JWB

Carleton UNIVERSITY

FINAL
EXAMINATION
APRIL 2001

DURATION: 3 HOURS

No. of Students: 135

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 six (6) pages.

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

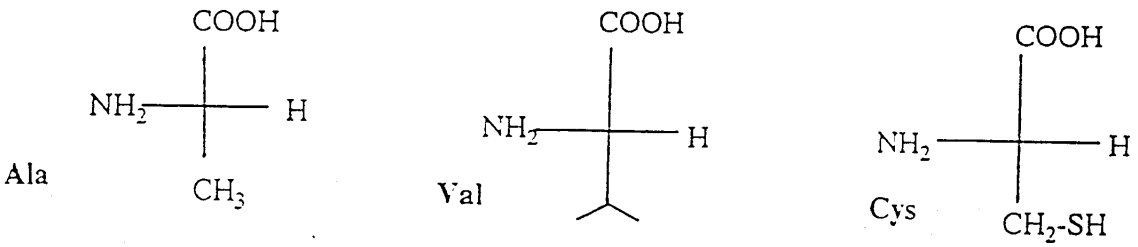
In addition to this question paper, students require: an examination booklet yes☐ no☐
a Scantron sheet yes☐ no☒

Marks (total=100)

15 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 how 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 Val-Ala-Cys, clearly indicating the N terminal amino acid and the C terminal amino acid.

(e) Indicate how a single chain of this tripeptide might interact with an adjacent identical chain via covalent bonding interactions.

(f) Indicate a reagent used to protect the N-terminus of a peptide chain while it is being selectively cleaved with the enzyme "carboxypeptidase"

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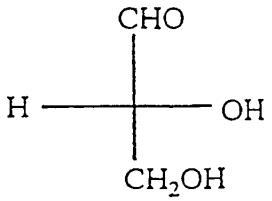
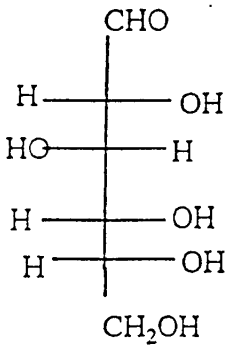
10 2. (a) Below is depicted the structure (Fischer projection) of the simplest carbohydrate, glyceraldehyde.

Is this in the D or L form?
Is this in the R or S form? Explain your answers



(b) Below is the open chain structure of glucose, an aldo-hexose. Is this the D or L form? Explain.



(c) This open chain form does not accurately represent the structure of glucose.

Rather, a cyclic structure with a 6-membered ring is a much better form-draw it and give the 2 possible structures known as the α and β anomers.

(d) In aqueous solution, the anomers reach an equilibrium state via a process called "mutarotation".Provide a possible mechanism for this process.
(e) Which anomer is favoured in the equilibrium?
(f) Why is this "counterintuitive" from the point of view of "simple" conformational analysis of 6-membered rings?
(g) What is the rationale for this "anomeric effect"?

5 3. Distinguish between the following pairs of terms. Use examples and drawings wherever possible.
(a) Acetal vs. ketal
(b) Hemi-acetal vs. hemi-ketal
(c) Boat and Chair conformations of cyclohexane
(d) cis- and trans-4-t-butylcyclohexanol
(e) An oligopeptide vs. a protein

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20 4. Provide structures for the products in each of the following reactions of carbonyl compounds:

(a) ethanal + dimethylamine

(b) butanone + 2,4-dinitrophenylhydrazine

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

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

(e) cyclopentane carboxaldehyde + $NaBH_4$, followed by aqueous acid

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

(g) cyclopentanone + phenyllithium, followed by aqueous acid

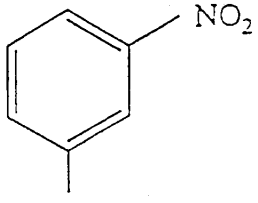
(h) ethylethanoate + excess phenylmagnesium bromide, then aqueous acid

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

(j) cyclopentanone + triphenylmethylphosphonium bromide in base

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)



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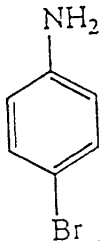

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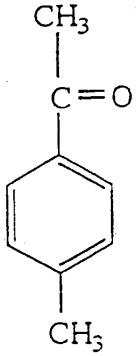

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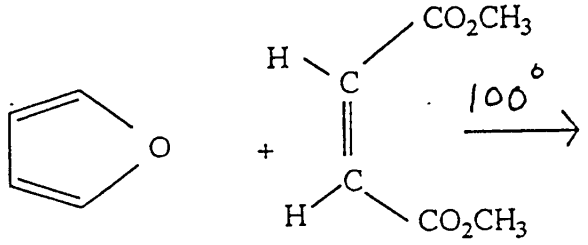
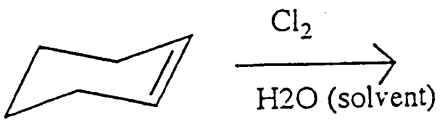
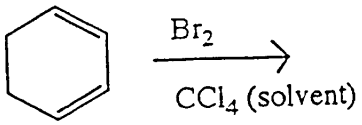
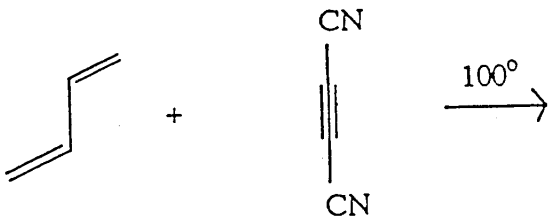
10 6. For each of the following reactions, provide the structures of the major products and a mechanistic rationale ("arrow pushing") for their formation.

