Carleton UNIVERSITY

FINAL
EXAMINATION
APRIL 2002

DURATION: 3 HOURS No. of Students: 150

Department Name & Course Number: Chemistry 65.224*,226*,228*
Course Instructor(s) G. W. Buchanan

AUTHORIZED MEMORANDA
None

Students MUST count the number of pages in this examination question paper before beginning to write, and report any discrepancy to a proctor. This question paper has 6 pages.

This examination question paper MAY be taken from the examination room.

In addition to this question paper, students require: an examination booklet yes X no ___
a Scantron sheet yes ___ no X

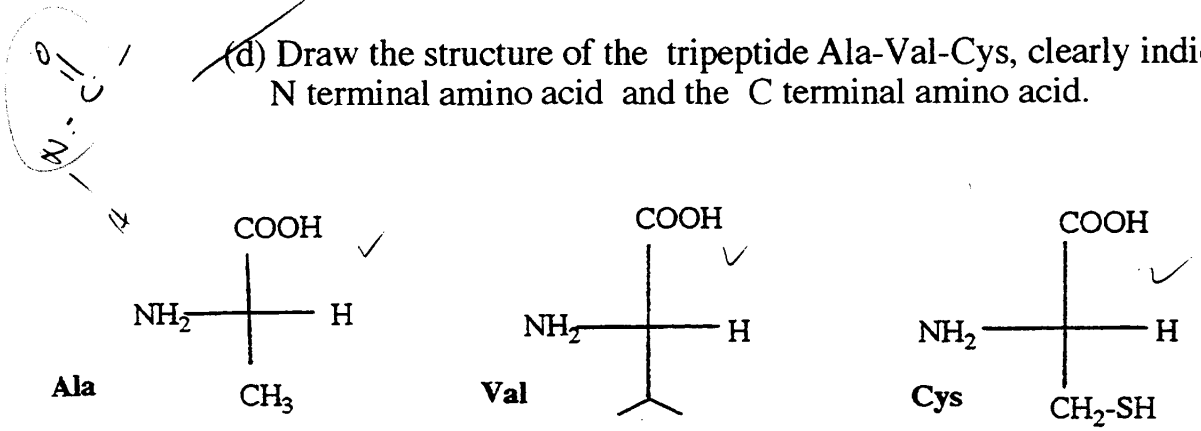
Marks (total=100)

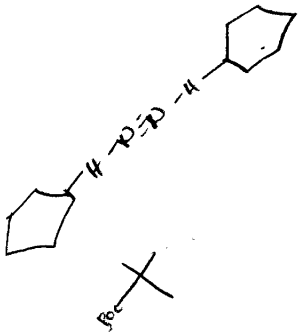
10 1. (a) Describe the general features of protein structure with respect to their primary , secondary , tertiary and quaternary features.

(b) What is a denatured protein and under what conditions may it arise?

(c) Below are shown the structures of the amino acids alanine, cysteine and valine.Indicate whether these are in the D or L configurations and explain via the convention known as a Fischer projection.

(d) Draw the structure of the tripeptide Ala-Val-Cys, clearly indicating the N terminal amino acid and the C terminal amino acid.





10 2. (i) In order to synthesize specific peptides, deactivation (protection) of the NH_2 function of amino acids is necessary. Show how this is done to make "t-Boc" protected alanine.

(ii) Outline the role of DCC (dicyclohexyl carbodi-imide) in the coupling reaction of "t-Boc alanine" with the ethyl ester of Valine.

(iii) Show how the Merrifield solid phase synthesis (using chlorinated polystyrene) can be used to prepare the tripeptide Cys-Val-Ala.

15 3. Provide structures for the products in each of the following reactions of carbonyl compounds:

(a) ethanal + methylamine

(b) butanone + 2,4-dinitrophenylhydrazine (any isomers?)

