Student Name: _____ Student No: _____

Chemistry 1AA3 **Final Exam** **April 2013**

McMaster University **VERSION 1**

Instructors: P. Berti, D. Brock, P. Lock, H. Stover

Duration: 180 min.

This exam contains 24 numbered pages printed on both sides. There are 36 multiple-choice questions appearing on pages numbered 3 to 21. Page 22 is extra space for rough work. Page 23 includes some useful data and equations. There is a periodic table on page 24. You may tear off the last page to view the periodic table and to do your rough work.

You must enter your name and student number on the question sheets, 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.

All questions are each worth 2 marks; the total marks available are 72. 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. Keep your eyes on your own paper - looking around the room may be interpreted as an attempt to copy.

Only Casio FX 991 MS 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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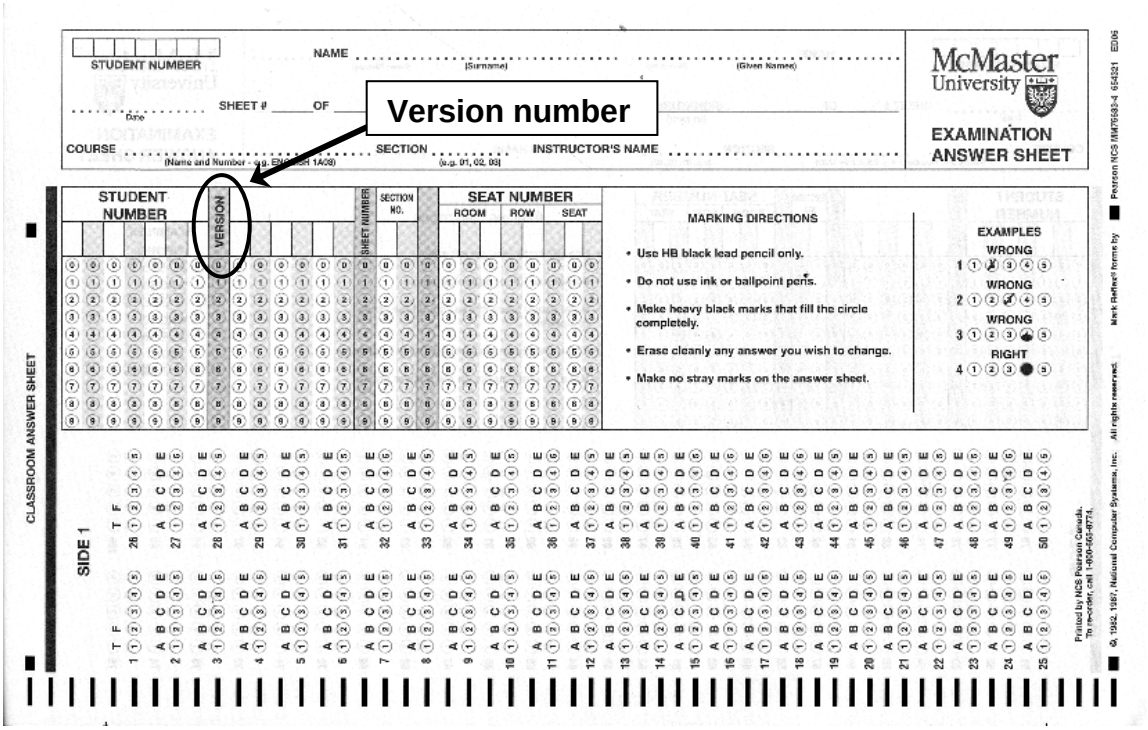
Student Name: _____ Student No: _____

OMR EXAMINATION - STUDENT INSTRUCTIONS

NOTE: IT IS YOUR RESPONSIBILITY TO ENSURE THAT THE ANSWER SHEET IS PROPERLY COMPLETED: YOUT EXAMINIATION RESULT DEPENDS UPON PROPER ATTENTION TO THESE INSTRUCTIONS.

The scanner, which reads the sheets, senses the bubble shaded areas by their non-reflection of light. A heavy mark must be made, completely filling the circular bubble, with an HB pencil. Marks made with a pen will NOT be sensed. Erasures must be thorough or the scanner will still sense a mark. Do NOT use correction fluid on the sheets. Do NOT put any unnecessary marks or writing on the sheet.

