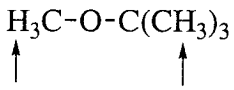
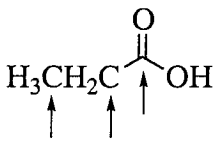
Advanced Organic Chemistry

10% (1) Take examples to expain the following terms:
(a) Basicity and nucleophilicity
(b) Tautomerism

10% (2) (a) Which of the underlined protons absorbs further downfield in ^1H nmr spectrum and explain.

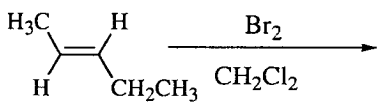


(b) Rank the indicated carbons in order of decreasing chemical shift in ^{13}C nmr spectrum and explain.

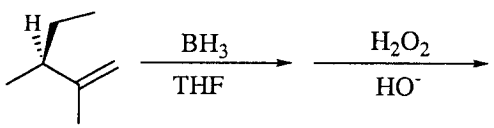


20% (3) For each of the following reactions, provide the following informations.
(a) Give the Fisher projections of all products (including stereoisomers).
(b) If more than one product is formed give the sterochemical relationship (if any) of each pair of products.
(c) Assign the R,S configuration of the asymmetric carbons.

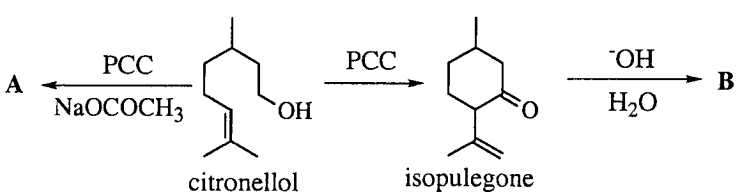
(1)



(2)

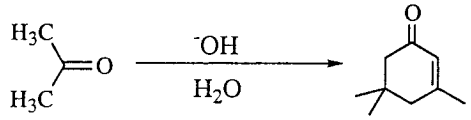


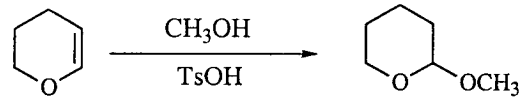
20%(4) Oxidation of citronellol, a constituent of rose and geranium oils, with PCC [CrO_3()$_2$] in the presence of added $NaOCOCH_3$ forms compound **A**. **A** has a molecular ion in its mass spectrum at 154 and a strong peak in its IR sprectrum at 1730 cm^{-1}, in addition to C-H stretching absorptions. Without added $NaOCOCH_3$, oxidation of citronellol with PCC yields isopulegone, which is then converted to **B** with aqueous base. **B** has a molecular ion at 152, and a peak in its IR spectrum at 1680 cm^{-1} in addition to C-H stretching absorptions.

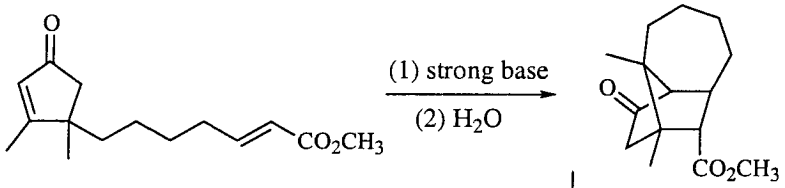


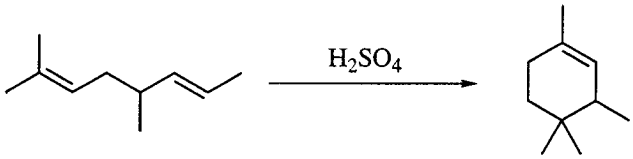
a. Identify the structure of A and B and explain the difference of IR spectrum absorptions.
b. Draw a mechanism for the conversion of citronellol to isopulegone.
c. Draw a mechanism for the conversion of isopulegone to B

28% (5) Draw a stepwise mechanism for the following reactions:

