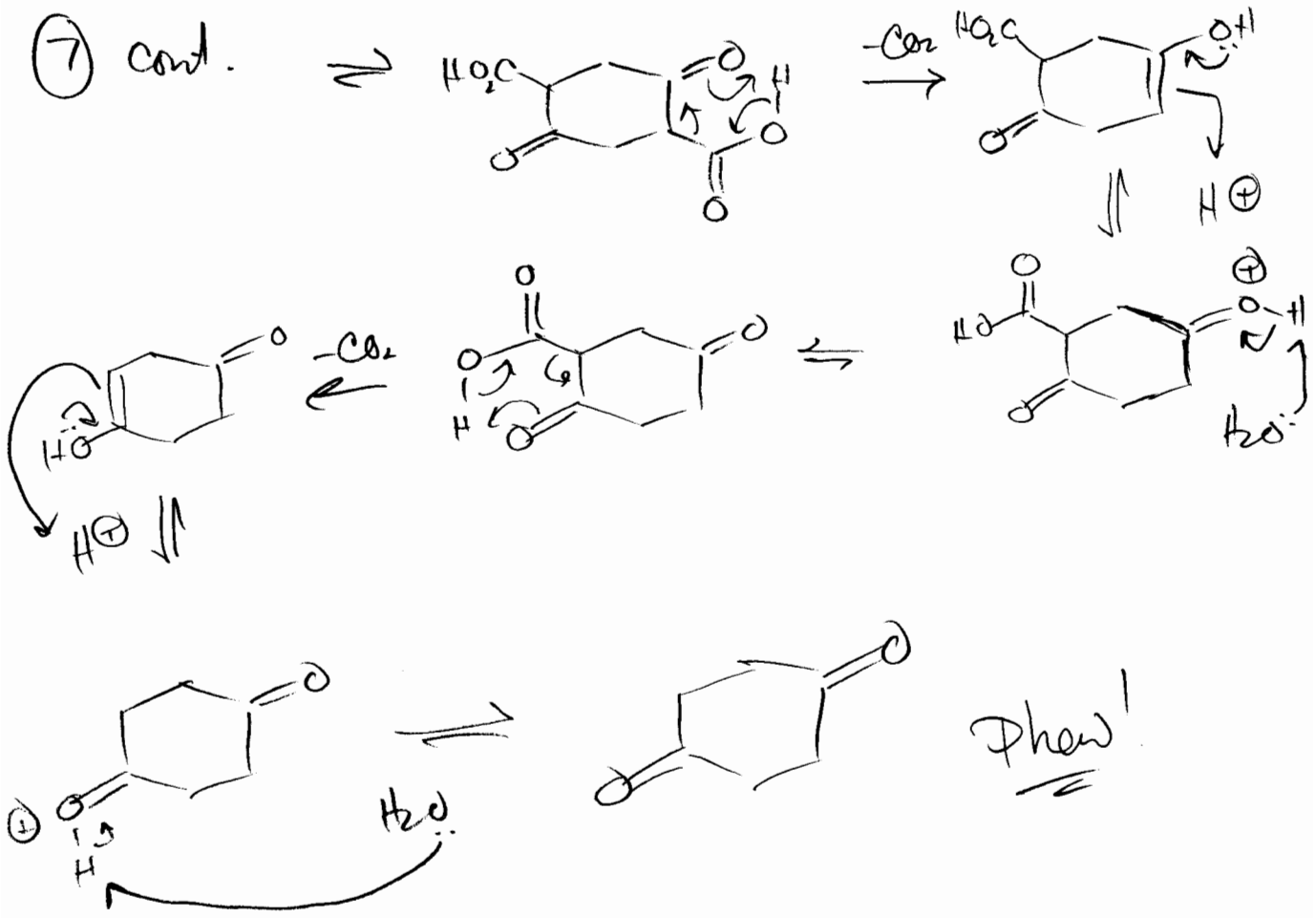
Problem Set 6 Answer Key



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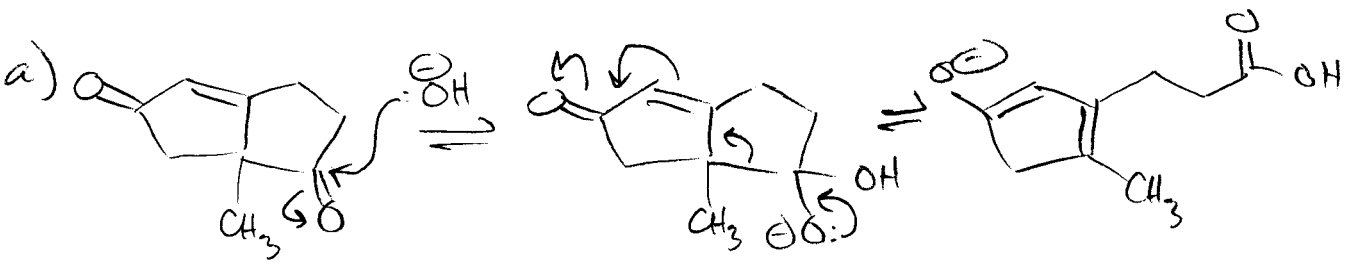
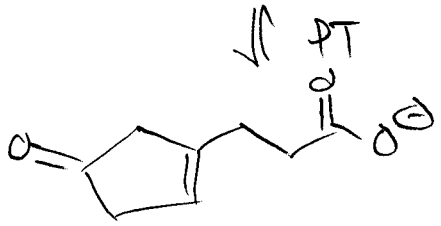
Problem Set 6 Answer Key

(8)

a)



- carboxylate is unreactive (not electrophilic)



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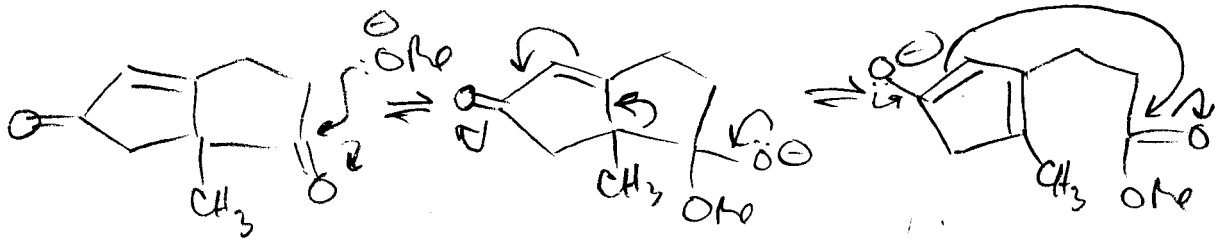