1. On SIDE 1 (red side) of the form, in the top box, in pen, print your student number, name, course name, and the date in the spaces provided. Then you MUST write your signature, in the space marked SIGNATURE.
2. In the second box, with a pencil, mark your student number, exam version number in the space provided and <u>fill in the corresponding bubble numbers underneath</u>.
3. Answers: mark only ONE choice from the alternatives (A,B,C,D,E) provided for each question. The question number is to the left of the bubbles. Make sure that the number of the question on the scan sheet is the same as the number on the test paper.
4. Pay particular attention to the Marking+ Directions on the form.
5. Begin answering the question using the first set of bubbles, marked “1”.



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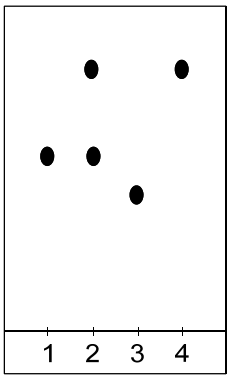
Student Name: _____ Student No: _____

VERSION **1**.
Enter your version number in the correct column on
your scan sheet (see p. 2 for details).

1. Consider the following TLC (thin layer chromatography) plate. Spot 1 is a sample of pure starting material, while spot 4 is a sample of pure product. Spots 2 & 3 are reaction products obtained from two different students. Which of the following conclusions would be **incorrect** regarding this TLC?



A) Sample 3 has no product.
B) The starting material and product appear to be pure.
C) Student 3 did something different than student 2.
D) Sample 2 has a 100% yield.
E) The product travelled further with the solvent than the starting material.

2. A 0.125 M aqueous solution of a weak acid (HA), volume = 25.0 mL, was titrated with a 0.100 M NaOH solution. HA and NaOH react in a 1:1 mole ratio. The pH at the equivalence point was 11.13. What is the **pK_a** of HA?

A) 9.5
B) 8.9
C) 10.1
D) 9.2
E) 9.7

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3. The following compounds are available as 0.10 M aqueous solutions:

   pyridine ($pK_b = 8.82$)
   triethylamine ($pK_b = 3.25$)
   NH_3 ($pK_b = 4.74$)
   NaOH
   $HClO_4$
   phenol ($pK_a = 9.96$)
   HClO ($pK_a = 7.54$)

   Identify **two solutions** that could be used to prepare a pH 5 buffer.

   A) HClO and NaOH
   B) phenol and NaOH
   C) pyridine and $HClO_4$
   D) $HClO_4$ and NaOH
   E) triethylamine and $HClO_4$

4. In order to prepare a buffer of pH 4.60, you start with 500.0 mL of 0.100 M benzoic acid (C_6H_5COOH) and add NaOH(s). What **mass (in g) of NaOH** is required? Assume there is no volume change upon NaOH(s) addition.

   Data:
   $K_a(C_6H_5COOH) = 6.3 \times 10^{-5}$

   A) 4.97
   B) 5.55
   C) 3.18
   D) 1.43
   E) 8.72

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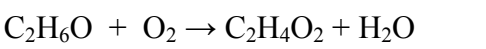
5. The oxidation of ethanol to acetic acid in presence of excess oxygen is found to be pseudo-first order in ethanol. Use the data in the table below to estimate the rate constant for this reaction.



$C_2H_6O + O_2 \rightarrow C_2H_4O_2 + H_2O$

time (h)	[ethanol] (mM)
1.00	0.020
1.10	0.019

A) 2.3×10^{-4} s^{-1}
B) 3.0×10^{-4} s^{-1}
C) 1.1×10^{-4} s^{-1}
D) 6.8×10^{-5} s^{-1}
E) 1.4×10^{-4} s^{-1}

6. If $v = 8 \times 10^{-7}$ M/s for an enzymatic reaction, where [E] = 1 μM, [S] = 50 μM and $k_{cat} = 3$ s^{-1}, what is $\boldsymbol{K_M}$?

A) 1.4×10^{-3} M
B) 7.9×10^{-5} M
C) 1.4×10^{-4} M
D) 3.7×10^{-4} M
E) 3.7×10^{-5} M

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7. The rate of flashing of a firefly was measured to be 0.5 s^{-1} at 298 K and 1 s^{-1} at 318 K, respectively. What is the activation energy of this process, according to the Arrhenius equation?