(c) cyclopentanone + 1,3-propandiol , with acid catalyst

(d) cyclopentane carboxaldehyde + $LiAlH_4$, followed by aqueous acid

(e) Diethylamine + butanone

(f) 2-pentanone + hydroxylamine (indicate any isomers)

(g) cyclopentanone + phenyllithium, followed by aqueous acid

(h) ethylethanoate + excess phenylmagnesium bromide, then aqueous acid

(i) benzoic acid + $LiAlH_4$, followed by aqueous acid

(j) cyclopentanone + triphenylethylphosphonium bromide in base

5 4. Distinguish between the following pairs of terms:

(i) cisoid vs. transoid diene (ii) bonding vs. antibonding orbital
(iii) R and S configurations (iv) aromatic vs. non aromatic hydrocarbon
(v) a monoterpene vs. a sesquiterpene

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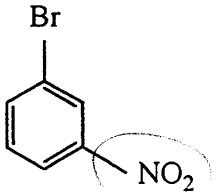
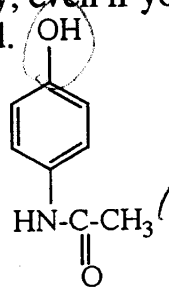
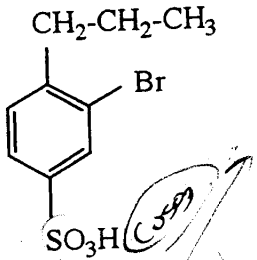
10 5. Provide synthetic schemes for the following "target" molecules **from benzene** NB. (i) Show your strategy, even if you do not know all the reagents to be used.

(a) 

(b) 

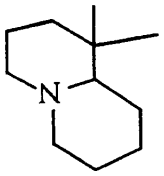
(c) 

10 6. (a) For each of the following compounds, draw the most stable conformations, clearly indicating which substituents are axial and which are equatorial. Assume the following order of relative size of the substituents: t-butyl > CH_3 > OH

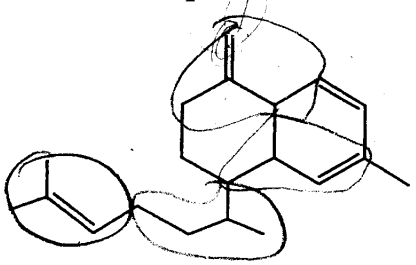
(i) cis-4-t-butylcyclohexanol (ii) trans-1,2-dimethylcyclohexane
(iii) cis-3-methylcyclohexanol (iv) trans-1,4-dimethylcyclohexane
(v) cis-1,2-cyclohexane diol

(b) For each of the five compounds above, indicate, with a brief rationale, which will be optically active (chiral) and which will not.

5 7. The 3° amine depicted below can be degraded to 4,4-dimethyl-1,5,8 nonatriene via the "Hofmann degradation" reaction. Show the reagents required for such a degradation and give a mechanistic rationale via "arrow pushing"

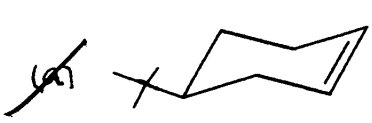


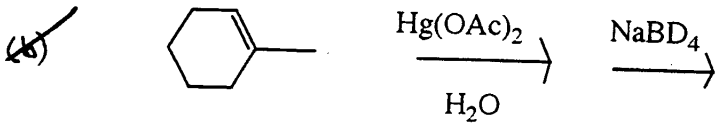
5 8. (a) The terpenoid structure below, isolated from a termite, can be formally derived from four isoprene units. Show how this could arise.
(b) Calculate the position of the UV maximum absorption for this compound using the data table shown below.

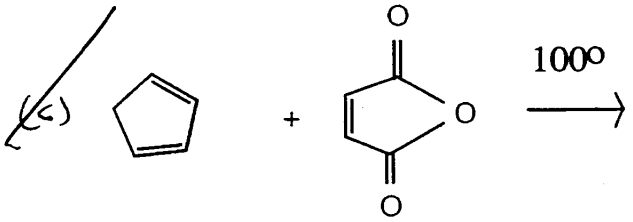


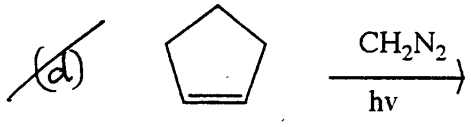
Base diene value	253
Each added alkyl group	+5
Each double-bond exocyclic in a six-membered ring	+5
Each additional conjugated double bond	+30

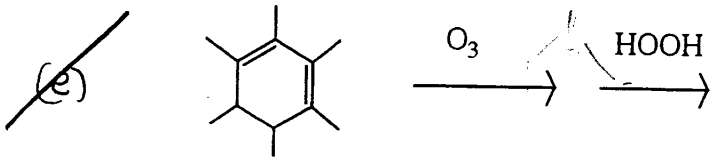
15 9. Provide structures for the major organic products of each of the following reactions. Include stereochemical details where relevent.