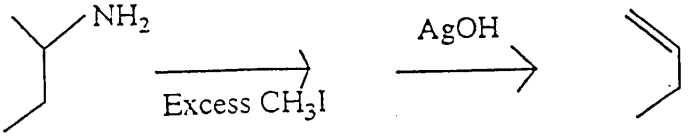
(a) 

(b) 

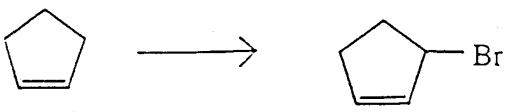
NB specify stereochem

(c) 

(d) 

(e) 

10 7. Indicate the reagents needed to carry out the following transformations

(a) 

(b) 

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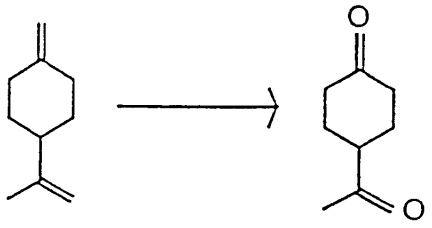
7. Contd

(c)



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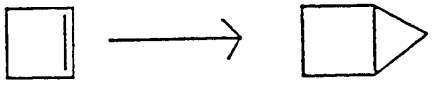

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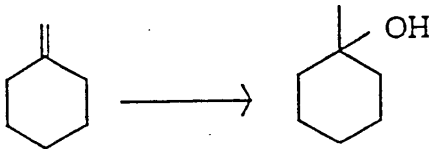

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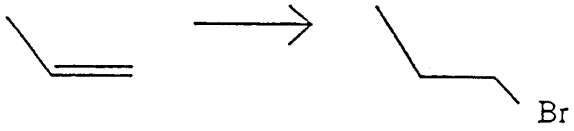
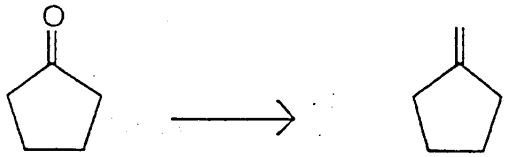


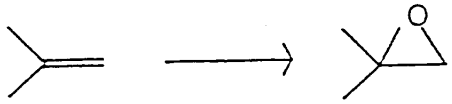
(g)

(h)

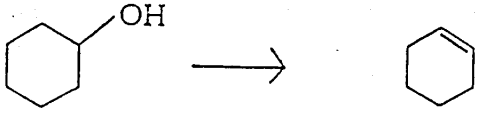


(with no other isomers formed)

(i)



(j)



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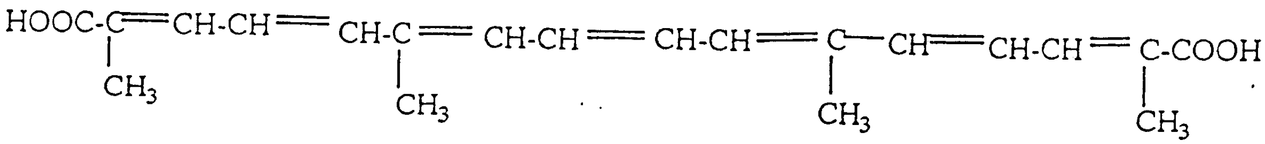
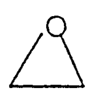
5 7. Below is the structure of Crocetin, the yellow pigment isolated from saffron.
(a) Indicate a possible biosynthetic origin based on combinations of isoprene units.

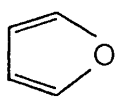


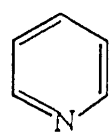
(b) Calculate the position of maximum UV absorption for Crocetin using the data table shown below.

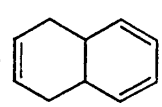
Base diene value	217
Each added alkyl group	+5
Each double-bond exocyclic in a six-membered ring	+5
Each additional conjugated double bond	+30

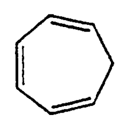
9. Indicate, with a brief rationale, which of the following species will be aromatic.

(

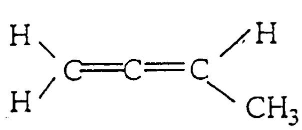
(b) 

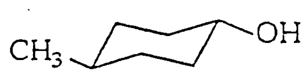
(c) 

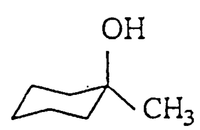
(d) 

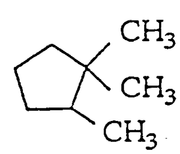
(e) 

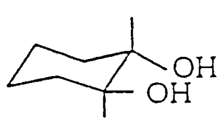
5 10. Indicate, with a brief rationale, which of the following species will be optically active.











5 11. Provide mechanisms ie "arrow pushing" to account for each of the following rearrangements.