   A) 26.6 kJ/mol
   B) 25.2 kJ/mol
   C) 31.8 kJ/mol
   D) 27.3 kJ/mol
   E) 29.2 J/mol

8. Indicate the **incorrect** statement regarding activation energies:

   A) In unimolecular decomposition reactions, molecules start breaking apart when they gain energy equivalent to the activation energy of decomposition.
   B) Activation energies can be positive or negative, depending on the type of reaction.
   C) Activation energies influence reaction rates.
   D) Activation energies can be measured by comparing reaction rates at different temperatures.
   E) According to collision theory, the activation energy corresponds to the minimum amount of kinetic energy molecules need to react during collisions.

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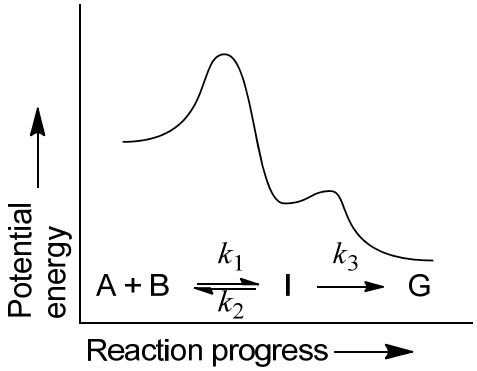
9. A researcher set out to measure the kinetic constants for an enzyme, but there was a mistake in the enzyme concentration. He thought it was 1.0 μM, but it was really 0.5 μM. What effect would this mistake have on the apparent kinetic constants?

   A) k_{cat} would be too high, but K_M would be correct
   B) k_{cat} would be correct, but K_M would be too high
   C) k_{cat} and K_M would both be too low
   D) k_{cat} and K_M would both be too high
   E) k_{cat} would be too low, but K_M would be correct

10. Which statement about the reaction profile below is **incorrect**?



   A) $k_1 > k_2$
   B) The rate-limiting step is A + B → I.
   C) The first elementary step involves the association of A and B to form intermediate I.
   D) The reaction could be zero order with respect to [B].
   E) $k_2 < k_3$

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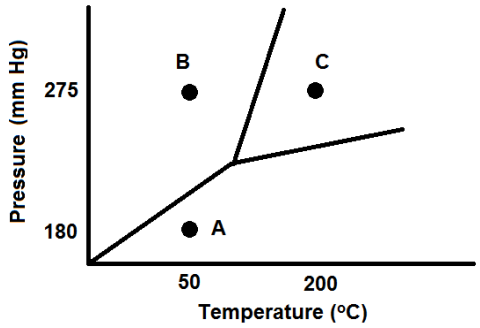
11. For each of the points A, B and C (each marked with a "●"), which of the following statements is **incorrect**?



A) Transforming from B into C involves a process called melting (fusion).
B) It is possible to transform A into C, or C into A, without observing a phase boundary.
C) The critical temperature is approximately 100 °C.
D) The triple point pressure, P, is: 180 mm Hg < P < 275 mm Hg.
E) Point A is in the region where only vapour exists.

12. A sealed vessel contains equal amounts (mol) of each of BrCl, Cl_2, NaCl, PCl_3 and PCl_5 at –34°C. Assuming no reactions take place between them, which species would have the highest vapour pressure at this temperature?

A) BrCl
B) PCl_3
C) NaCl
D) PCl_5
E) Cl_2

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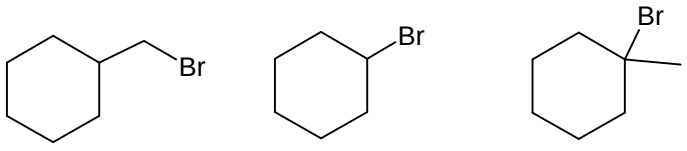
13. Solid CO_2 (0.35 mol) is reacted with CH_3MgBr (0.28 mol) in ether solvent. The product of the reaction is isolated in aqueous solution (assume 100% yield) and excess $CO_2(s)$ is removed. Then, HCl(aq) (0.16 mol) is added. What is the **pH** of the solution that results?

