Name: _____ Student number: _____

Chemistry 1AA3 **April, 2005**

VERSION 1

Instructors: M. Austen, M. Brook, P. Lock, B. McCarry

Duration: 3 hours

MCMASTER UNIVERSITY FINAL EXAMINATION

This test contains 30 numbered pages. There are **40** multiple-choice questions appearing on pages numbered 3 to 26. Pages 27 and 28 are for your rough work. Page 29 includes some useful data and equations, and there is a periodic table on page 30. You may tear off the last page to view the periodic table and the data provided.

You must enter your name and student number on this question sheet, as well as on the answer sheet. Your invigilator will be checking your student card for identification. **You are responsible** for ensuring that your copy of the question paper is complete. Bring any discrepancy to the attention of your invigilator.

Questions 1 to 30 are each worth 2 marks, questions 31 – 40 are each worth 3 marks; the total marks available are 90. There is **no** additional penalty for incorrect answers.
BE SURE TO ENTER THE CORRECT VERSION OF YOUR TEST (shown near the top of page 1), IN THE SPACE PROVIDED ON THE ANSWER SHEET.

ANSWER ALL QUESTIONS ON THE ANSWER SHEET, IN PENCIL.
Instructions for entering multiple-choice answers are given on page 2.
SELECT ONE AND ONLY ONE ANSWER FOR EACH QUESTION from the answers **(A)** through **(E). No work written on the question sheets will be marked**. The question sheets may be collected and reviewed in cases of suspected academic dishonesty.

Academic dishonesty may include, among other actions, communication of any kind (verbal, visual, *etc*.) between students, sharing of materials between students, copying or looking at other students' work. If you have a problem please ask the invigilator to deal with it for you. Do not make contact with other students directly. Try to keep your eyes on your own paper – looking around the room may be interpreted as an attempt to copy.

Only Casio FX 991 electronic calculators may be used; but they must NOT be transferred between students. Use of periodic tables or any aids, other than those provided, is not allowed.

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You are writing VERSION 1 of this exam. Make sure you have correctly entered your version number ("1") in the correct column on your scan sheet (see p. 2 for details).

Questions 1 through 30 are worth two (2) marks each.

1. Commercial ethanol is produced by the reaction of ethene with water at 600K.

   $CH_2{=}CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$ $\quad K_p = 9.0 \times 10^3$

   Ethene and water when placed in a reaction vessel at 600K had initial partial pressures of 100 atmospheres (atm). What is the **equilibrium partial pressure of ethene** at 600K?

(A) 0 atm
(B) 0.11 atm
(C) 50 atm
(D) 99.9 atm
(E) 100 atm

2. The K_a of citric acid ($C_6H_8O_7$) is 7.5×10^{-4}. Calculate the **pH** of a 0.50 M solution of aqueous citric acid.

(A) 0.30
(B) 1.71
(C) 3.12
(D) 4.43
(E) 10.88

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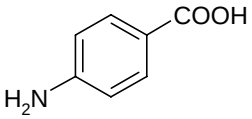
3. A first-year student determined the solubility of 4-aminobenzoic acid (a UV-absorbing compound used in sunscreen lotions, molar mass = 137.1 g/mol) by preparing a saturated solution and determining the pH to be 2.93. Calculate the **solubility** of 4-aminobenzoic acid in water (in g/L) if the pK_a of 4-aminobenzoic acid is 4.40.



4-aminobenzoic acid

(A) 4.3×10^{-5} g/L

(B) 4.9 g/L

(C) 10 g/L

(D) 270 g/L

(E) 4060 g/L

4. You wish to make a buffer of pH = 4.0. You have HCl(aq) and NaOH(aq) available. Choose **one other** solution you will **use to make your buffer**.

(A) NaCl(aq)

(B) NaOCl(aq), $K_b = 3.4 \times 10^{-7}$

(C) H_2CO_3(aq), $K_{a1} = 4.5 \times 10^{-7}$, $K_{a2} = 4.7 \times 10^{-11}$

(D) HCOOH(aq), $K_a = 1.8 \times 10^{-4}$

(E) CH_3NH_2(aq), $K_b = 4.4 \times 10^{-4}$

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5. Alazarin yellow R is an acid-base indicator with a pK_a of 11.0. The acidic form is yellow and the basic form is red. A few drops of this indicator are added to the titration of methylamine (pK_b = 3.36) with HCl. Find the **FALSE** statement(s) about this titration experiment.

   (i) The alazarin yellow R indicator is an appropriate choice for locating the equivalence point of this titration.

