

5.451 F2005  
 Problem Set 3.

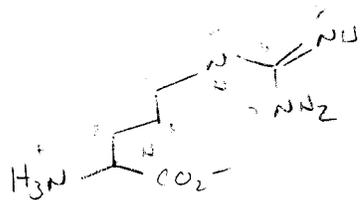
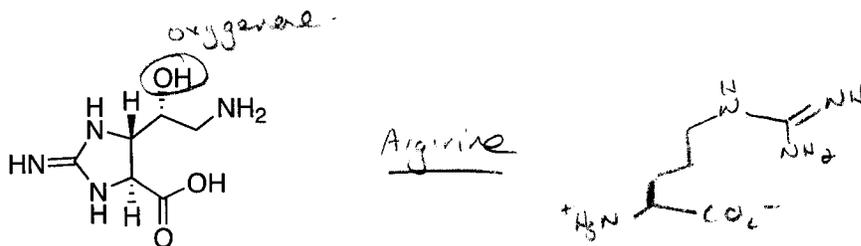
1. (25 pts) Using your knowledge of the 20 proteogenic amino acids, propose the starting material as well as a mechanism of biosynthesis for the following alkaloid. General acid bases catalysis and an oxygenase reaction is utilized.

see JOC (2002)

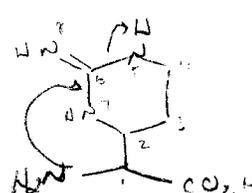
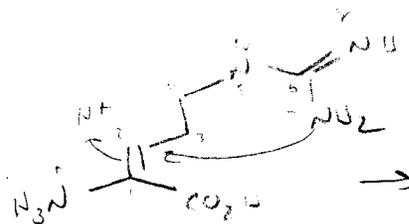
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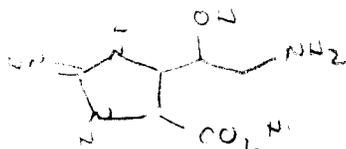
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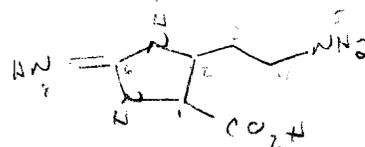
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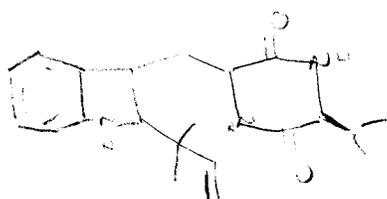
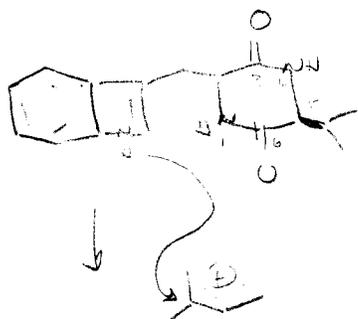
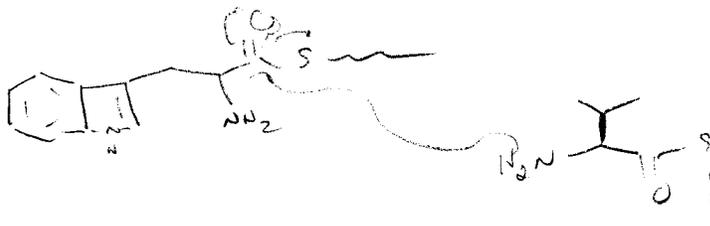
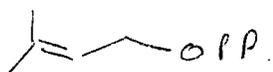
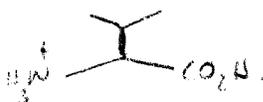
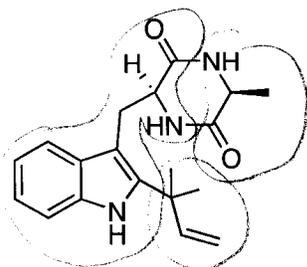


