Chem 30C, Winter 2008

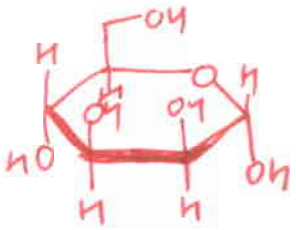
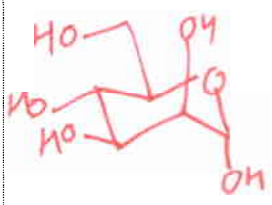
Final Exam

Prof. Ohyun Kwon, UCLA

Your Name (Please Print)

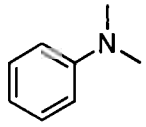
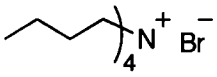
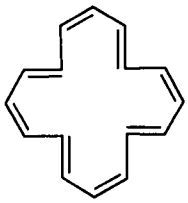
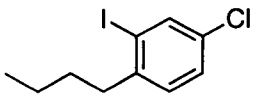
Question	Your points
1 (16 points)	16
2 (9 points)	9
3 (8 points)	8
4 (12 points)	12
5 (22 points)	22
6 (24 points)	21 21
7 (20 points)	19 19
8 (14 points)	18 18
9 (16 points)	16
10 (12 points)	12
11 (15 points)	15
12 (13 points)	13
13 (19 points)	19
Total (200 points)	200

1. (a) (6 points) Write a Fisher projection of D-mannose, a Haworth projection of α-D-mannose and a chair conformation of α-D-mannose.

Fisher projection	Haworth projection	A chair conformer
		
D-mannose	α-D-mannose	α-D-mannose

2 each

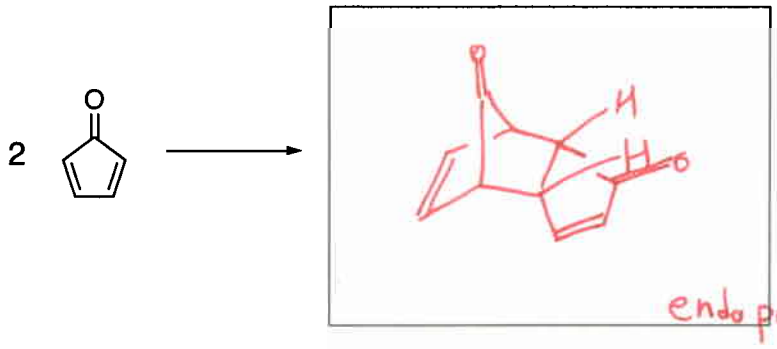
(b) (10 points) Name the following molecules.

	N,N-dimethylaniline
	tetrahydrofuran (THF)
	tetrabutylammonium bromide (TBAB)
	C16] annulene
	1-butyl-4-chloro-2-iodobenzene

2 each

16

2. (9 points) All attempts to synthesize cyclopentadienone yield only a Diels-Alder adduct. On the other hand, cycloheptatrienone has been prepared by several methods and is stable. Draw a structural formula for the Diels-Alder adduct formed from two cyclopentadienones (specify relative stereochemistry). And explain what accounts for the marked difference in stability of these ketones.

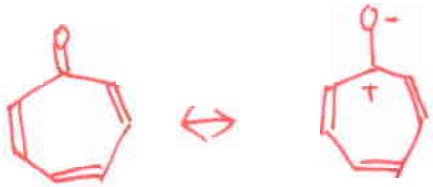


3

→ A major contributing resonance structure for cyclopentadiene has only four π electrons (anti-aromatic) therefore extremely unstable & highly reactive

3

→ On the other hand a major contributing resonance structure for cycloheptatriene has six π electrons (aromatic!) therefore very stable & highly unreactive



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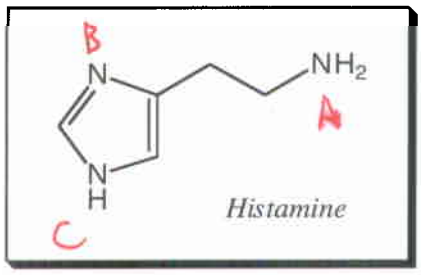
5

3. (8 points) *Histamine*, an important chemical in our bodies, functions as a neurotransmitter and a potent vasodilator. It is the agent that causes many symptoms of the common cold (hence antihistamine drugs being sold over the counter). Rank the basicity of each nitrogen in histamine and explain why.



A > B > C : basicity 2

(A) is a normal, 1° aliphatic amine

nitrogen is sp^3 hybridized & least electronegative 2

(B) lone pair electrons on this nitrogen is sp^2 hybridized

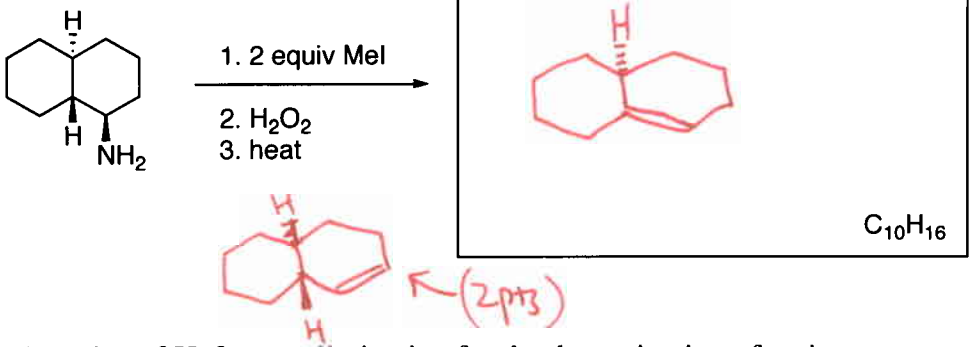
therefore, less prone to protonation 2

(C) lone pair electrons on this nitrogen is a part of

aromatic (6 π electrons) system and least available for protonation 2

8

4. (a) (3 points) Propose a structural formula for compound **A**, $C_{10}H_{16}$, and account for its formation.