   (ii) The indicator starts to change from red to orange at about pH = 12 and completes the change from orange to yellow at about pH = 10.

   (iii) The indicator will be yellow over the entire buffer region of the titration curve.

(A) i

(B) ii

(C) iii

(D) i, iii

(E) ii, iii

6. Choose the **FALSE** statements about acids, bases, electrophiles and nucleophiles.

   (i) The carbon atom of a carbonyl group can act as an electrophile.

   (ii) Alkyl lithium reagents, such as $LiCH_2CH_3$, are strong Lewis bases (nucleophiles), but are weak Brønsted bases.

   (iii) In water, $C_3H_7O^-$ (propoxide) is a strong base, but $C_2H_5COO^-$ (propanoate) is a weak base because of its increased charge delocalization.

   (iv) $HBrO_3$ is a weaker acid than $HBrO_2$.

(A) i, ii

(B) i, iv

(C) ii, iii

(D) ii, iv

(E) iii, iv

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7. The dimethyl acetal of ethanal is 1,1-dimethoxyethane ($CH_3CH(OCH_3)_2$). It can be prepared in an equilibrium reaction by heating a dilute solution of ethanal in methanol at 65°C with a small amount of concentrated H_2SO_4 added as a catalyst.

$$CH_3CHO + 2\,CH_3OH \overset{H_2SO_4}{\rightleftharpoons} CH_3CH(OCH_3)_2 + H_2O$$

Which statement(s) about this reaction is/are **FALSE**?

(i) The reaction will reach equilibrium more slowly in the absence of H_2SO_4.

(ii) The rate of acetal formation will be slower at 25°C than at 65°C.

(iii) The addition of a dehydrating agent will drive the equilibrium to the right.

(iv) Dilution of the H_2SO_4 with water will not affect the position of the equilibrium.

(A) i

(B) ii

(C) iii

(D) iv

(E) iii, iv

8. Course-correcting rockets on spacecraft use the spontaneous reaction between liquid hydrazine (N_2H_4) and liquid N_2O_4 to produce $N_2(g)$ and $H_2O(g)$ for thrust. If the initial rate of consumption of N_2O_4 on firing a rocket thruster was 2.4 mole s^{-1}, what was the **rate of production of $N_2(g)$?**

(A) 0.8 mole s^{-1}

(B) 2.4 mole s^{-1}

(C) 3.6 mole s^{-1}

(D) 4.8 mole s^{-1}

(E) 7.2 mole s^{-1}

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9. For the reaction $X(g) + Y(g) \rightarrow Z(g)$, the following observations are made. As the concentration of X is increased by a factor of 1.5, the rate increases by a factor if 2.25. In a second experiment, as the concentration of X is doubled and the concentration of Y is doubled, the rate increases by a factor of 11.3. What is **the rate law** for this reaction?

(A) Rate = $k [X][Y]$

(B) Rate = $k [X]^2[Y]$

(C) Rate = $k [X][Y]^{1.5}$

(D) Rate = $k [X]^2[Y]^{1.5}$

(E) Rate = $k [X]^2[Y]^2$

10. A certain reaction occurs in two steps. The first step has an E_a (activation energy) of 40 kJ and is endothermic by 18 kJ. The second step has an E_a of 37 kJ. If the E_a of the first step of the *reverse* reaction is 47 kJ, what is the **ΔH** of the **overall forward reaction**?

(A) 8 kJ

(B) 10 kJ

(C) 19 kJ

(D) 28 kJ

(E) 37 kJ

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11. The rate constant, k, for a reaction is 1.30 mol L^{-1} s^{-1} at 427 °C and 23.1 mol $L^{-1}s^{-1}$ at 527 °C. The activation energy is 134 kJ mol^{-1}. The value of **the Arrhenius pre-exponential factor (A)** is:

(A) 4.1×10^{-8} mol L^{-1} s^{-1}

(B) 1.3 mol L^{-1} s^{-1}

(C) 1.3×10^{10} mol L^{-1} s^{-1}

(D) 4.4×10^{14} mol L^{-1} s^{-1}

(E) 4.4×10^{14}

12. The rate constant is k = 1.94×10^{-4} L mol^{-1} s^{-1} at 30.0 °C for the elementary reaction,

$$BH_4^-(aq) + NH_4^+(aq) \rightarrow H_3B{\cdot}NH_3(aq) + H_2(g)$$

The reaction has an activation energy of 161 kJ mol^{-1}. What is the value of the **rate constant at 40.0 °C**?