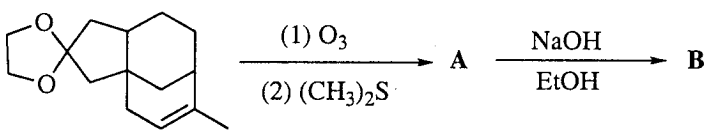
(1) 3 

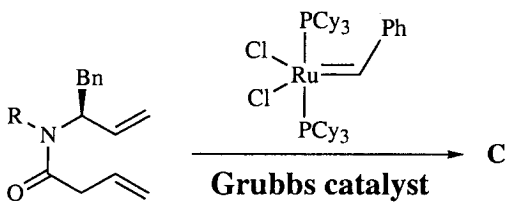
(2) 

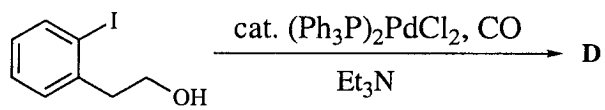
(3) 

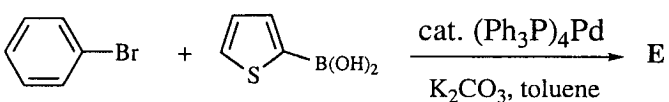
(4) 

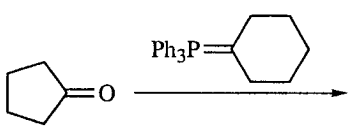
12% (6) Identiy products (A ~ F) for each of the following reactions :

(1) 

(2) 

(3) 

(4) 

(5) 

94 學年度下博士班資格考試

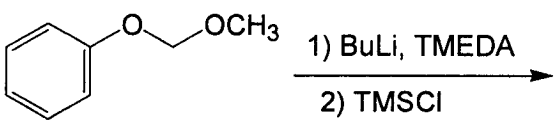
Advanced Organic Chemistry

(1) Give the order of reactivity of the halides (Cl^-, Br^-, I^-) toward *n*-butylbrosylate in acetone when (a) $(C_4H_9)_4N^+$ and (b) Li^+ is the cation of the halide salt. Give an explanation. 8%

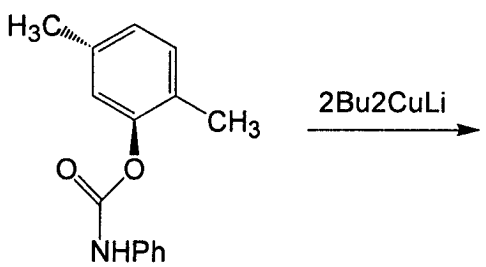
(2) Explain each of the following terms. Give an example of reaction: 16%
(a) Fisher Indole Synthesis
(b) Jones reagent
(c) Collins oxidation
(d) Birch reduction

(3) Give the products and stereochemistry (if necessary) of the following reactions. (mechanism is not required) 15%

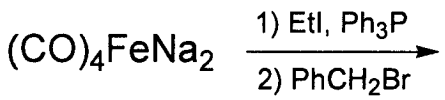
(a)



(b)

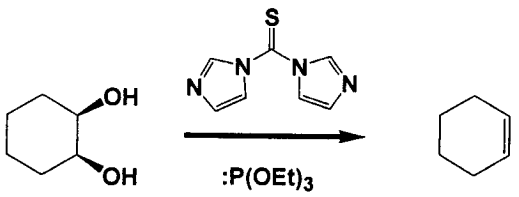


(c)

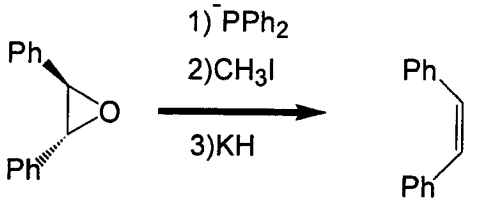


(4) Propose the reasonable mechanisms for each of the following reactions using curved arrow formalism. 16%

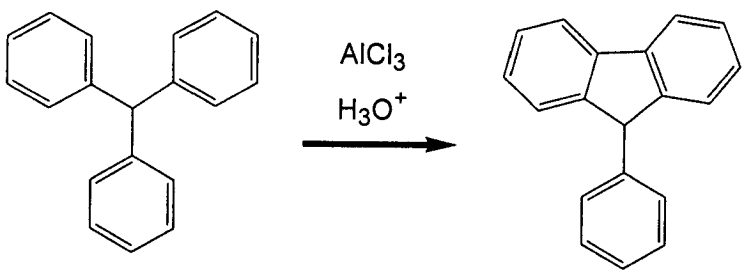
(a)