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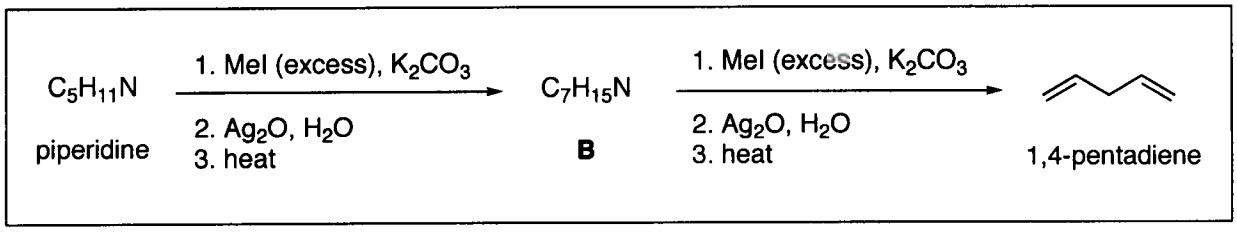
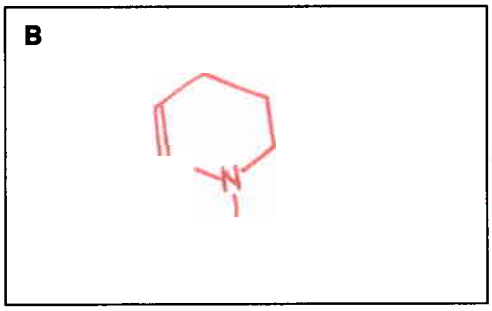
(2pts)

(b) (9 points) The value of Hofmann elimination for the determination of amine structures was first illustrated by the following series of experiments. Based on the results shown below.



i. Draw the structure of compound **B**.



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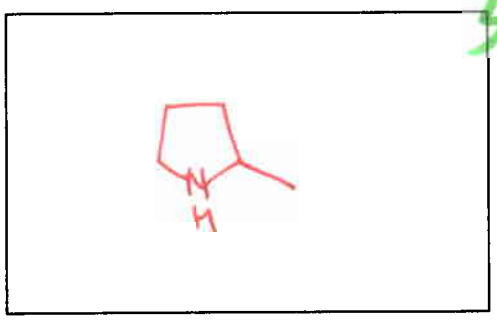
ii. Propose two additional structures (with molecular formula $C_5H_{11}N$) that are also consistent with the results above.



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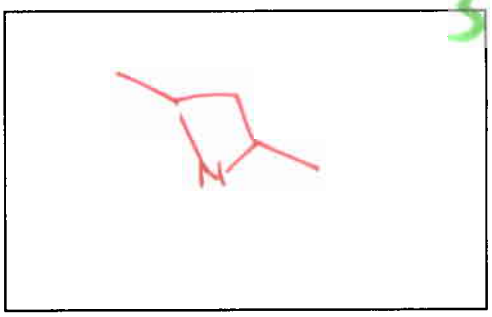

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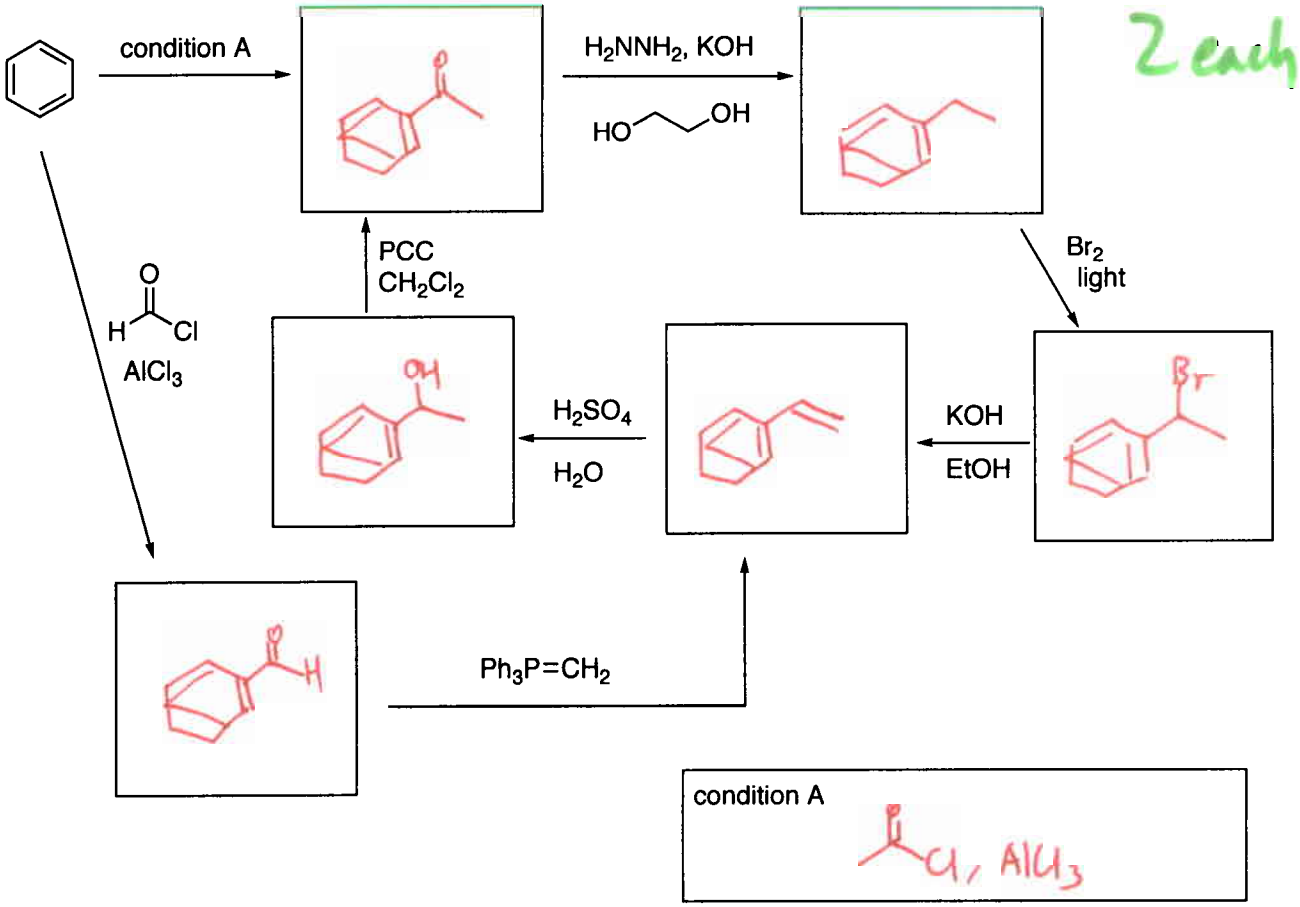
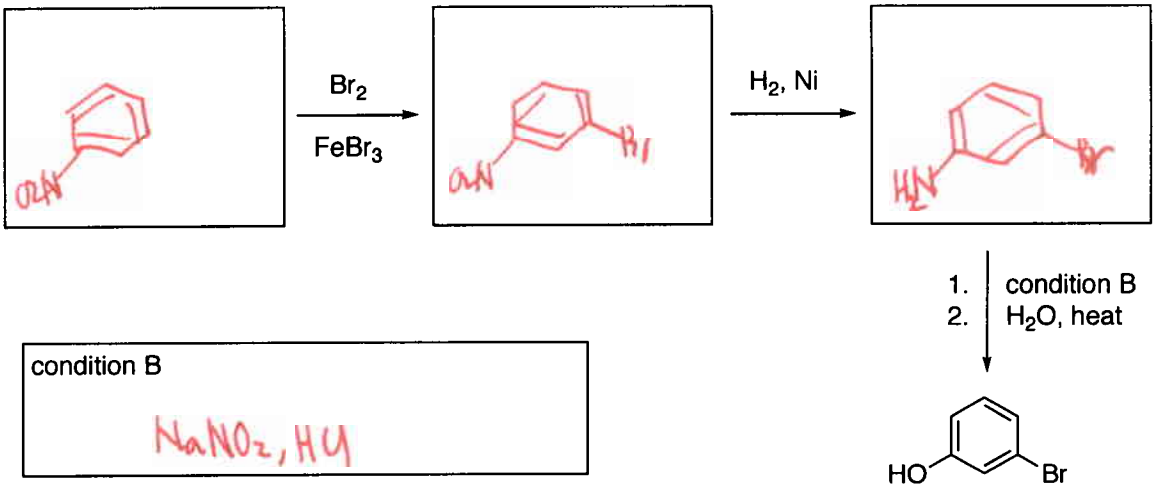
5. (22 points) Provide structures of the products or reaction conditions.