(A) 1.1×10^{24} L mol^{-1} s^{-1}

(B) 1.0×10^{24} L mol^{-1} s^{-1}

(C) 8.4×10^{2} L mol^{-1} s^{-1}

(D) 7.9 L mol^{-1} s^{-1}

(E) 1.5×10^{-3} L mol^{-1} s^{-1}

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13. Dinitrogen pentoxide (N_2O_5) undergoes a rapid, first order reaction with water to produce nitric acid. Thirty seconds after placing 0.010 mole of N_2O_5 in 1.00 L of water, the pH of the solution was 1.80. What is the **half-life** of N_2O_5 in water?

$$N_2O_5(aq) + H_2O(l) \rightarrow 2\ HNO_3(aq)$$

(A) 13 seconds

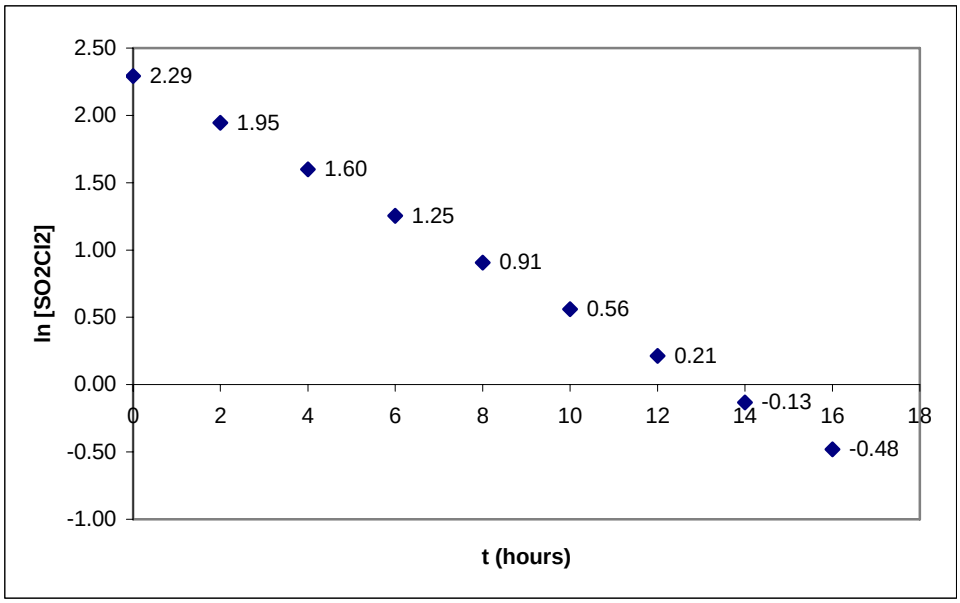
(B) 20 seconds

(C) 30 seconds

(D) 60 seconds

(E) 89 seconds

14. Based on the data shown in the plot below, calculate the value of the **rate constant, k,** for the reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$



(A) There is insufficient data to calculate k.

(B) $4.81 \times 10^{-5}\ s^{-1}$

(C) $0.30\ s^{-1}$

(D) 240 s

(E) $0.173\ s^{-1}$

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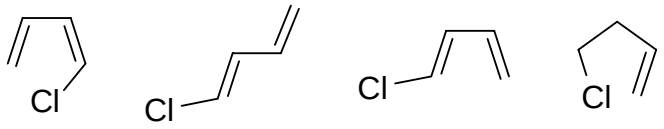
15. Which of the following statements are **TRUE** regarding the structures shown below?



A **B** **C** **D**

(i) **A** is a *Z*-isomer.

(ii) **A** and **B** are geometric isomers.

(iii) **A** and **C** are geometric isomers.

(iv) **B** and **D** are structural isomers.

(v) **B** and **C** are geometric isomers.

(A) i, ii, iii

(B) i, iii, v

(C) ii, iii, iv

(D) ii, iii, v

(E) iv, v

16. How many **structural isomers** are possible for the formula $C_3H_4Cl_2$?

(A) 9

(B) 8

(C) 7

(D) 6

(E) 5

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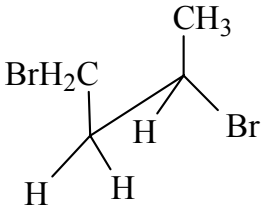
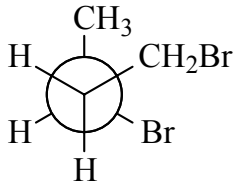
17. Which of the projections shown below represents the **lowest energy conformation** of 1,3-dibromobutane, viewed along the **C2-C3 bond**?