    Data:
    pK_a (CH_3COOH) = 4.74

    A) 4.74
    B) 4.53
    C) 4.88
    D) 4.95
    E) 4.62

14. Given the following structures, which of the statements below is **incorrect**?



(I) (II) (III)

    A) Molecule II can react with some nucleophiles *via* an S_N1 mechanism.
    B) When II undergoes a successful substitution reaction with CH_3COONa (where CH_3COO^- is a nucleophile) the product is an ester.
    C) Molecule I will react with nucleophiles *via* a two-step substitution mechanism.
    D) Reaction of III with water will produce an alcohol *via* an S_N1 mechanism.
    E) Reaction of I with OH^- will produce an alcohol *via* an S_N2 mechanism.

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15. Which statement about hybridization is **incorrect**?

A) In alkenes the unhybridized p-orbitals form a π-bond and force the substituents attached to the alkene C atoms to become eclipsed.
B) sp^2-hybridized orbitals are lower in energy than sp^3-hybridized orbitals.
C) sp-, sp^2-, and sp^3-hybridized orbitals can sometimes form π-bonds.
D) For a carbon atom the angle between sp^2-hybrid orbitals is greater than the angle between sp^3-hybrid orbitals.
E) For a given atom, sp-hybrid orbitals are separated by a 180° angle.

16. Indicate the correct **condensed structural formula** for 3-bromopentane.

A) $CH_3CH_2CBr_2CH_2CH_3$
B) $CH_3CH_2CHBrCH_2CH_3$
C) $CH_3CHBrCH_2CH_2CH_3$
D) $CH_3CH_2CHBrCH_2CH_2CH_3$
E) $(CH_3)_3CHBrCH_2CH_3$

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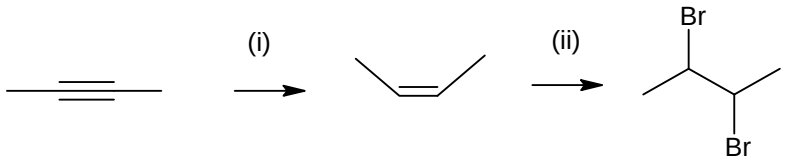
17. Which of the following are **propagation steps** in the halogenation of an alkane?

i) $CH_3CH_3 + Cl\cdot \rightarrow HCl + CH_3CH_2\cdot$
ii) $CH_3CH_2\cdot + CH_3CH_2\cdot \rightarrow CH_3CH_2CH_2CH_3$
iii) $CH_3CH_2\cdot + Cl_2 \rightarrow CH_3CH_2Cl + Cl\cdot$
iv) $Cl\cdot + CH_2{=}CH_2 \rightarrow ClCH_2CH_2\cdot$
v) $Cl_2 + h\nu \rightarrow 2Cl\cdot$

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

18. Which **reagents** are needed to carry out the following synthesis?



	(i)	(ii)
A)	excess H_2, Pd/C	Br_2, hν
B)	excess H_2, Lindlar's catalyst	HBr
C)	excess H_2, Lindlar's catalyst	Br_2
D)	excess H_2, Ni	Br_2
E)	excess H_2, Pt	HBr

19. Which of the following statements is **incorrect**?

A) Cycloalkanes with 5- and 6-membered rings have non-planar arrangements of carbon atoms.
B) For a given C-C bond, all eclipsed conformations are higher in energy than all staggered conformations.
C) The boat conformation of cyclohexane contains a greater number of axial substituents than the chair conformation.
D) Cyclopropane has a planar arrangement with respect to the carbon atoms.
E) The boat conformation of cyclohexane contains a greater number of eclipsed interactions than the chair conformation.

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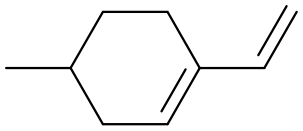
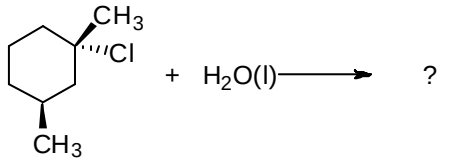
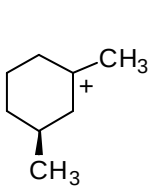
20. For the following molecule, **how many** sp^3- and sp^2-hybridized carbon atoms are there, and how many π- and σ–bonds are there?