(a)



2 each

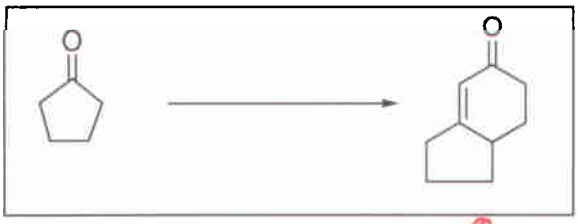
(b)

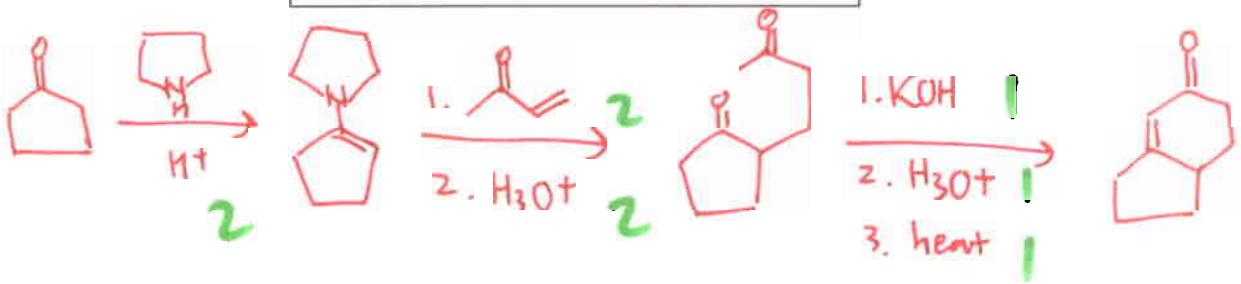


22

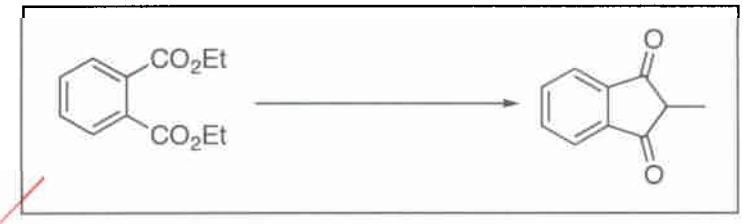
6. Propose a synthesis for the following transformations.

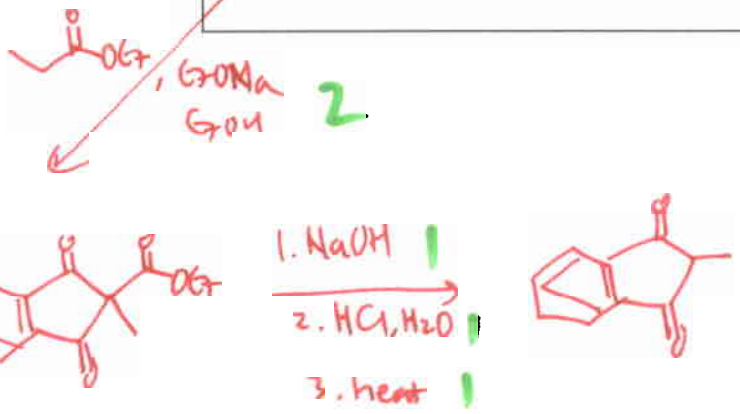
(a) (10 points)



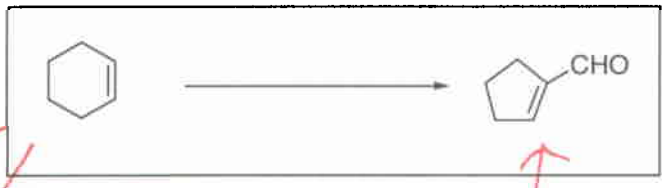


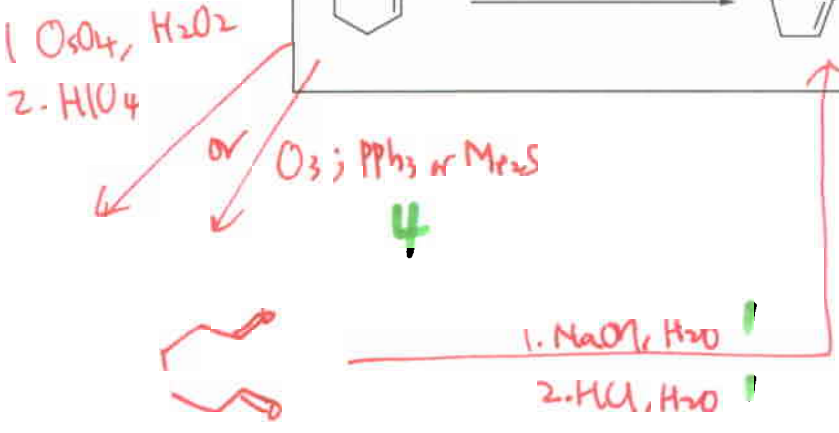
(b) (6 points)





