

National Exams December 2018

04-BS-12, Organic Chemistry

3 hours duration

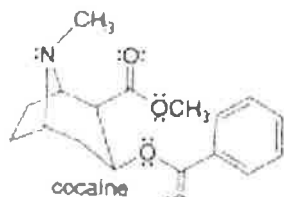
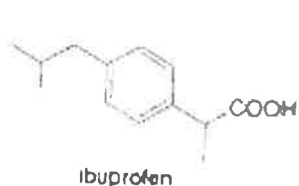
NOTES:

1. If doubt exists as to the interpretation of any question, the candidate is urged to submit with the answer paper, a clear statement of any assumptions made.
2. This is a CLOSED BOOK EXAM.
Approved Sharp or Casio calculator is permitted.
Candidates are allowed to bring ONE aid sheet 8.5" X 11" hand-written on both sides containing notes and formulae.
3. TEN (10) questions constitute a complete exam paper.
The first 10 questions as they appear in the answer book will be marked.
4. Each question is of equal value.

Question 1:

Many drugs are Bronsted-Lowry acids or bases.

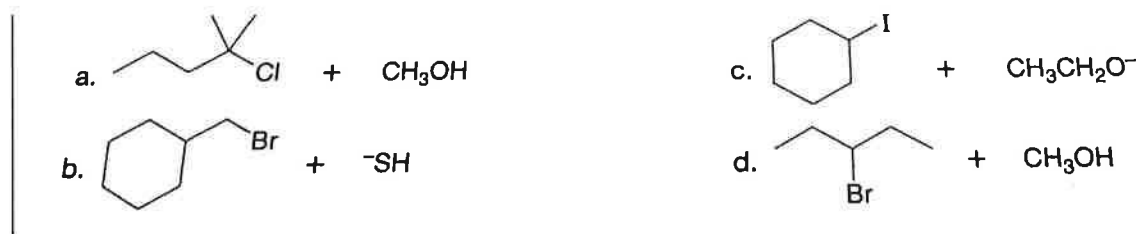
- a) What is the most acidic proton in the analgesic ibuprofen? Draw the conjugate base.
- b) What is the most basic electron pair in cocaine? Draw the conjugate acid.



Question 2:

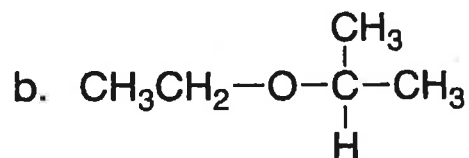
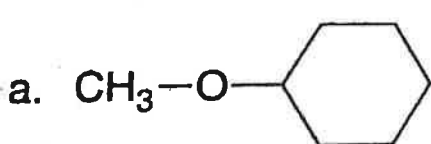
For each alkyl halide, and nucleophile

- a) Draw the product of the nucleophilic substitution
- b) Determine the likely mechanism (S_N1 or S_N2) for each reaction.



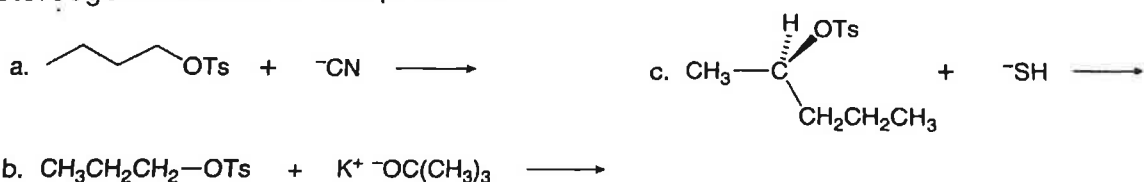
Question 3:

Draw two different routes to each ether and state which route, if any, is preferred.



