

National Exams December 2019

04-BS-12, Organic Chemistry

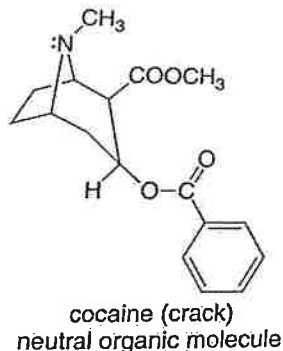
3 hours duration

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. Candidates are allowed to bring ONE aid sheet 8.5" X 11" hand-written on both sides containing notes and formulae. A Casio or Sharp approved calculator is permitted.
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.

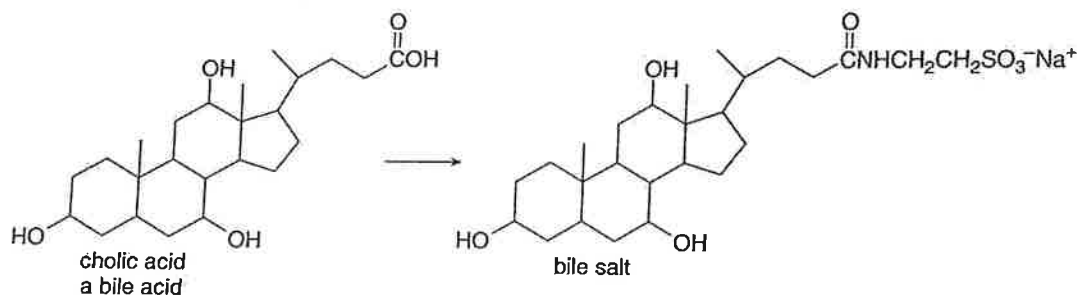
Question 1:

Cocaine is a widely used addictive drug. It is usually obtained as its hydrochloride salt, but can be converted to crack, the neutral molecule, by treatment with a base. Which of the two compounds has a higher boiling point? How does the relative solubility explain why crack is usually smoked but cocaine hydrochloride is injected directly into the bloodstream?



Question 2:

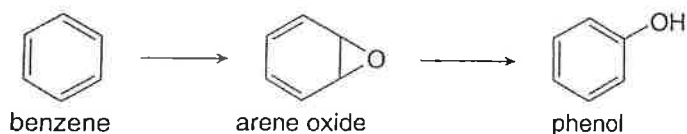
Cholic acid, a compound called a bile acid, is converted to a bile salt in the body. Bile salts have properties similar to soaps and they help to transport lipids through aqueous solutions. Explain why this is so.



Question 3:

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.

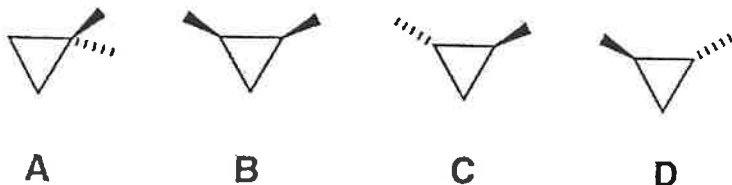
- Classify each of these reactions as oxidation, reduction or neither
- Explain why phenol is more water soluble than benzene. Suggest why this might be important.



Question 4:

Given are four isomeric dimethylcyclopropanes.

- How are the compounds in each pair related (enantiomers, diastereomers, constitutional isomers) A and B? A and C? B and C? C and D?
- Label each of the compounds as chiral or achiral.
- Which of the compounds alone would be optically active?
- Which of the compounds have a plane of symmetry?
- How do the boiling points in each pair compare – A and B? B and C? C and D?
- Which of the compounds are meso compounds?
- Would an equal of compounds C and D be optically active? B and C?