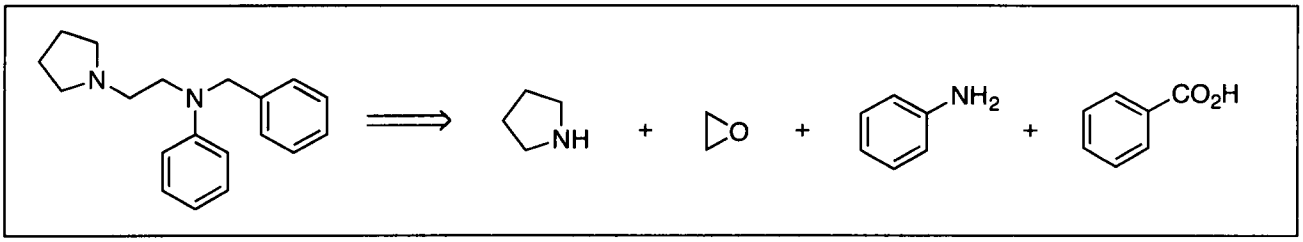
(c) (8 points)

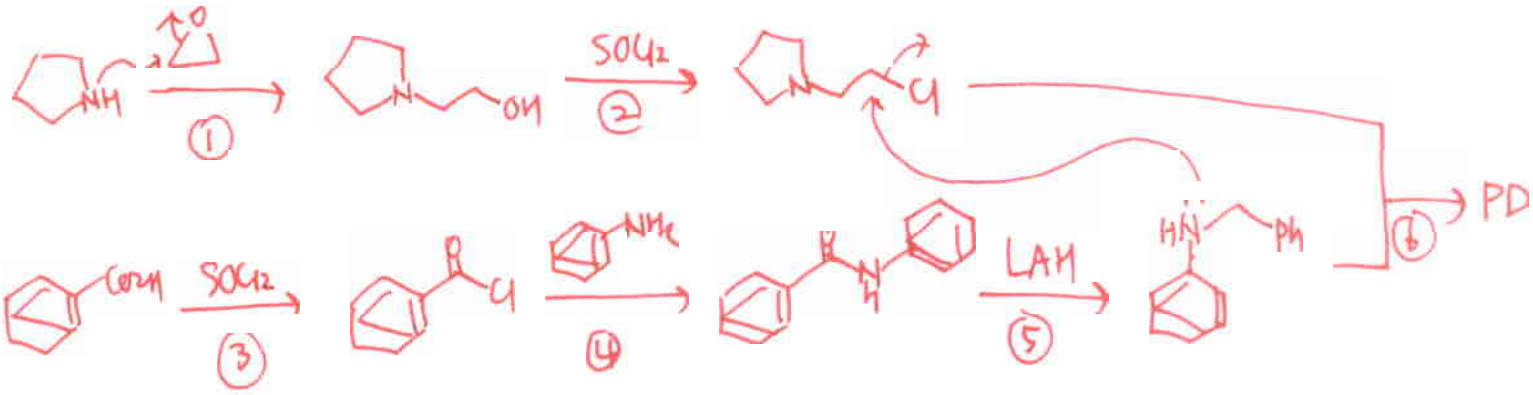




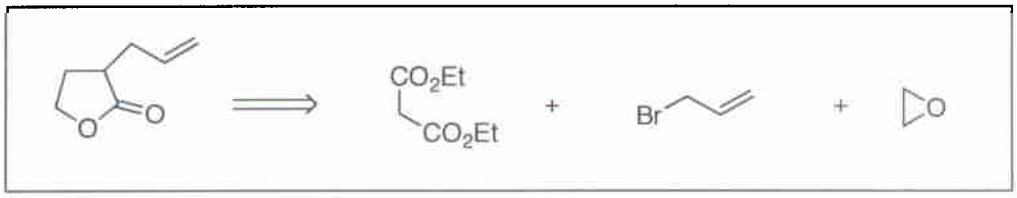
7. Propose a synthesis for the following molecules using the given starting materials.

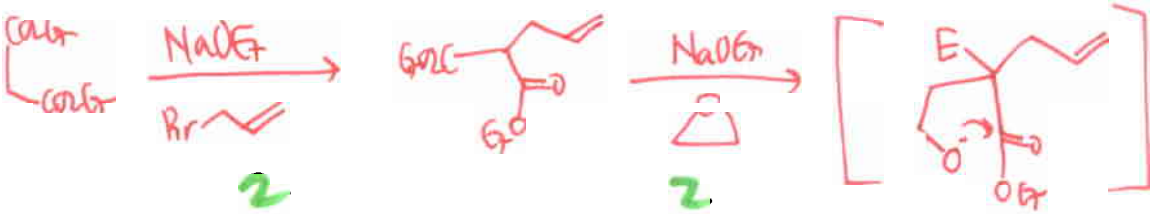
(a) (12 points) antihistamine histapyrrodine

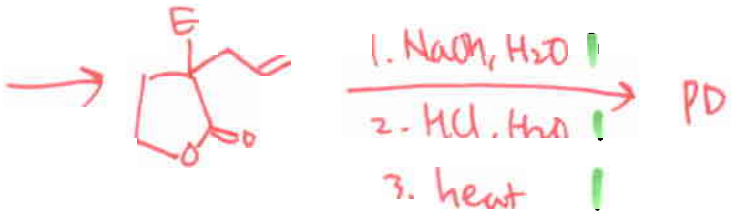




(b) (8 points)



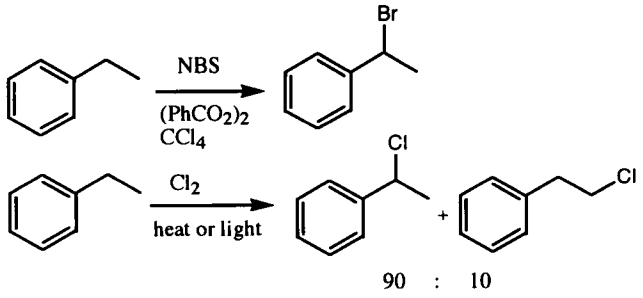




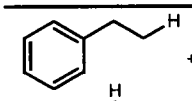
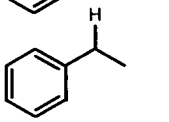
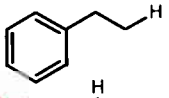
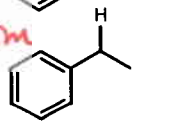
19

18

8. (14 points) Chlorination of ethylbenzene under radical reaction conditions is less regioselective than bromination as shown below. Explain why by applying a postulate proposed in 1955 by George Hammond and by drawing energy diagrams for relevant reactions.