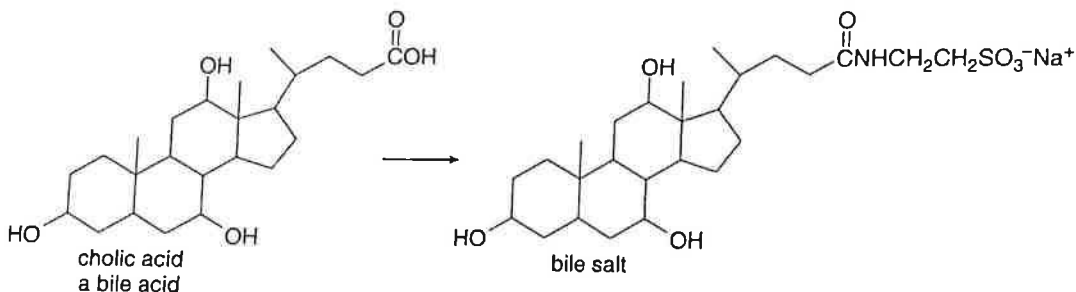
Question 4:

Draw the products of each reaction and include the stereochemistry at any stereogenic centres in the products.



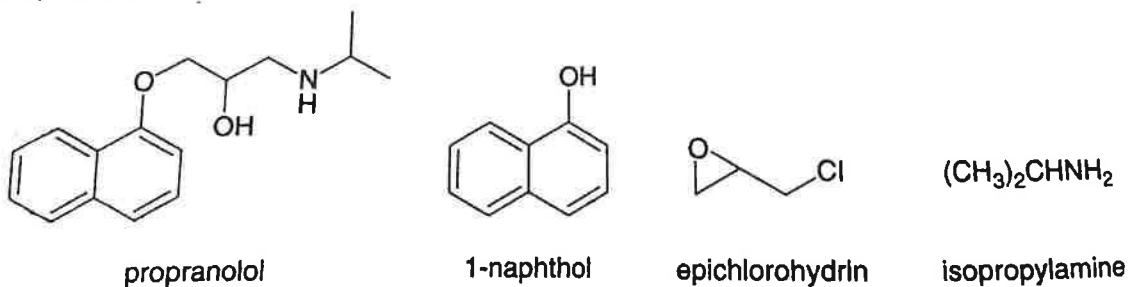
Question 5:

Cholic acid, a compound called a bile acid, is converted to a bile salt in the body. Bile salts have properties similar to soaps and they help to transport lipids through aqueous solutions. Explain why this is so.



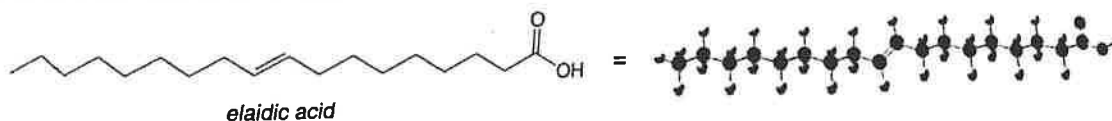
Question 6:

Propranolol, an antihypertensive agent used to treat high blood pressure can be prepared from 1-naphthol epichlorohydrin and isopropylamine using two successive nucleophilic substitution reactions. Devise a stepwise synthesis of propranolol from these starting materials.