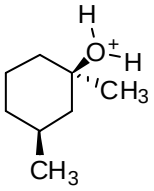
	sp^3	sp^2	π-bonds	σ-bonds
A)	5	4	9	2
B)	5	4	2	23
C)	4	5	9	23
D)	4	5	2	10
E)	5	4	2	10

21. Indicate all possible intermediate(s) and product(s) of the following reaction.

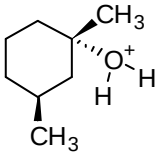




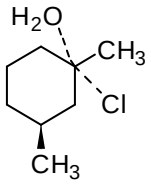
(i)



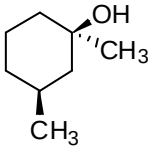
(ii)



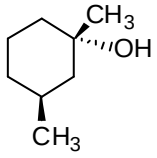
(iii)



(iv)



(v)



(vi)

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

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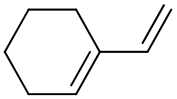
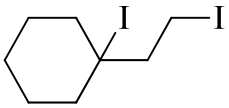
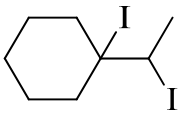
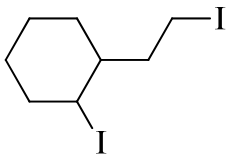
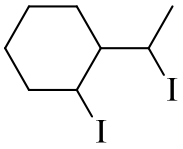
22. What would the **product** be for the reaction of excess HI with the molecule below?

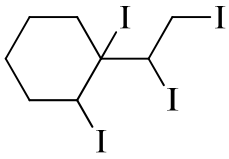


A) 

B) 

C) 

D) 

E) 

23. A student reacts a long chain carboxylic acid (oleic acid; 1.250 g, MW 282.46 g mol^{-1}) with an alcohol in the presence of a catalytic amount of acid. After work-up and purification, the result is a solid (1.238 g), obtained in 75.1% yield. What was the alcohol?

A) hexanol
B) benzyl alcohol
C) isopropanol
D) phenol
E) methanol

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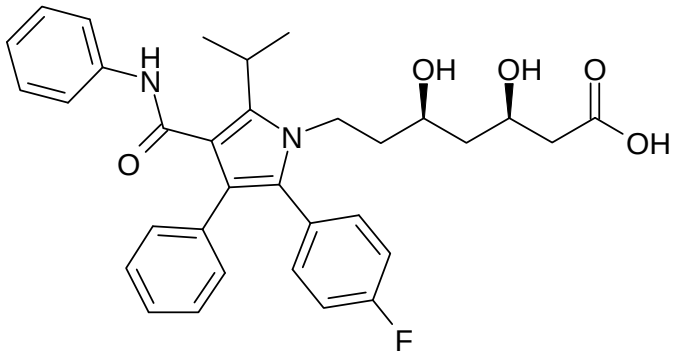
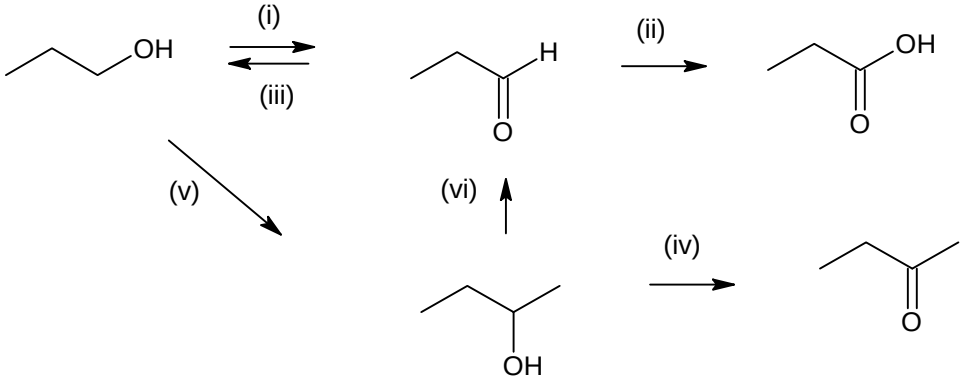
24. The **functional groups** present in Lipitor® (shown below) include:



A) phenol, carboxylic acid, aldehyde
B) alkene, carboxylic acid anhydride, ether
C) amine, alkyl halide, alkyne
D) alcohol, aryl halide, amide
E) ester, ketone, arene

25. Choose the **incorrect** statement regarding the reagents needed for the steps shown below.



A) Steps (ii) and (iv) can both be achieved by reaction with $KMnO_4$(aq).
B) Step (v) can be achieved *via* an oxidation reaction, followed by a Grignard reaction and acid work-up.
C) Step (i) can be achieved by reaction with PCC in CH_2Cl_2.
D) Step (vi) can be achieved by reaction with H_2O, and H_3O^+(aq).
E) Step (iii) can be achieved by reaction with $NaBH_4$ followed by addition of H_3O^+(aq).