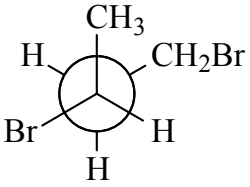
(A)



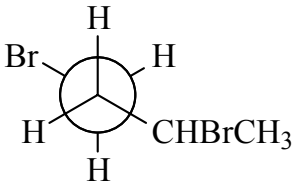
(B)



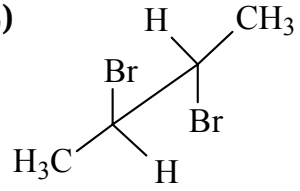
(C)



(D)



(E)



18. Select the **TRUE** statements regarding physical properties:

(i) The boiling point of hexanal is higher than that of hexane.

(ii) The vapour pressure of ethanol is higher than that of ethane.

(iii) The reason that propanone has a higher boiling point than propane is because of hydrogen bonding.

(iv) The dominant intermolecular force in 3-octene is the dipole-dipole force.

(v) Ethers can participate in hydrogen bonding.

(A) i, ii

(B) i, iv

(C) i, v

(D) ii, iv

(E) iii, iv, v

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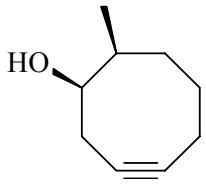
19. **Name** the following molecule according to IUPAC rules:



(A) *cis*-8-methylcyclooct-3-ynol

(B) *cis*-5-methylcyclooctyn-4-ol

(C) *Z*-8-methylcyclooct-3-ynol

(D) *Z*-5-methylcyclooctyn-4-ol

(E) *cis*-4-hydroxy-5-methylcyclooctyne

20. In an experiment you react butanone with isopropyl magnesium bromide in ether solvent, and then you add a solution of dilute acid. The IUPAC **name of the organic product** expected from this reaction is:

(A) 3-methylhexan-3-ol

(B) 5-methylhexan-3-ol

(C) 2,3-dimethylpentan-2-ol

(D) 2,3-dimethylpentan-3-ol

(E) 2-isopropylbutan-2-ol

21. Which of the following statements is **FALSE**?

(A) A nucleophile is an electron-rich species.

(B) A tertiary carbocation can act as an electrophile.

(C) An S_N1 reaction is faster in polar solvents than in nonpolar solvents.

(D) An S_N1 reaction goes through a trigonal bipyramidal transition state.

(E) An S_N2 reaction has a one-step reaction mechanism.

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22. Which of the following statements about the double bond in ethene are **TRUE**?

(i) The C atoms are *sp* hybridized.

(ii) The π bond is derived from the overlap of p orbitals.

(iii) The π bond's electron density is located in the H-C-C plane.

(iv) The C-C π bond is more reactive bond than the σ C-C bond.

(v) The C-C σ (sigma) and C-C π (pi) bonds are of equal strength.

(A) i, iii

(B) ii, iii

(C) ii, iv

(D) iii, v

(E) iv, v

23. Acetylsalicylic acid (ASA), which is a molecule used for pain relief, is shown below.

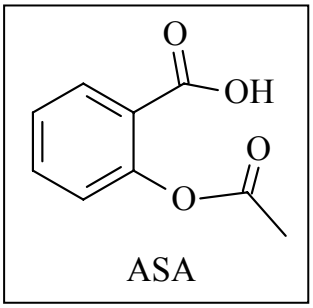
Which of the following statements about acetylsalicylic acid is/are **TRUE**?

(i) ASA contains at least one carbonyl group.

(ii) There are only 4 C-O sigma (σ) bonds in ASA.

(iii) There are only five degrees of unsaturation in ASA.

(iv) ASA contains an ether functional group.



ASA

(A) i

(B) ii

(C) i, ii

(D) i, iv

(E) ii, iii

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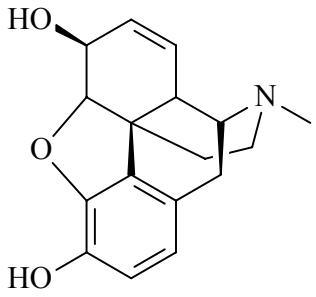
24. The alkaloid morphine is shown below. Which of the following statements about this molecule are **TRUE**?



Morphine

(i) Morphine contains a secondary amine group.

(ii) Morphine contains a secondary alcohol group.

(iii) There are exactly 6 sp^2 hybridized atoms in morphine.

(iv) Morphine contains at least one quaternary carbon atom.