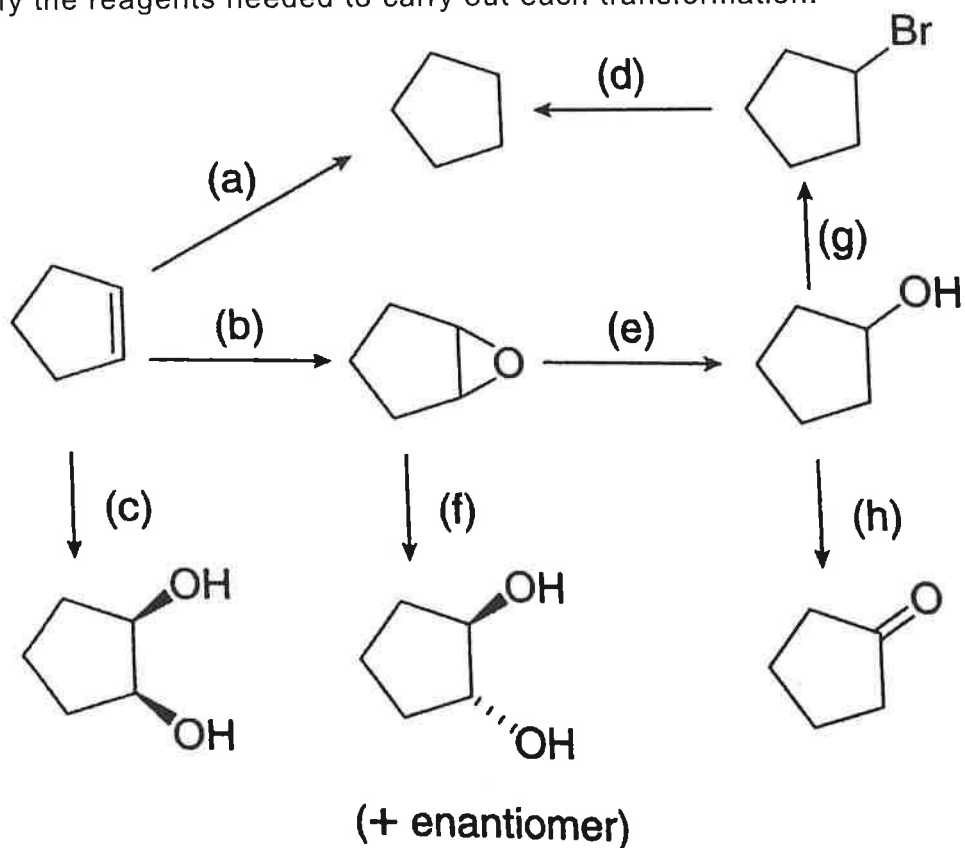
Question 7:

Although naturally occurring unsaturated fatty acids have the Z configuration, elaidic acid, a C18 fatty acid having an E double bond is present in processed foods such as margarine and cooking oils. Predict how the melting point of elaidic acid compares with the melting points of stearic and oleic acids.



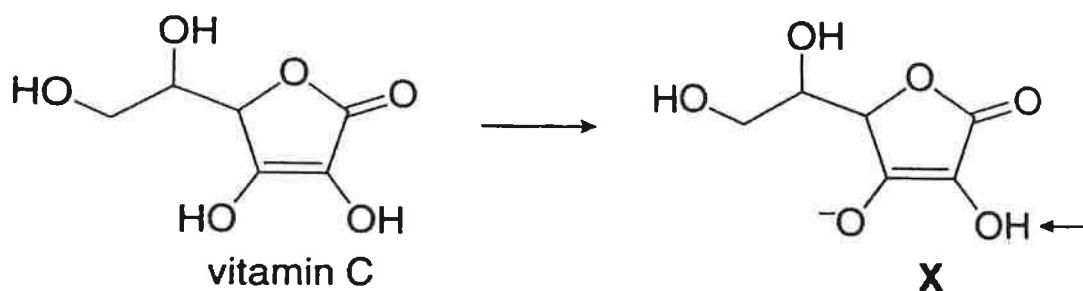
Question 8:

Identify the reagents needed to carry out each transformation.



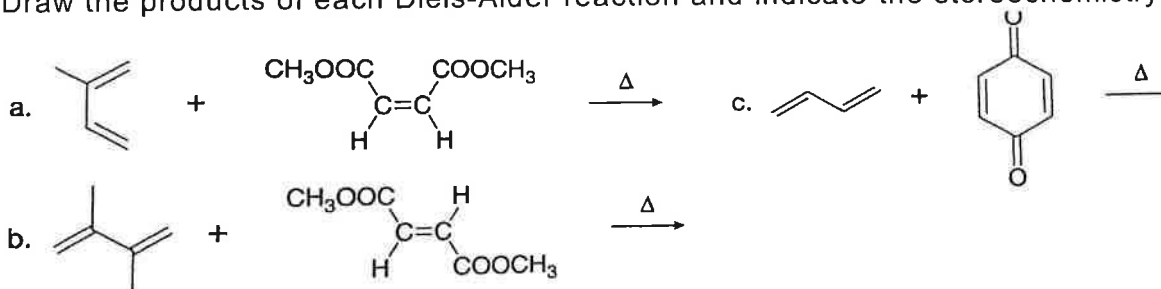
Question 9:

In cells, Vitamin C exists largely as its conjugate base X. X is an antioxidant because radicals formed in oxidation processes abstract the indicated H atom forming a new radical that halts oxidation. Draw the structure of the radical formed by H abstraction and explain why this H atom is the most easily removed.