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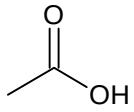
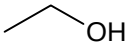
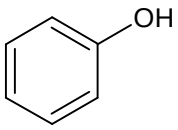
26. Which statement(s) is/are **correct** regarding the molecules shown below?







$pK_a = 4.74$ $pK_a = 15.9$ $pK_a = 10$

(i) The conjugate base of phenol is a stronger base than CH_3COONa.
(ii) Ethanol is a weaker acid than phenol.
(iii) When $NaHCO_3$ ($pK_b = 7.64$) is added to solutions of each of the three molecules above, a gas will be produced in each case.

A) iii
B) i
C) i, ii
D) ii, iii
E) i, iii

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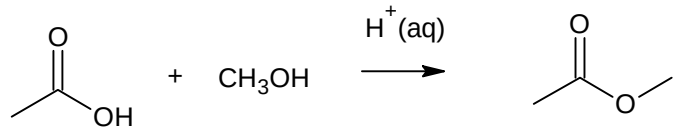
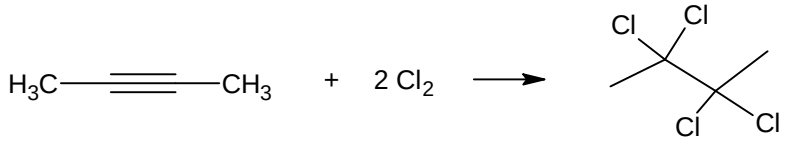
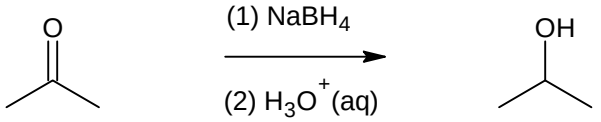
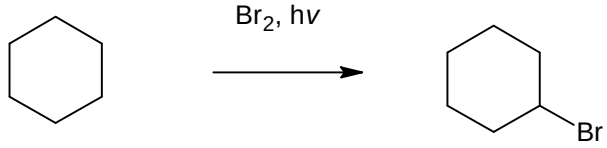
27. Which of the following are **addition reactions**?

(i) 

(ii) 

(iii) 

(iv) 

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

28. Identify the **incorrect** statement about *E*/*Z* isomers:

A) *E* and *Z* are different configurations that a molecule can have.
B) *E*-isomers of alkenes generally have higher melting points than their *Z*-isomers.
C) 1-bromocyclopentene can only exist as the *E*-isomer.
D) *E*-isomers are sometimes referred to as *trans*-isomers.
E) A $-CH_2CH_3$ group has higher priority than an -OH group because it has a higher mass.

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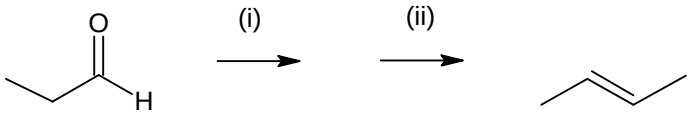
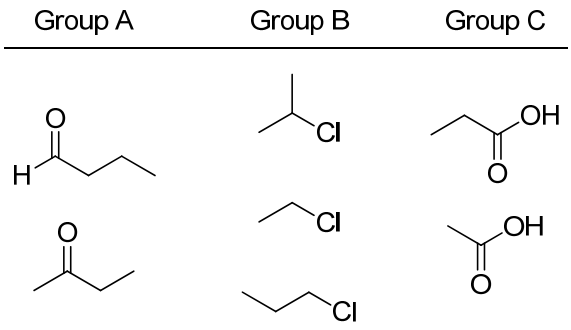
29. Which **reagents** are needed to carry out the following synthesis?