(A) i, ii

(B) i, iv

(C) ii, iii

(D) ii, iv

(E) iii, iv

25. Tollen's reagent contains the silver ammonia complex ion, $Ag(NH_3)_2^+(aq)$. Reaction with an aldehyde produces a "silver mirror", *i.e.*, metallic silver. During this reaction **the aldehyde**:

(A) is reduced to an alcohol.

(B) changes to a ketone.

(C) oxidizes the ammonia solution.

(D) makes a new complex ion with silver.

(E) is oxidized to a carboxylic acid.

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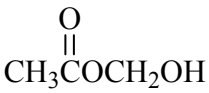
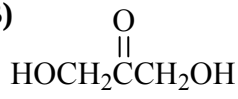
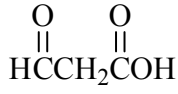
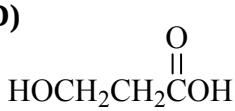
26. A certain organic compound has the formula $C_3H_6O_3$, but its structure is not known. In the lab you perform several chemical tests in order to identify the compound. You make the following observations about the unknown compound:
    - It decolourizes a few drops of $KMnO_4(aq)$.
    - It does not react with a solution of Ag^+ ions in ammonia.
    - Bubbles of a gas are observed upon addition of $NaHCO_3(aq)$.

Which of the **structures** shown below **best fits these observations**?

(A) 

(B) 

(C) 

(D) 

(E) 

27. In a test tube a hydrocarbon reacts with bromine and, as a result, litmus paper held over the mouth of the test tube turns red. Which of the following statements are **TRUE** about this reaction?

    (i) The hydrocarbon may have double bonds.
    (ii) The hydrocarbon cannot have double bonds.
    (iii) The hydrocarbon oxidizes the bromine.
    (iv) There are single bonds in this hydrocarbon.
    (v) A substitution reaction with bromine occurs.

(A) i, iii
(B) ii, iii
(C) i, iv, v
(D) ii, iv, v
(E) iii, iv

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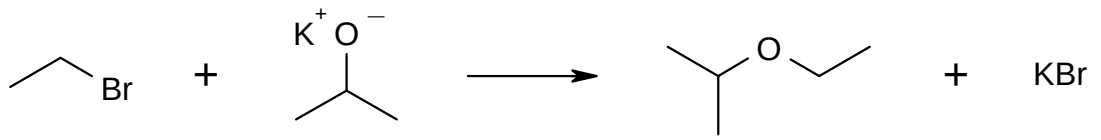
28. The following reaction occurs readily at 25 °C.



Which of the following statements is/are **FALSE**?

(i) This is an S_N2 reaction.

(ii) Changing the initial concentration of $KOCH(CH_3)_2$ will not affect the reaction rate.

(iii) The same product would be obtained if CH_3CH_2OK was reacted with $BrCH(CH_3)_2$.

(A) i

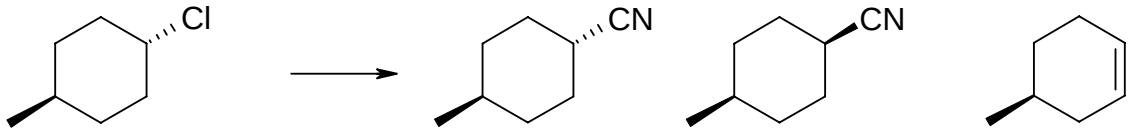
(B) ii

(C) iii

(D) i, ii

(E) ii, iii

29. Which of the following statements is/are **TRUE**?



1 **A** **B** **C**

(i) **1** can be converted to a mixture of **A** and **B** using NaOH.

(ii) Treatment of **1** with cool NaCN will form mostly **B**.

(iii) Treatment of **1** with aqueous H_2SO_4 will lead to the formation of **C**.

(iv) Treatment of **1** with H_2 in the presence of Pt will form **C**.

(A) None is true.