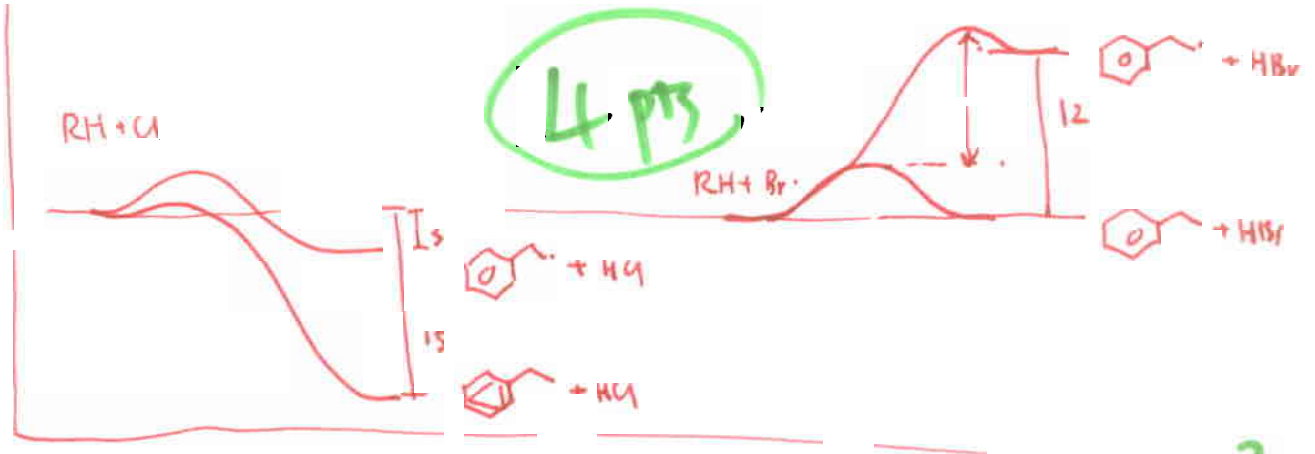
Heats of Reaction for Hydrogen Abstraction in Ethyl Benzene

Reaction Step	ΔH° (kcal/mol)
	12
	0
	-3
	-15

(1) Rate-determining step in radical halogenation is the abstraction of a hydrogen atom by a halogen (or succinimide) radical 2

(2) The table shows that (homo)benzylic chlorination is exothermic and that (homo)benzylic bromination is endothermic (or neutral) 2 2

(3) Hammond postulate states that transition state for an exothermic rxn looks more like reactant and that for an endothermic rxn resembles products. 2 2

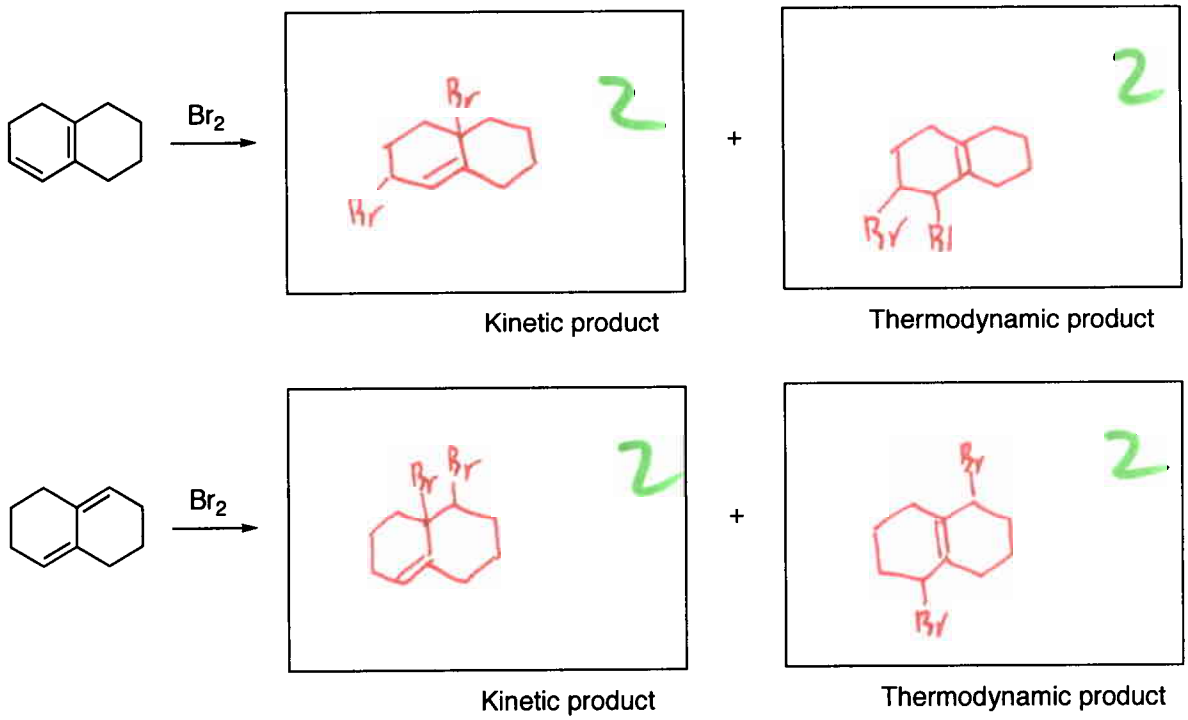


→ therefore, the TS energy diff. for chlorination between the benzylic chlorination and homobenzylic chlorination is a lot smaller than that for bromination 2