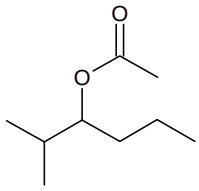


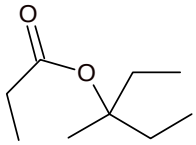
	(i)	(ii)
A)	H_2, Pt	dilute HCl(aq)
B)	H_2, Pt	conc. H_2SO_4(aq)
C)	(1) $NaBH_4$, (2) H_3O^+(aq)	conc. H_2SO_4(aq)
D)	(1) CH_3MgBr/ether, (2) H_3O^+(aq)	conc. H_2SO_4(aq)
E)	CH_3MgBr/ether	dilute HCl(aq)

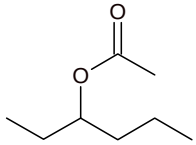
Continued on next page…

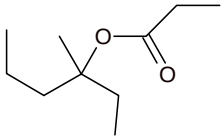
30. A combinatorial library was built by reacting the carbonyl compounds in group A with the Grignard reagents formed from the halides in group B, followed by esterification of the resulting product with the acids in group C. Which of the following compounds **could not** be part of the resulting combinatorial library?

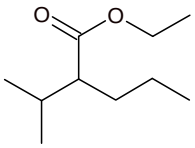


A) 

B) 

C) 

D) 

E) 

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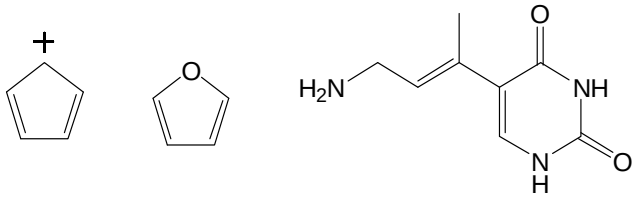
31. Which of the following planar structures would be aromatic?

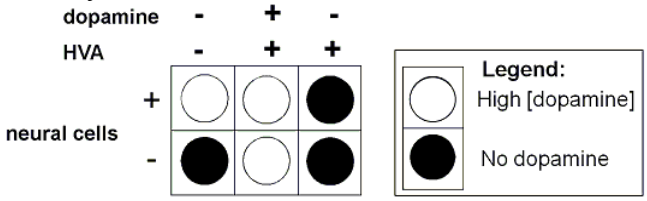


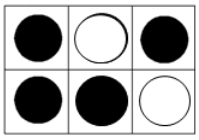
(i) (ii) (iii)

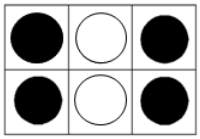
A) i, ii
B) i
C) ii, iii
D) i, iii
E) ii

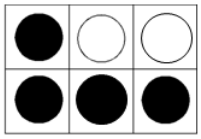
32. If neural cells were accidentally omitted from all the control wells in the bee neural cell assay, as discussed in class, **what would the control wells look like**?

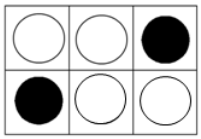
Normally, the control wells look like this:

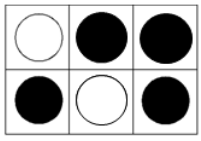


A)


B)


C)


D)


E)


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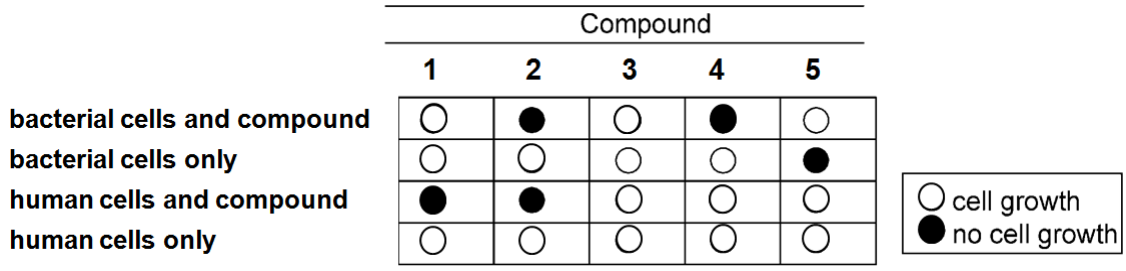
33. A high-throughput assay was developed to find inhibitors for an enzyme which catalyzes the reaction A → G + H. The product G has an absorbance which can be detected with a spectrophotometer. Each test well contains a solution of the enzyme, the substrate, A, and a test inhibitor. One of the control wells contains a solution of G only. What **type of well/result** is the latter?