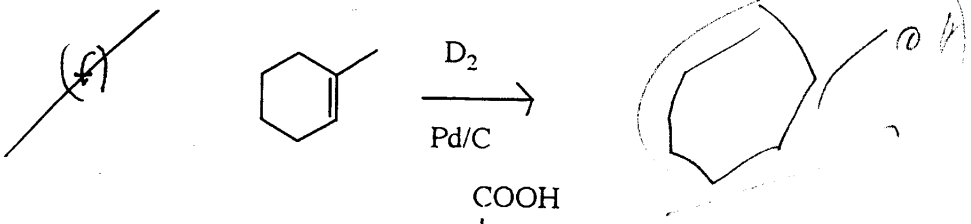
(a) 

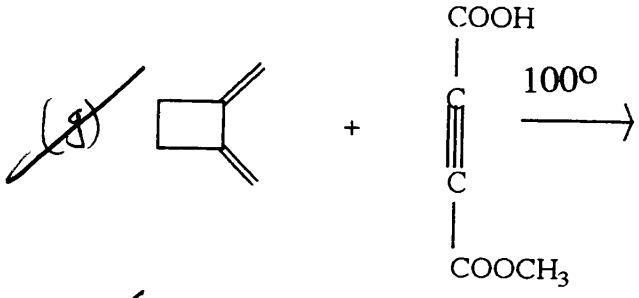
(b) 

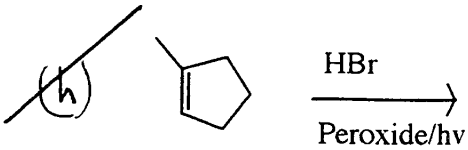
(c) 

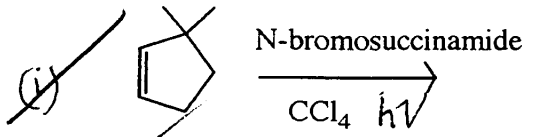
(d) 

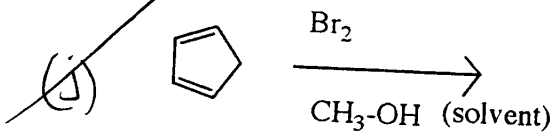
(e) 

(f) 

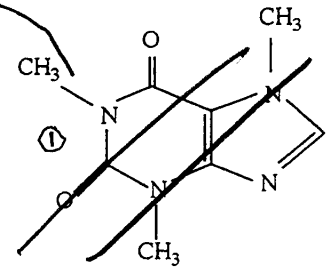
(g) 

(h) 

(i) 

(j) 

5 10. For each of the ten structures shown below, select the appropriate name from the following list.
cocaine, ecstacy, codeine, caffeine, naloxone, heroin, methadone, amphetamine, morphine, adrenaline



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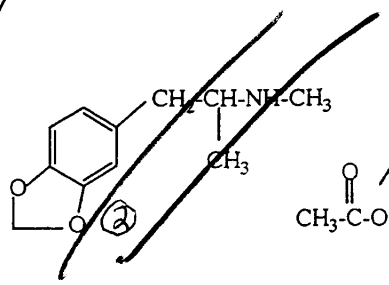

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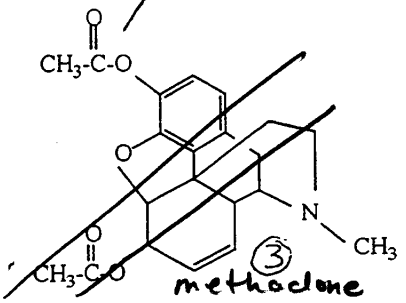
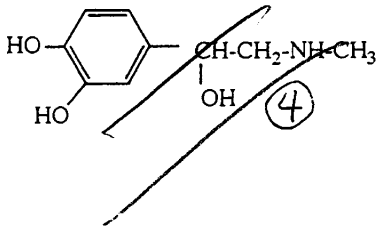