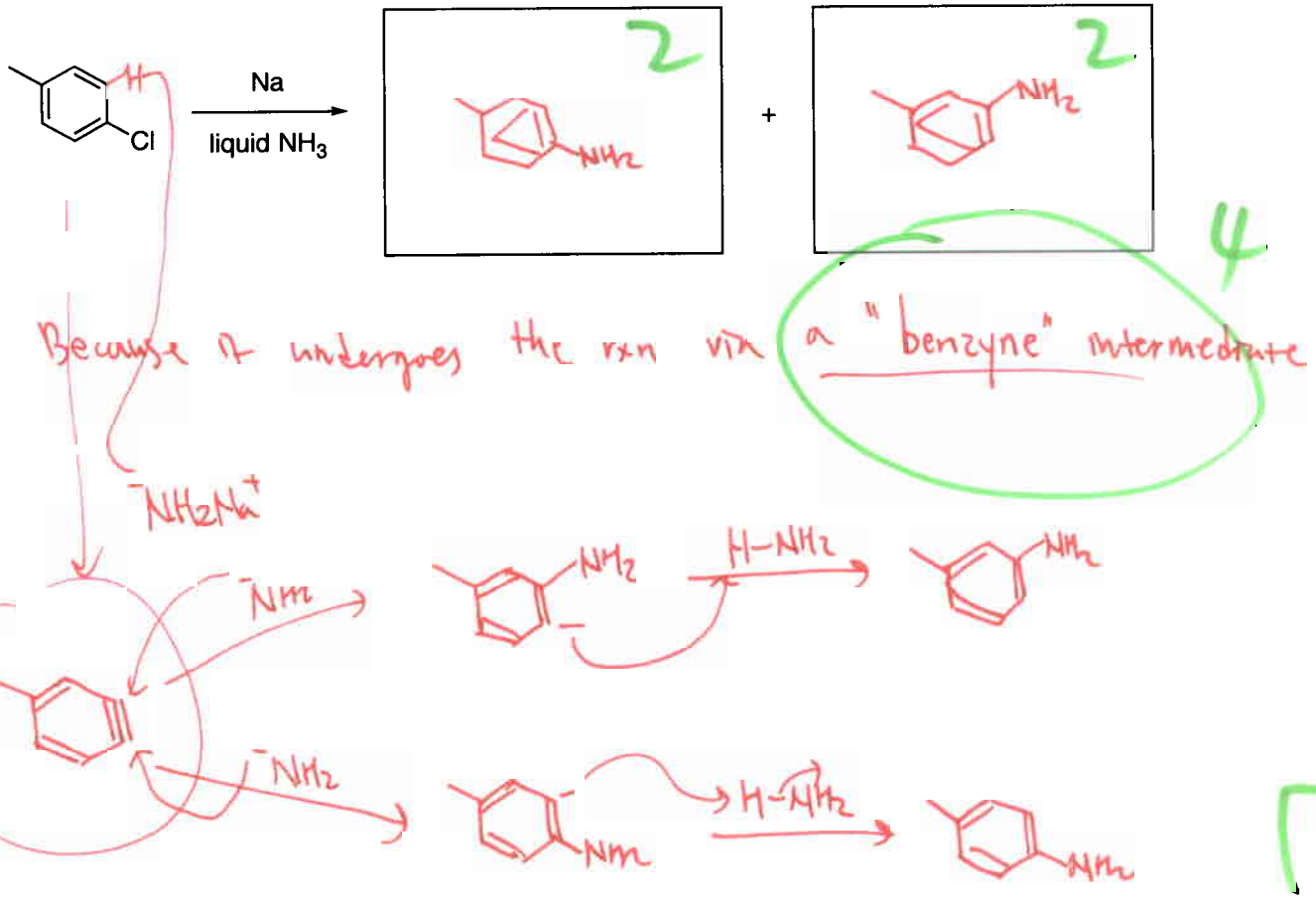
→ That's why benzylic bromination is exclusive & 9:1 mixture of benzylic/homobenzylic chlorination 2

18

9. (a) (8 points) Predict the structures of the expected kinetic and thermodynamic products from addition of one mole of HBr to the following dienes.

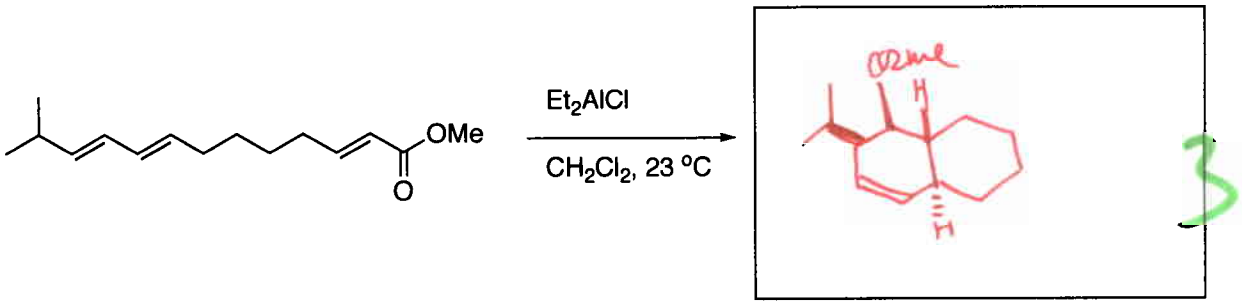


(b) (8 points) Provide structures of the following nucleophilic aromatic substitution and briefly explain why the reaction provides two products instead of one (simple substitution product).

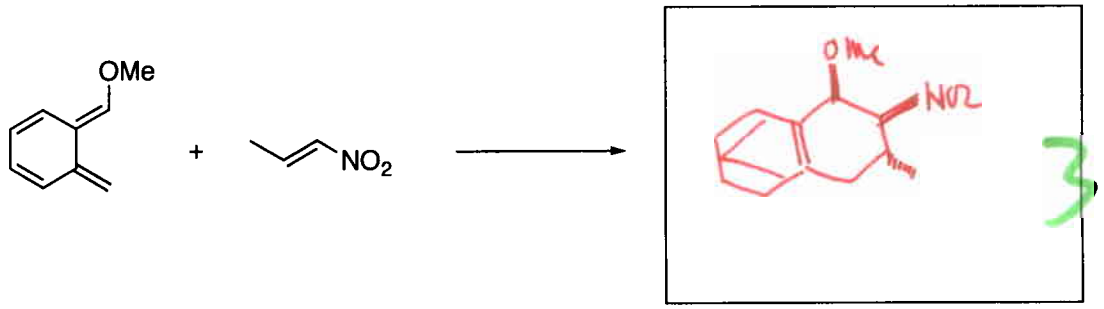


10. (12 points) Predict the structures of the products of the reactions shown below. Specify the relative stereochemistry of the chiral centers in the products if there is more than one chiral center.

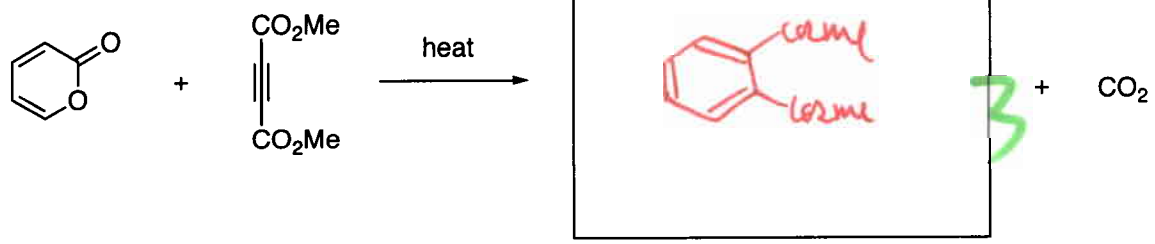
(a) Use of Lewis acid (Et_2AlCl) improves the *endo* selectivity.