Question 10:

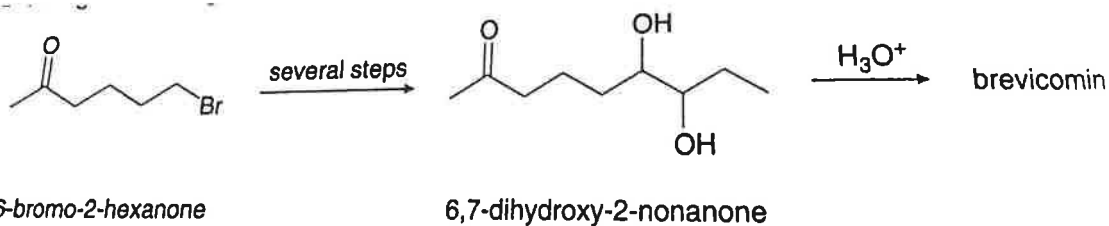
Draw the products of each Diels-Alder reaction and indicate the stereochemistry



Question 11:

Brevicomin, the aggregation pheromone of the western pine bark beetle, contains a bicyclic bridged ring system that resembles frontalin. Brevicomin is prepared by the acid catalyzed cyclization of 6,7-dihydroxy-2-nonanone.

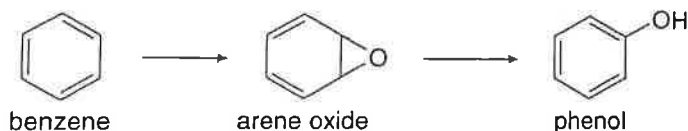
- Suggest a structure for brevicomin
- Devise a synthesis of 6,7-dihydroxy-2-nonanone from 6-bromo-2-hexanone. You may also use three carbon alcohols and any required organic and inorganic reagents.



Question 12:

Hydrocarbons like benzene are metabolized in the body to arene oxides, which rearrange to form phenols. This is an example of a general process in the body in which an unwanted compound (benzene) is converted to a more water soluble derivative or a metabolite so that it can be excreted more readily from the body.

- Classify each of these reactions as oxidation, reduction or neither
- Explain why phenol is more water soluble than benzene. Suggest why this might be important.



Question 13:

- A low resolution mass spectrum of the neurotransmitter dopamine gave a molecular ion at $m/z=153$. Two possible molecular formulas for this molecule are $C_8H_{11}NO_2$ and $C_7H_{11}N_3O$. A high resolution mass spectrum provided an exact mass at 153.0680. Which of the possible molecular formulae is the correct one?
- Morphine, heroin and oxycodone are three addicting analgesic narcotics. How could IR spectroscopy be used to distinguish these compounds from each other?



- Propose a structure consistent with each set of spectral data.
 - $C_4H_8Br_2$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 1.87 (singlet 6H), 3.86 (singlet 2 H)
 - $C_3H_6Br_2$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 2.4 (quintet), 3.5 (triplet)
 - $C_5H_{10}O_2$: IR peak at 1740 cm^{-1} ; NMR (ppm) 1.15 (triplet, 3H), 2.30 (quartet, 2H), 1.24 (triplet 3 H), 4.72 (quartet 2H)
 - $C_6H_{14}O$: IR peak at $3600-3200\text{ cm}^{-1}$; NMR (ppm) 0.8 (triplet, 6H), 1.5 (quartet, 4H), 1.0 (singlet, 3H), 1.6 (singlet, 1H)
 - $C_6H_{14}O$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 1.10 (doublet, 30 units), 3.60 (septet, 5 units)