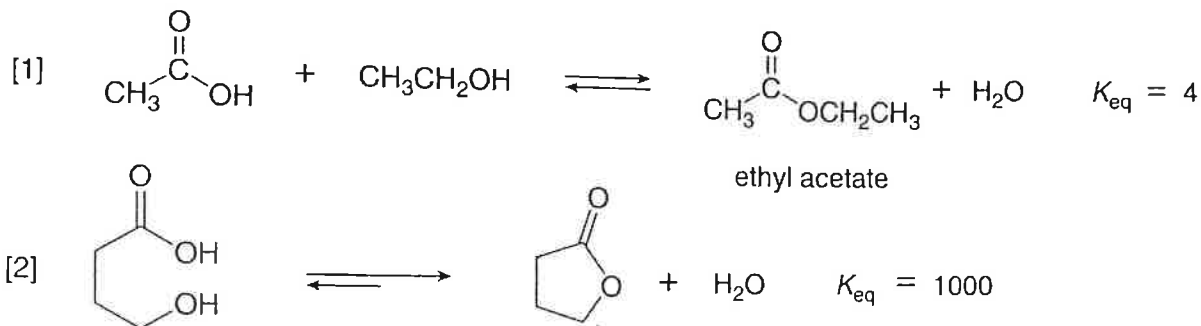
Question 5:

Draw an energy diagram for each reaction. Label the axes, the starting material, the product, the transition state, ΔH_o and E_a .

- A concerted exothermic reaction with a low energy of activation
- A one step endothermic reaction with a high energy of activation.
- A two step reaction $A \rightarrow B \rightarrow C$ in which the reactive energy of the compounds is $A < C < B$ and the step $A \rightarrow B$ is rate determining.
- A concerted reaction with $\Delta H_o = -20$ kcal/mol and $E_a = 4$ kcal

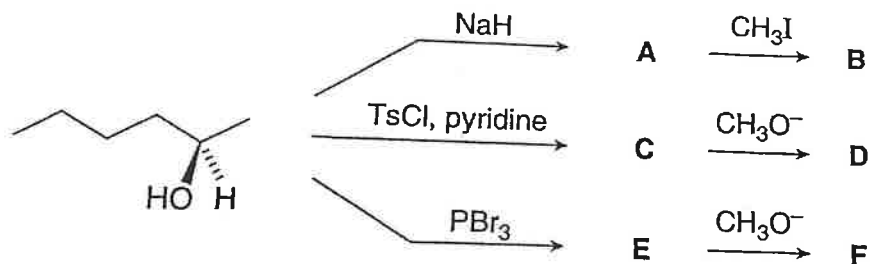
Question 6:

Esterification is the reaction of a carboxylic acid ($RCOOH$) with an alcohol ($R'OH$) to form an ester ($RCOOR'$) with the loss of water. Equation 1 is an example of an intermolecular esterification reaction. Equation 2 is an example of an intramolecular esterification reaction; that is the carboxylic acid and the alcohol are contained in the same starting material, forming a cyclic ester as the product. The equilibrium constants for both reactions are given. Explain why K_{eq} is different for these two apparently similar reactions.



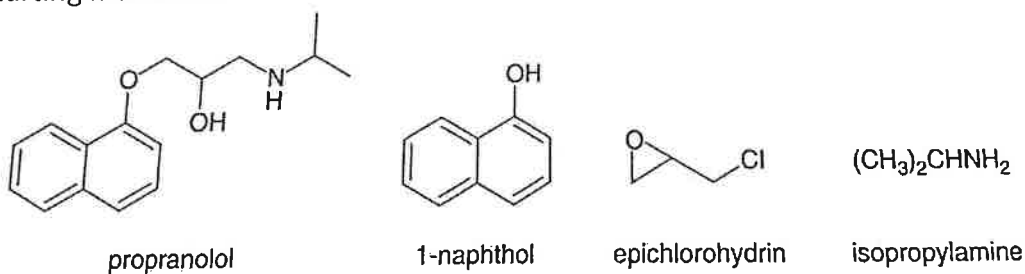
Question 7:

Identify compounds A-F in the following reactions. How are compounds B and D related? How are compounds B and F related?