(B) i, iii

(C) ii

(D) iv

(E) ii, iii

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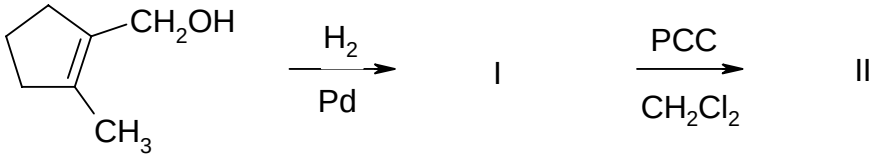
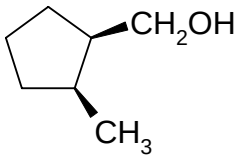
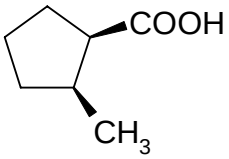
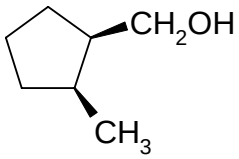
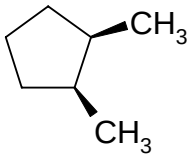
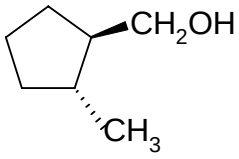
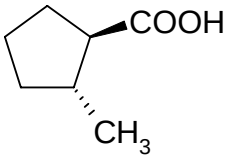
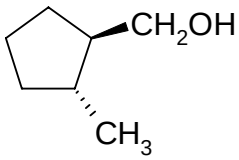
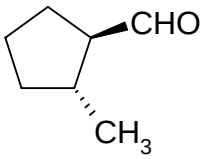
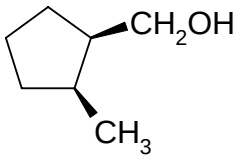
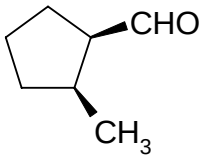
30. Predict the **structures of products I and II** which result from the following two-stage reaction sequence:



	Product I	Product II
(A)		
(B)		
(C)		
(D)		
(E)		

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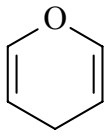
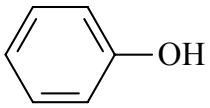
Questions 31 through 40 are worth three (3) marks each.

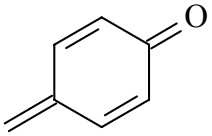
31. You perform the combustion of 18.26 g of an unknown organic compound ($C_xH_yO_z$) in excess oxygen. The combustion produces 28.0 L of carbon dioxide gas and 10.5 g of liquid water at 20°C and 1 atm. Of the options given below, which molecule **most likely** represents your **unknown compound**?



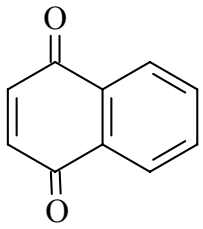
(A)



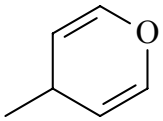
(B)



(C)



(D)



(E)

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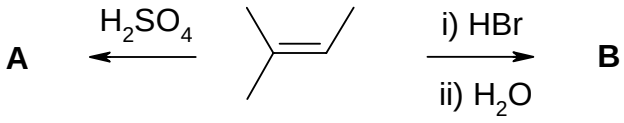
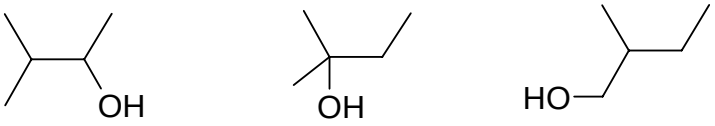
32. **Predict the major products** of the reactions of 2-methylbut-2-ene with the following species in two separate chemical reactions:

(a) with dilute aqueous H_2SO_4

(b) with HBr followed by treatment with H_2O.