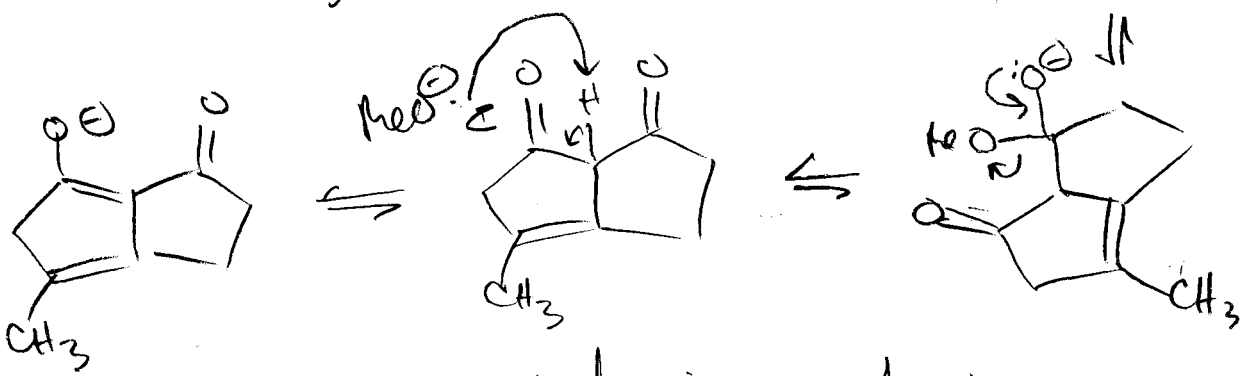

Ester generated in 2nd step can undergo Claisen condensation w/ enolate

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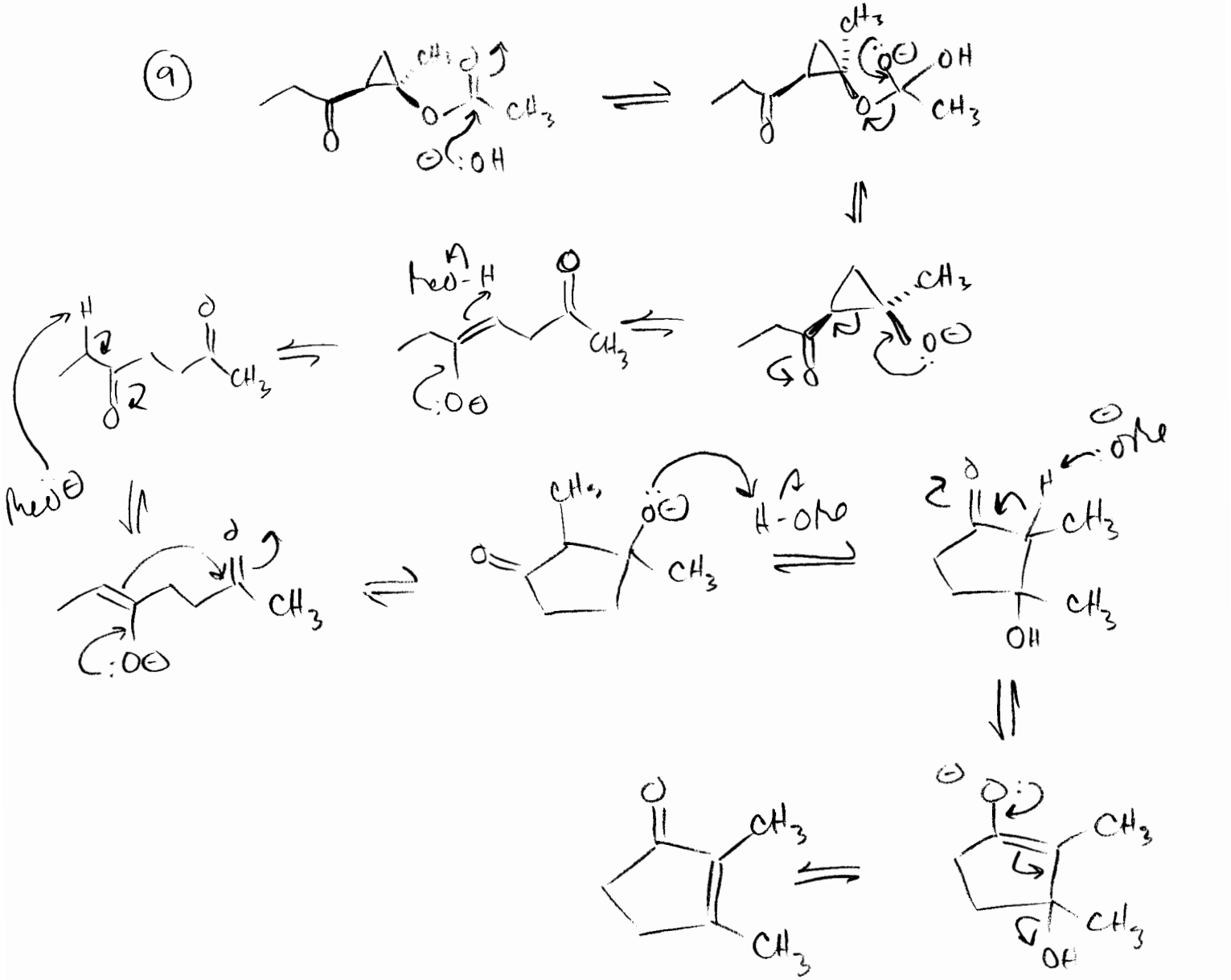

Remember: C-C bonds in cyclopropane frequently act more like π-bonds than σ-bonds.