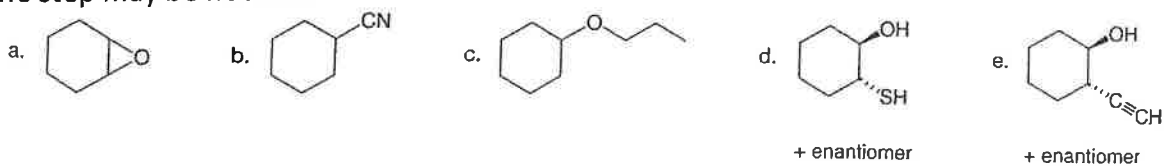
Question 8:

Propranolol, an antihypertensive agent used in the treatment of 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 9:

Devise a synthesis of each compound from cyclohexene as the starting material. More than one step may be needed.



Question 10:

a) 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?

b) Morphine, heroin and oxycodone are three addicting analgesic narcotics. How could IR spectroscopy be used to distinguish these compounds from each other?

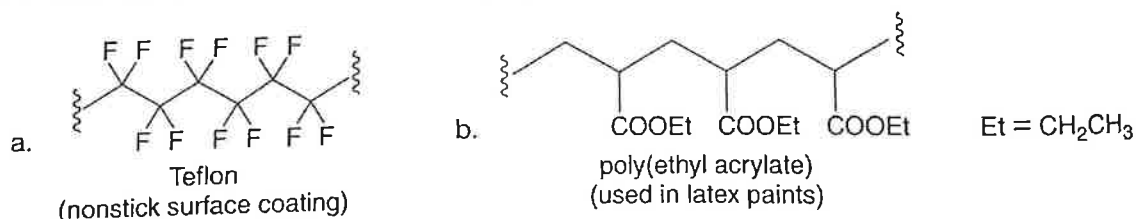


c) Propose a structure consistent with each set of spectral data.

- i) $C_4H_8Br_2$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 1.87 (singlet 6H), 3.86 (singlet 2H)
- ii) $C_3H_6Br_2$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 2.4 (quintet), 3.5 (triplet)
- iii) $C_5H_{10}O_2$: IR peak at 1740 cm^{-1} ; NMR (ppm) 1.15 (triplet, 3H), 2.30 (quartet, 2H), 1.24 (triplet 3H), 4.72 (quartet 2H)
- iv) $C_6H_{14}O$: 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)
- v) $C_6H_{14}O$: IR peak at $3000-2850\text{ cm}^{-1}$; NMR (ppm) 1.10 (doublet, 30 units), 3.60 (septet, 5 units)

Question 11:

What monomer is needed to form each polymer?

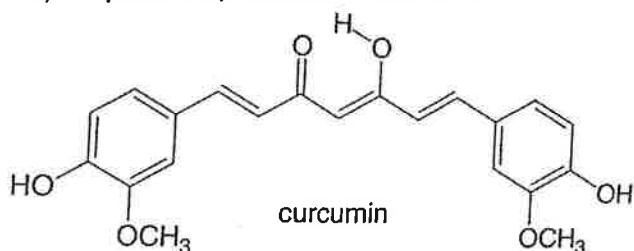


Draw the structure of poly (methyl methacrylate), a polymer used in Lucite and Plexiglas, and formed from radical polymerization of methyl methacrylate ($CH_2=C(CH_3)COOCH_3$).

Question 12:

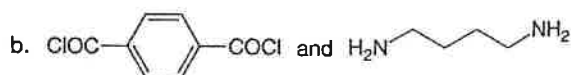
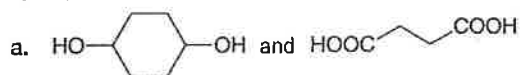
Curcumin is a yellow pigment isolated from turmeric, a tropical perennial in the ginger family and a principal ingredient in curry powder. It has long been used as an anti-inflammatory agent in traditional eastern medicine. In some preliminary research in mice, curcumin has been shown to correct the defect that causes cystic fibrosis, a fatal genetic disease.

- Enols, compounds that contain a hydroxyl group bonded to a C=C. are unstable and tautomerize to carbonyl groups. Draw the keto form of the enol of curcumin and explain why the enol is more stable than many other enols.
- Explain why the enol -OH proton is more acidic than the alcohol -OH proton.
- Why is curcumin coloured?
- Explain why curcumin acts as an anti-oxidant.



Question 13:

What polyester or polyamide can be prepared from each pair of monomers?



What monomers are needed to prepare each polymer?