A) false negative result
B) false positive result
C) positive control well
D) true positive result
E) negative control well

34. Compounds 1 to 5 were screened in multi-well plates for antibacterial activity. Antibacterial compounds prevent growth of bacterial cells, while not affecting growth of human cells. Which of the results below is most promising in terms of identifying a new antibacterial compound?



A) 1
B) 4
C) 3
D) 5
E) 2

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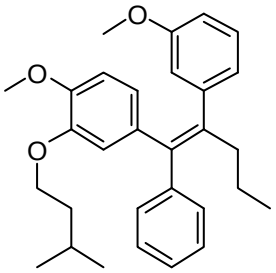
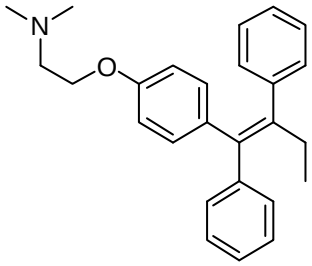
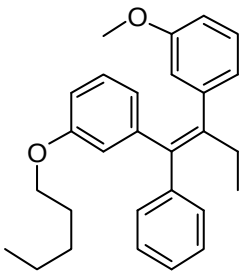
35. Indicate the **incorrect** statement concerning aromatic compounds:

A) π-bonds in aromatic systems are less reactive towards hydrogenation than those in linear mono, di and tri-alkenes.
B) Carbon, nitrogen and oxygen atoms that are part of an aromatic ring must contribute at least one π-electron to the aromatic system.
C) Aromatic systems are planar so as to allow maximum overlap between adjacent p-orbitals.
D) Aromatic systems involve a planar ring of sp^2-hybridized atoms with (4n + 2) π-electrons.
E) Cycloheptatriene can lose a hydrogen anion (hydride) to form an aromatic cation.

36. Determine the maximum size of the library that could be built based on the sites of diversity and substituents present in the three compounds below.







A) 16
B) 12
C) 22
D) 36
E) 44

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Student Name: _____ Student No: _____

Extra space for rough work.

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Student Name: _____ Student No: _____

General data and equations. Other data appear with the questions.

There is a periodic table on the next page.

STP = 273.15 K, 1 atm

R = 8.3145 J/K·mol = 0.08206 L·atm/K·mol

1 atm = 760 mm Hg = 101.325 kPa

1 J = 1 kg m^2 s^{-2} = 1 kPa·L = 1 Pa·m^3

1 cm^3 = 1 mL

$K_w = 1.0 \times 10^{-14}$

F = 96485 C/mol

$N_A = 6.022 \times 10^{23}$ mol^{-1}

0°C = 273.15 K

1 m = 10^9 nm = 10^{10} Å

1 g = 10^3 mg

$v_0 = k[A]^m[B]^n$	$v = \lim_{t \to 0} \frac{1}{g}\frac{\Delta[G]}{\Delta t} = \frac{1}{g}\frac{d[G]}{dt}$
$[A]_t = [A]_0 \bullet e^{-kt}$	$ln\frac{[A]_t}{[A]_0} = -kt$
$[A]_t = [A]_0 - kt$	$t_{1/2} = \frac{ln\,2}{k} = \frac{0.69}{k}$
$v_0 = k[A]^2$ or $k[A][B]$	$\frac{d[E \bullet S]}{dt} = 0$
$v_0 = \frac{k_{cat}[E]_0[S]}{K_M + [S]}$	$k = Ae^{-E_a/RT}$
$ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$	

Continued on next page…

Student Name: ______________________ Student No: ______________________

PERIODIC TABLE OF THE ELEMENTS

ALDRICH®

I 1	II 2	3	4	5	6	7	8	9	10	11	12	III 13	IV 14	V 15	VI 16	VII 17	VIII 18
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra 226.03	89 **Ac 227.03	104 Unq [261]	105 Unp [262]	106 Unh [263]												

Transition Metals (groups 3–12)

Atomic weights are based on ^{12}C = 12 and conform to the 1987 IUPAC report values rounded to 5 significant digits. Numbers in [ ] indicate the most stable isotope.

* Lanthanides	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
** Actinides	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]