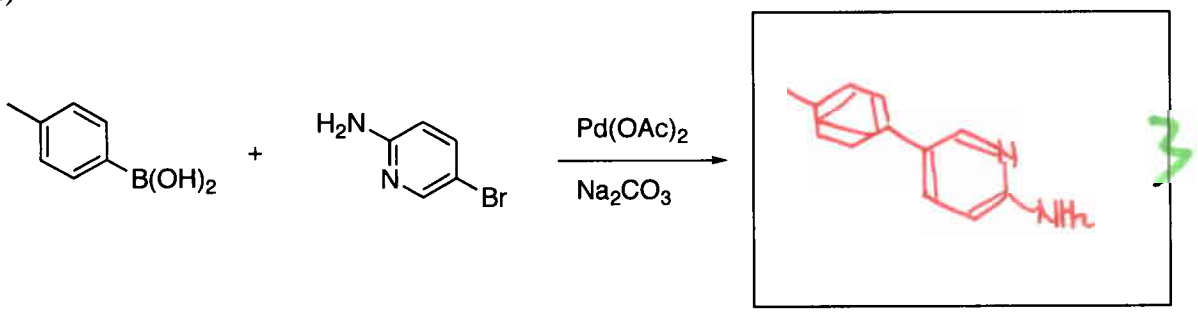
(b)



(c)



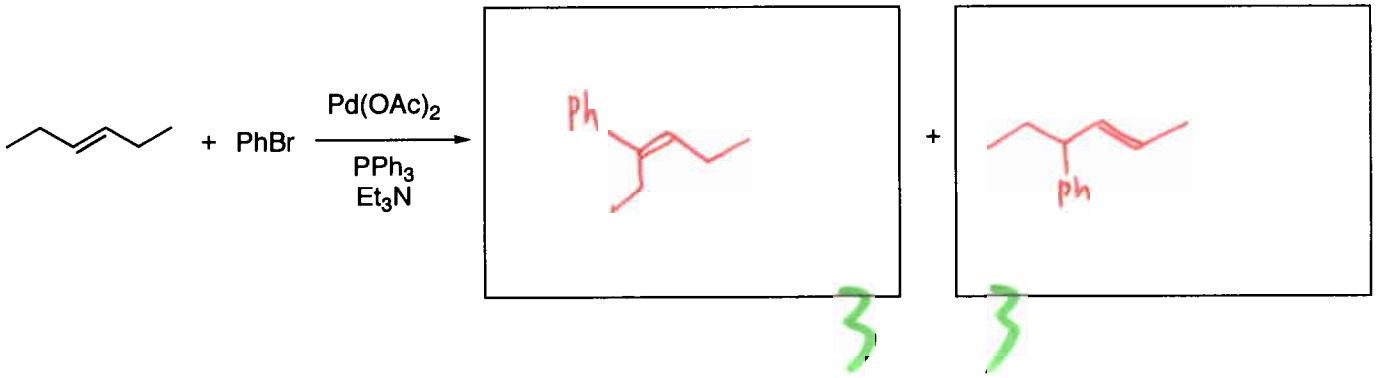
(d)



12

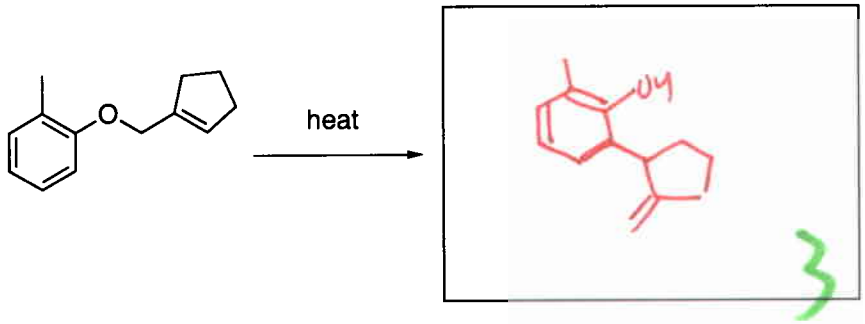
11. (15 points) Show the products of the reactions shown below.

(a)



3 3

(b)



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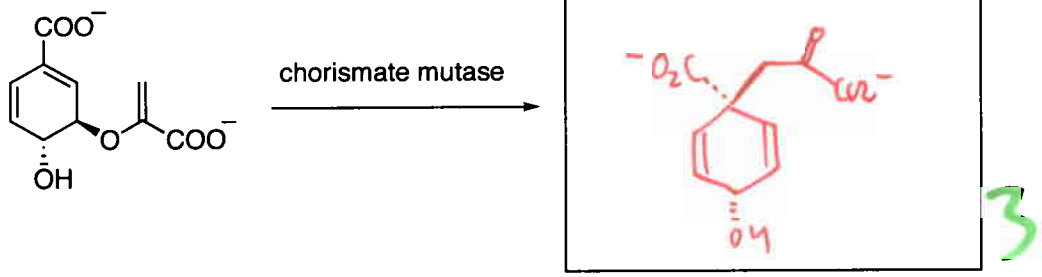
(c)



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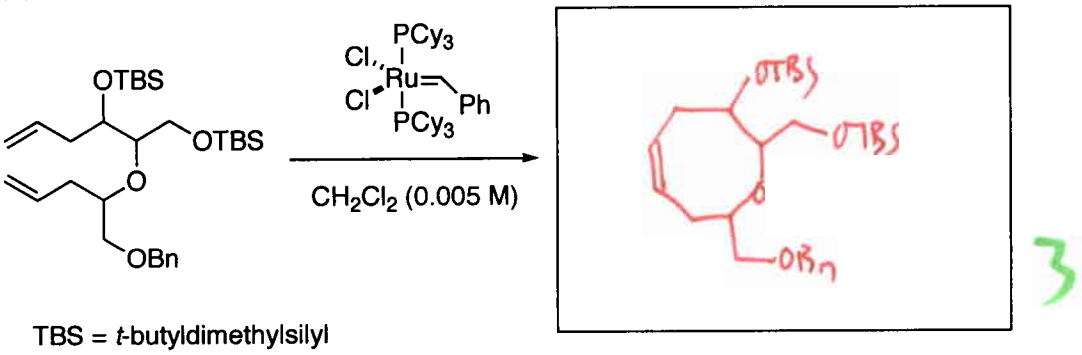
(d)

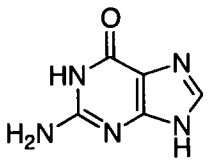
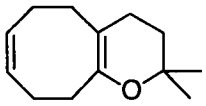
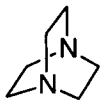


TBS = *t*-butyldimethylsilyl

3

15

12. (a) (9 points) Which of the compounds below are expected to be UV/Vis active and which are not? Briefly explain why.