Possible products



I II III

	Product A	**Product B**
(A)	I	I
(B)	I	II
(C)	II	I
(D)	II	II
(E)	III	III

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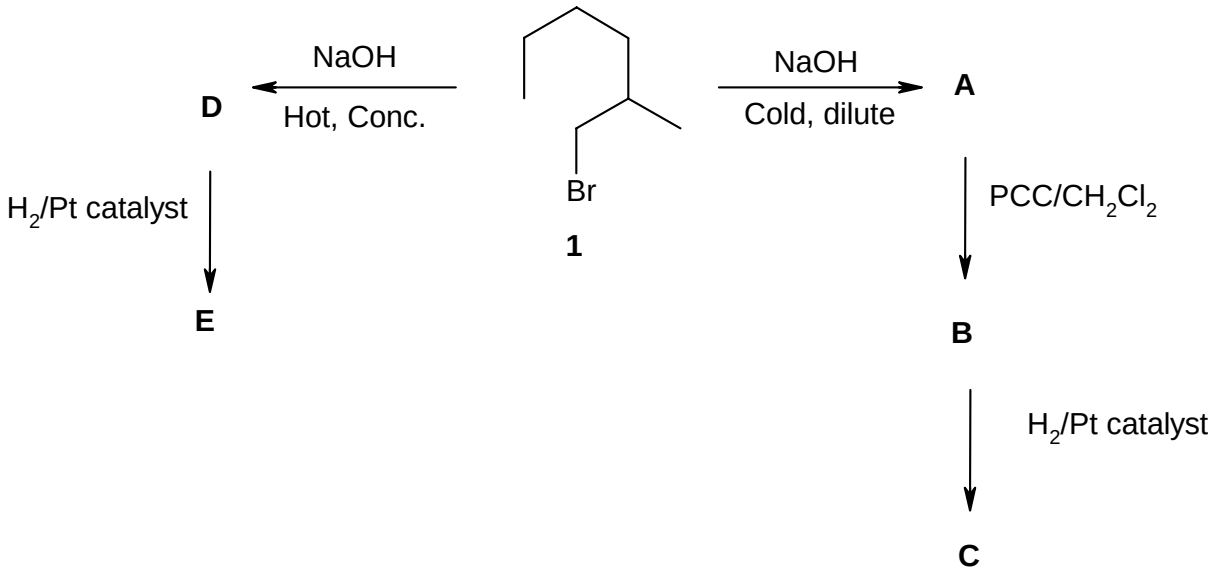
Use the reaction scheme below for the following 2 questions.

You may want to start by drawing structures of each product **A – E.**



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33. Which of the following statements are **FALSE** with respect to the reaction scheme above?

(i) Product **D** would not decolourize Br_2.

(ii) Product **D** is a primary alcohol.

(iii) The reaction that forms product **A** is an S_N2 process.

(iv) The reaction that forms product **B** is an oxidation and the reaction that forms product **E** is a reduction.

(v) The reaction of product **C** with NaBr will regenerate the starting material **1**.

(A) i, ii

(B) i, ii, v

(C) i, iii, iv

(D) ii, iii, iv

(E) iv, v

34. With respect to the reaction scheme above, which of the following statements are **TRUE**?

(i) Products **E** and **C** are the same compound.

(ii) Product **B** contains an aldehyde.

(iii) Treatment of compound **1** with magnesium in ether, followed by dilute acid will lead to the formation of product **E**.

(iv) Product **D** does not readily dissolve in water.

(v) The reactions to give products **A** and **D** are both nucleophilic substitutions.

(A) i, ii, v

(B) ii, iii, iv

(C) ii, iii, v

(D) iii, iv

(E) iv, v

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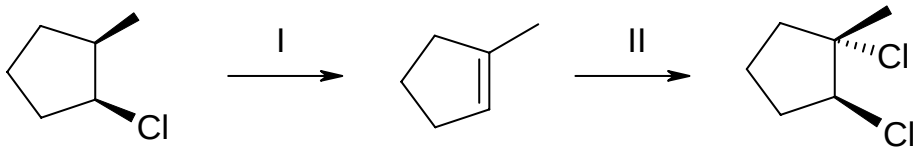
The following lists of chemical reagents and reaction conditions are to be used with the following 3 questions:

Reagents:	**a**. Br_2	**b**. Cl_2	**c**. Mg, ether
	d. NaOH (dilute)	**e**. NaOH (conc.)	**f**. Na
	g. HCl (dilute)	**h**. HCl (conc.)	**i**. H_2SO_4 (conc.)
	j. PCC, CH_2Cl_2	**k**. acidic $K_2Cr_2O_7$ (aq)	**l**. CH_3CH_2MgCl
	m. CH_3CH_2Cl	**n**. CH_3CH_2OH	**o**. NH_2NH_2

Conditions: (i) 25°C (ii) heat (iii) light (hν)

35. From the lists above **select the reagents and conditions** needed for each of the following two transformations:



	Reagent(s)/Conditions I	**Reagent(s)/Conditions II**
(A)	**d** (i)	**b** (iii)
(B)	**d** (ii)	**h** (ii)
(C)	**i** (ii)	**b** (i)
(D)	**e** (ii)	**g** (i)
(E)	**e** (ii)	**b** (i)