CO2



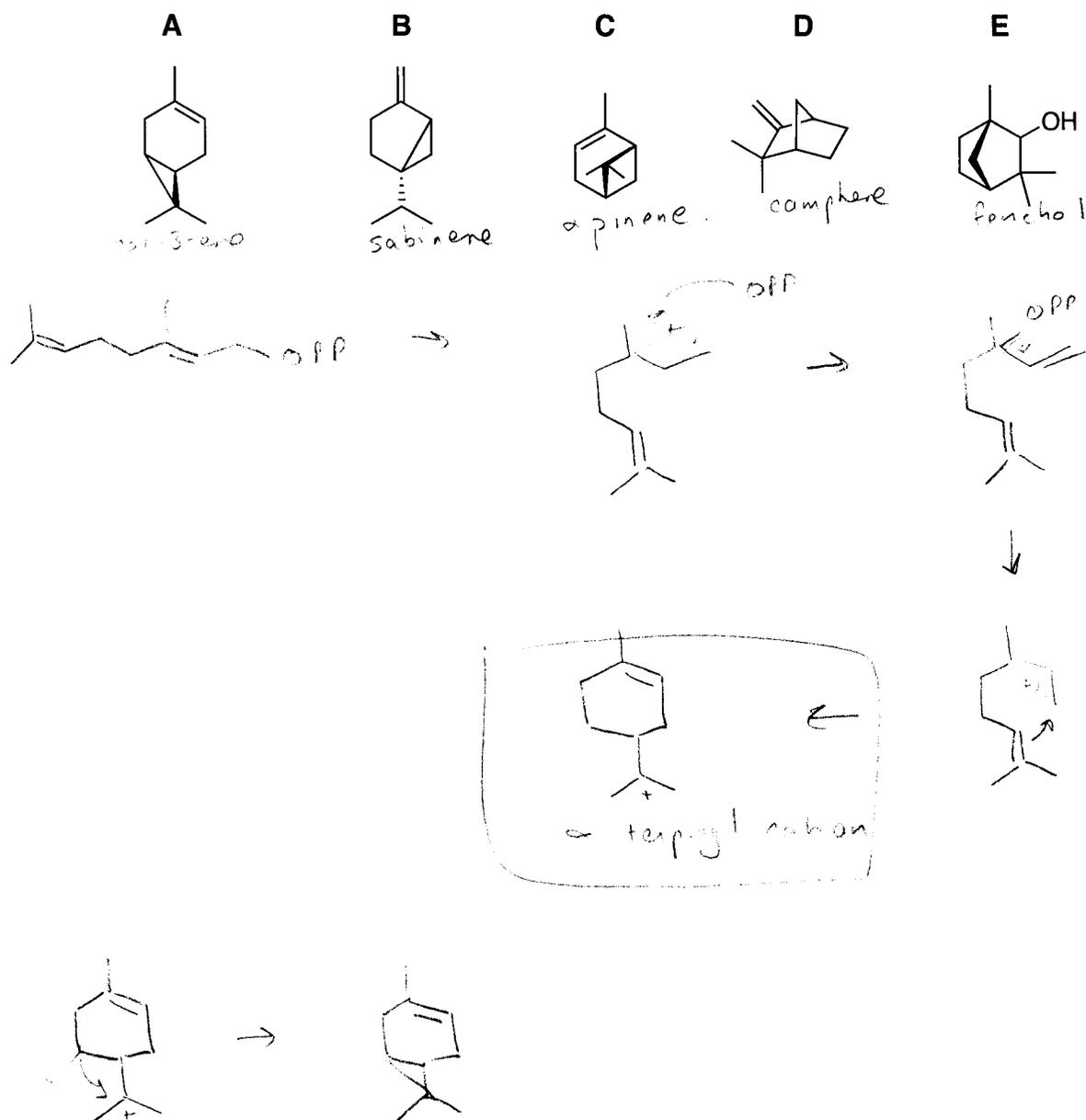
5.451 F2005  
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2. (25 pts) Propose 3 naturally occurring starting materials and a mechanism (using general acid/base catalysis) for assembling them to yield the following alkaloid.

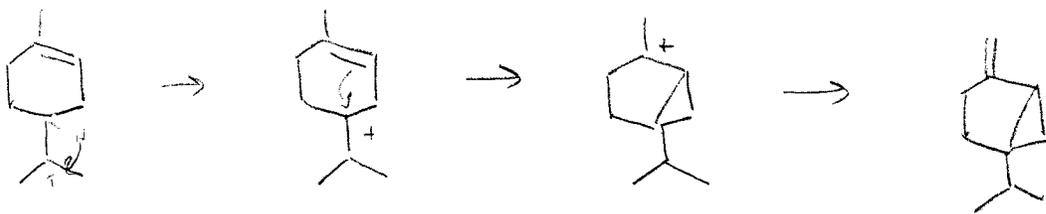


5.451 F2005  
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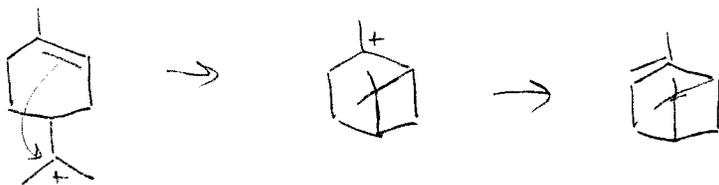
3. (25 pts) **A-E.** Monoterpene biosynthesis. Draw the mechanism of biosynthesis for each of the following monoterpenes starting from geranyl diphosphate. Include all intermediates and utilize arrows to indicate the flow of electrons. These reactions are enzymatically catalyzed by a terpene cyclase, so utilize general acid/base catalysis.



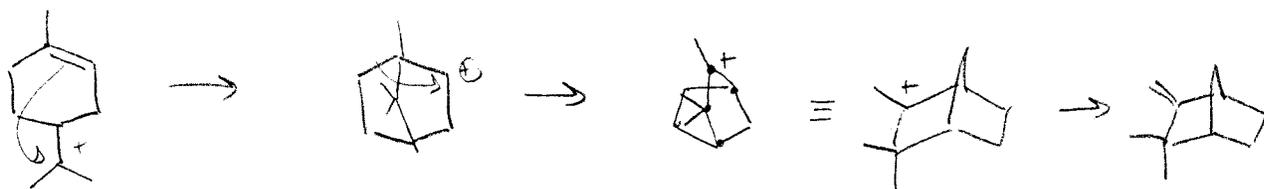
(B)



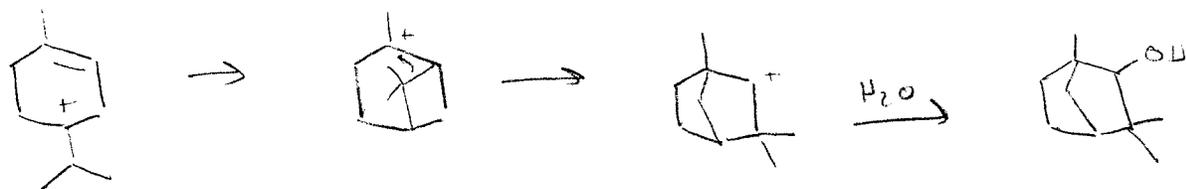
(C)



(D)



(E)



5.451 F2005  
 Problem Set 3.

4. (25 pts) Sesquiterpene biosynthesis. Propose a detailed mechanism of biosynthesis from farnesyl diphosphate for the following unusual sesquiterpene. (The last step that converts the intermediate to the final product is not typically observed in terpene biosynthesis.)