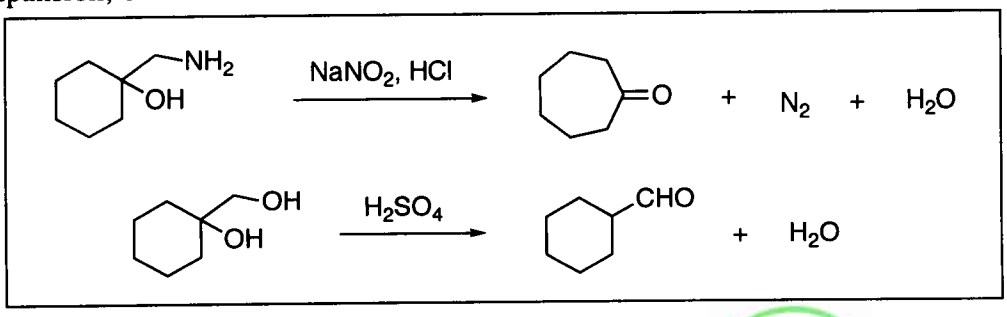
			
Yes or No	Yes 1	no 1	no 1
Why	contains a highly conjugated π system (chromophore) 2	no conjugated π system 2	no double bond 2

(b) (4 points) Define HOMO and LUMO.

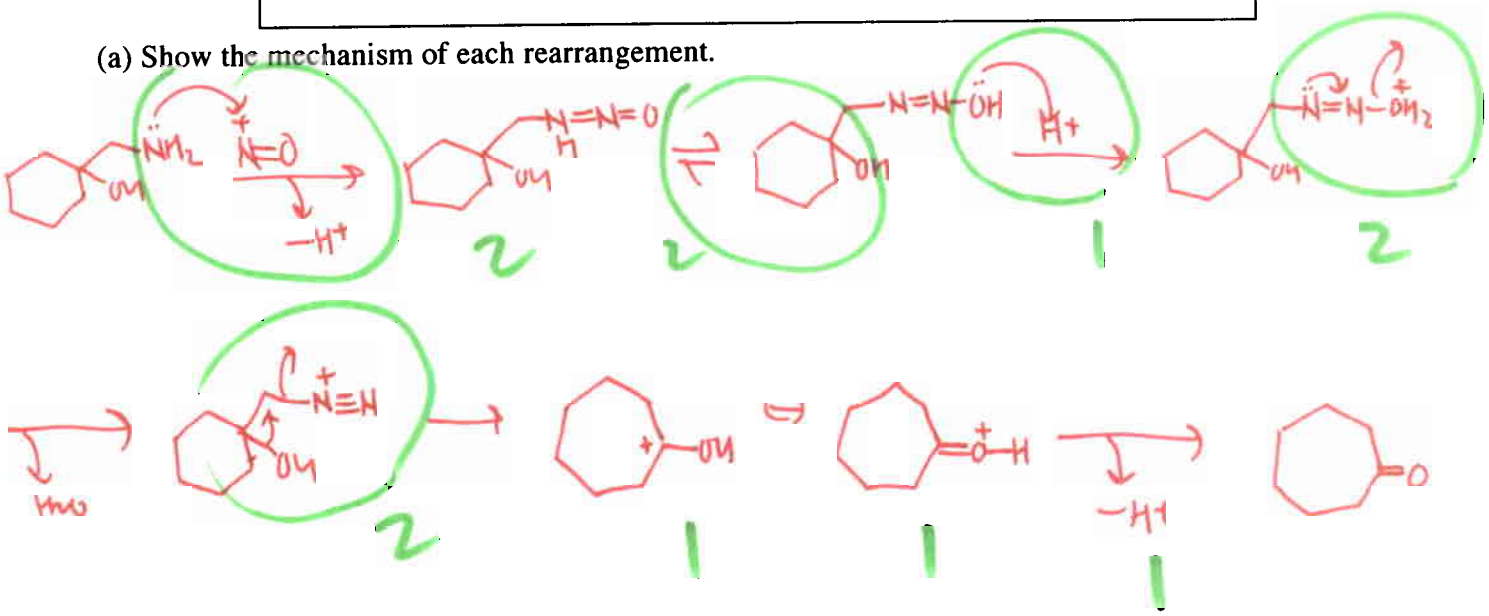
HOMO	Highest Occupied Molecular Orbital 2
LUMO	Lowest Unoccupied Molecular Orbital 2

13

13. (19 points) There exist similarities between the mechanism of nitrous deamination of 2-aminoalcohols and the pinacol rearrangement of 1,2-diols as shown below. However, the first reaction gives ring expansion, but not the second.



(a) Show the mechanism of each rearrangement.



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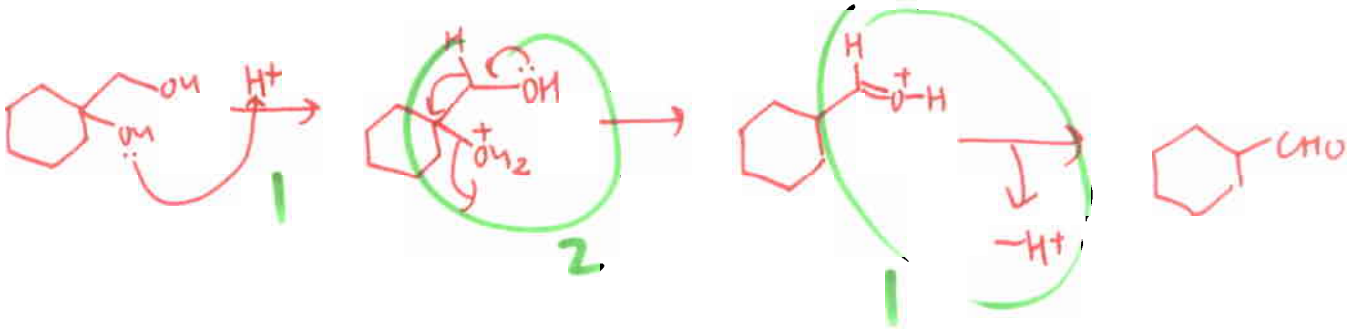
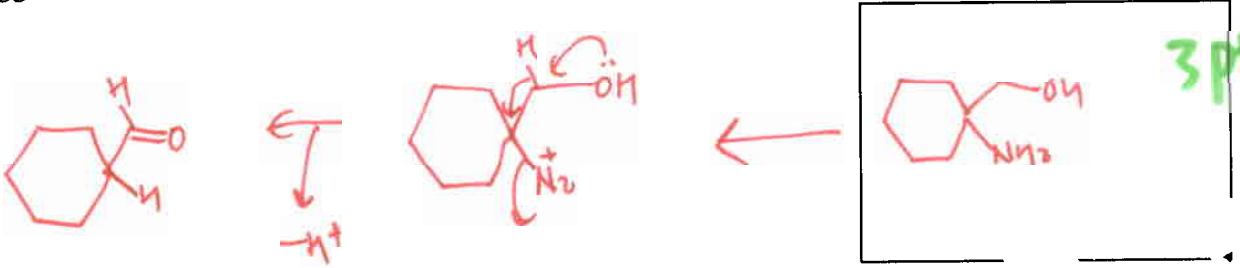


4

(b) Suggest a 2-aminoalcohol that would give cyclohexanecarbaldehyde as a product.



3 pts

19