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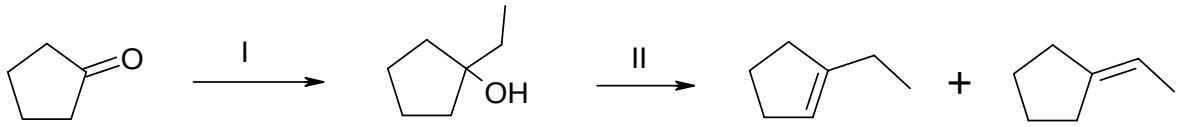
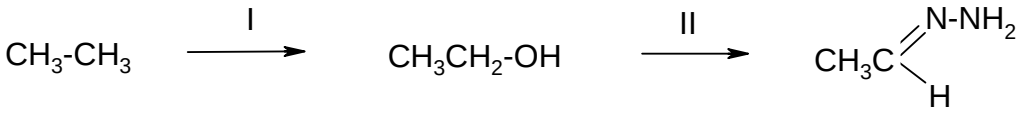
36. From the lists above **select the reagents and conditions** needed for the following two transformations:



	Reagent(s)/Conditions I	**Reagent(s)/Conditions II**
(A)	**a**, (iii); then **f**, (ii)	**i**, (ii)
(B)	**c**; then **m**, (ii)	**g**, (ii)
(C)	**f**; then **n**, (i)	**h**, (i)
(D)	**l**; then **g**, (i)	**e**, (ii)
(E)	**l**; then **g**, (i)	**i**, (ii)

37. From the lists above **select the reagents and conditions** needed for each of the following two transformations:



	Reagent(s)/Conditions I	**Reagent(s)/Conditions II**
(A)	**a**, (ii); then **d**, (i)	**o**, (ii)
(B)	**a**, (iii); then **d**, (i)	**j**; then **o**, (ii)
(C)	**b**, (iii); then **g**, (i)	**k**; then **o**, (ii)
(D)	**d**, (i)	**j**; then **o**, (i)
(E)	**e**, (ii)	**o**, (ii)

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38. CH_3MgBr (0.025 mol) was dissolved in diethyl ether (0.5 L). Solid CO_2 (44 g) was added. All the solvents and excess reagents were removed by evaporation, and the residue was dissolved in water (1 L). What is the **pH of the solution** (assume the yield of the reaction is 100%).

$K_a(CH_4) = 1 \times 10^{-50}$; $K_a(H_2CO_3) = 4.5 \times 10^{-7}$; $K_a(CH_3COOH) = 1.8 \times 10^{-5}$

(A) 5.4

(B) 7.0

(C) 8.6

(D) 11.8

(E) 12.3

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39. You are preparing a HCN / CN^- buffer of pH = 9.00. You need the pH to change by no more than 0.10 units when 1.0 g of NaOH are added to 2.0 L of the buffer. What is the **minimum concentration of HCN** in the buffer solution? (K_a of HCN = 6.2×10^{-10})

(A) 0.086 M

(B) 0.14 M

(C) 0.28 M

(D) 0.62 M

(E) 0.78 M

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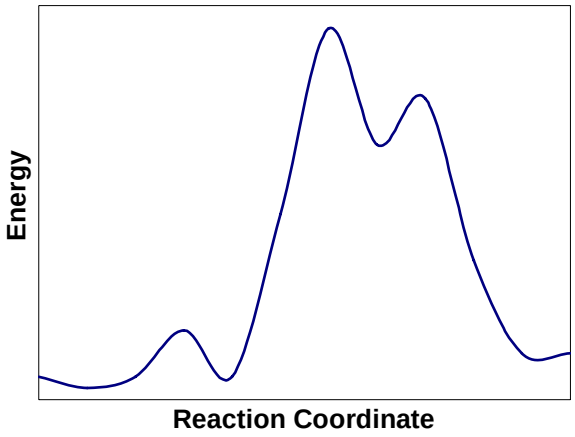
40. Based on what you know about **organic reaction mechanisms**, which one of the reactions below is likely to have a **reaction coordinate diagram** that has the following form?



(A) 2-methylpropan-2-ol + HBr → 2-bromo-2-methylpropane + H_2O

(B) 2-bromo-2methylpropane + H_2O → 2-methylpropan-2-ol + HBr

(C) propan-1-ol + HBr → 1-bromopropane + H_2O

(D) 1-bromopropane + OH^- → propan-1-ol + Br^-

(E) 1-bromopropane + OH^- → propene + H_2O + Br^-

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Data page

Some general data are provided on this page. Other data appear with the questions.

$R = 8.314 \text{ J / (K mol)} = 0.08206 \text{ L atm / (K mol)}$ $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

1 atm = 760 mm Hg = 101.325 kPa $0°C = 273.15 \text{ K}$

$k = Ae^{-Ea/RT}$ $[A]_t = [A]_o e^{-kt}$

$K_w = 1.0 \times 10^{-14}$ $K_b (CN^-) = 1.6 \times 10^{-5}$

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