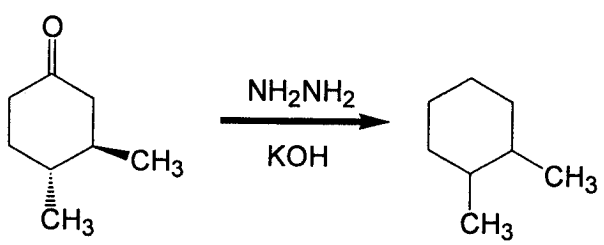
(b)



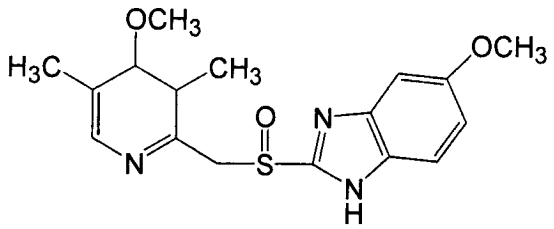
(c)



(d)



(5) Nexium is a proton pump inhibitor used to treat gastroesophageal reflux disease (i.e. heartburn). It has two pKa's of 4.0 and 8.8. 11%



(a) Assign the pKa values to their correct acdic/basic functional groups on the drug.

(b) Draw the structure of the predominant form of Nexium in the stomach at pH 1.5.

(c) Draw the structure of the predominant form of Nexium in the blood at pH 7.0.

(d) Draw the structure of the predominant form of Nexium in a buffered solution at pH 12.

(6) Show by constructing correlation diagrams, whether the following conrotatory thermal cyclo-reversion reactions are **symmetry** allowed. 10%

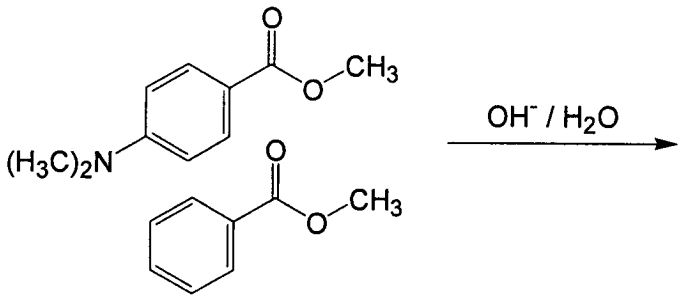
(a) cyclopropyl cation to ally cation
(b) cyclopropyl anion to ally anion

(7) Draw the structure of the unknown compound having the spectral data below. 8%

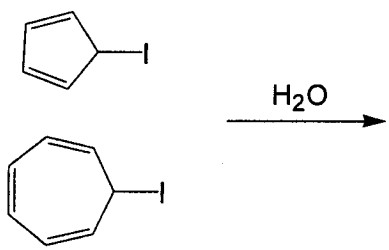
EA:	C, 82.42%; H, 8.59%; O, 8.99%
MS:	$M^+ = 188$
^{1}H NMR (ppm)	7.54 (1H, d, *J*=16), 7.30 (2H, dd, *J*=2, 8), 7.21 (2H, dd, *J*=7, 8), 7.14 (1H, dd, *J*=2, 7), 6.67 (1H, d, J=16), 1,21 (9H, s)

(8) In the following; for each set of reaction, there are two starting materials under the same conditions. One will react faster then the other. Draw the product that results from the **faster** reacting starting compound, and explain in short sentences why that one reacts faster then the other. 16%

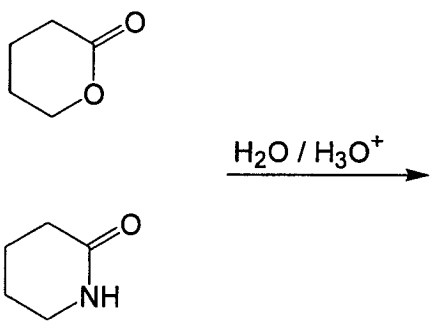
(a)



(b)



(c)



(d)