③ methadone



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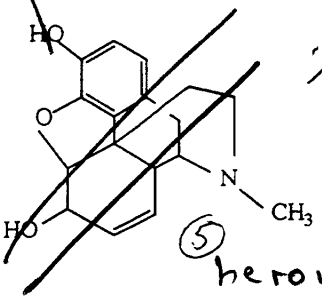
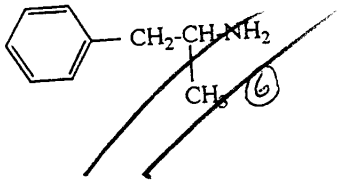


⑤ heroin



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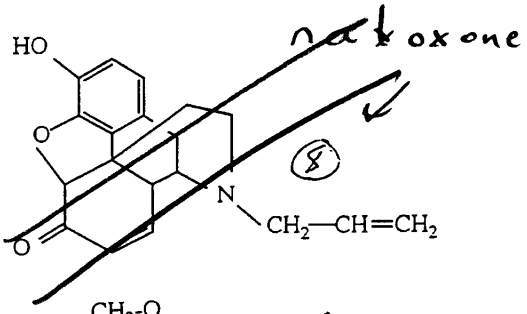
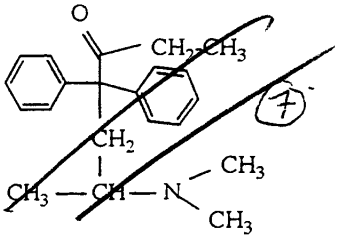


naltoxone

⑧



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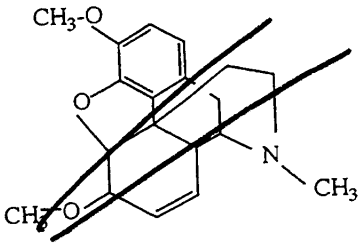
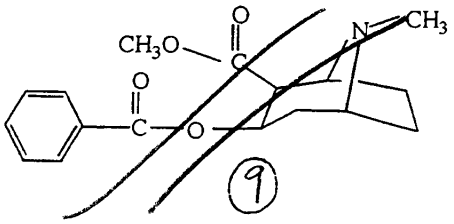


⑩ ~~Coke~~ Codeine



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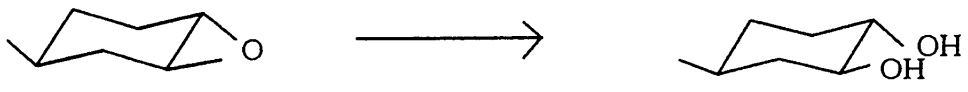
10 11. Provide reagents and mechanisms (ie arrow pushing) to explain the following interconversions.

(i)



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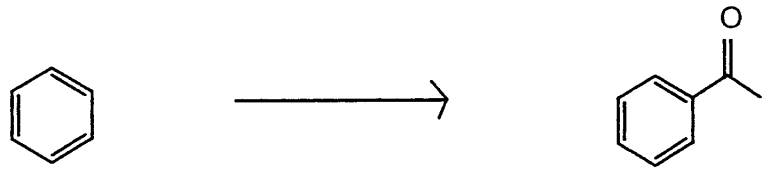

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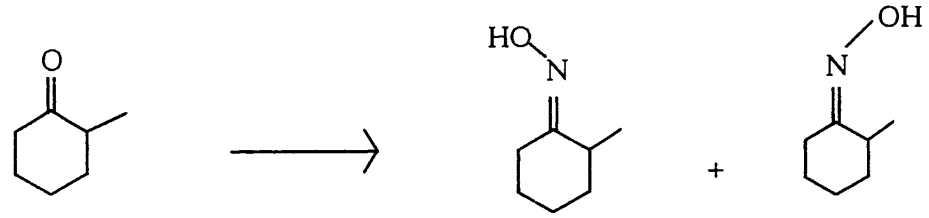

(iv)