

Name: \_\_\_\_\_

Student number: \_\_\_\_\_

**Chemistry 1AA3**

**Test 2**

**March 14, 2008**

**McMaster University**

**VERSION 1 ANSWERS & SOLUTIONS**

Instructors: P. Berti, P. Lock, J. Valliant

Duration: 120 minutes

This test contains 25 numbered pages printed on both sides. There are **30** multiple-choice questions appearing on pages numbered 3 to 21. Page 24 includes some useful data and equations. There is a periodic table on page 25. Page 22 & 23 may be used for rough work. You may tear off the last pages 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.

Questions 1 to 23 are each worth 2 marks, questions 24 – 30 are each worth 3 marks; the total marks available are 67. 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.

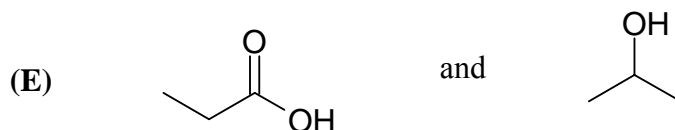
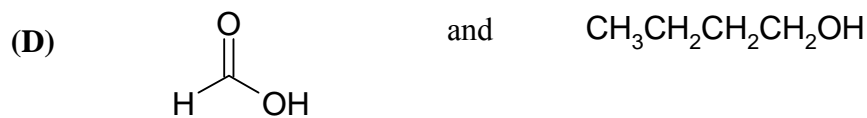
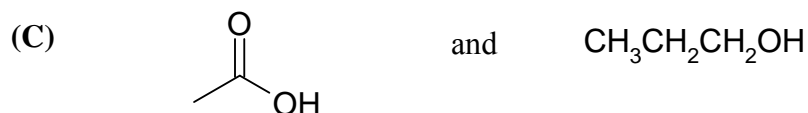
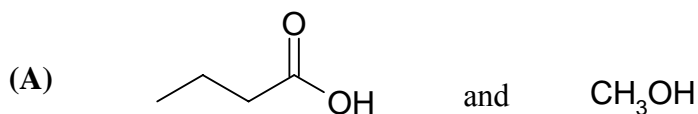
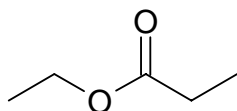
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**You are writing VERSION 1 of this test. Make sure you have correctly entered your version number ("1") in the correct column on your scan sheet (see p. 2 for details).**

**Questions 1 through 23 are worth two (2) marks each.**

- 1.** A reaction between **which two compounds**, in the presence of acid, yields the following product?



**ANS = (B)**

The product is an ester, which will result from the reaction of an alcohol with a carboxylic acid. The acid forms the root of the carboxylate group, and the alcohol becomes the substituent attached to the carboxylate, thus we need propanoic acid and ethanol.

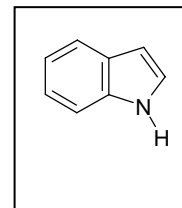
2. Which of the following statements is **FALSE**?

- (A) Hydrogenation of an alkene requires a catalyst because of the large bond energy of  $H_2$ .
- (B) The addition of HBr to 2-butene produces 1-bromobutene.
- (C) The charged carbon atom in a carbocation is  $sp^2$  hybridized.
- (D) PCC in  $CH_2Cl_2$  will oxidize *sec*-butanol to butanone.
- (E) Hydration of an alkene is favoured in the presence of dilute acid catalyst.

(A) TRUE. (B) FALSE – the reaction will follow Markovnikov's rule, to yield 2-bromobutane. (C) TRUE. (D) TRUE – PCC will accomplish one oxidation step (but not two). (E) TRUE.

3. The molecule shown below is indole. It is a planar molecule. Indicate the number of  **$sp^2$  and  $sp^3$  hybridized atoms**, the number of  **$\pi$  (pi) bonds** and the number of  **$\sigma$  (sigma) bonds**.

	$sp^2$	$sp^3$	$\pi$ bonds	$\sigma$ bonds
(A)	9	0	4	17
(B)	9	0	8	17
(C)	8	1	4	11
(D)	9	1	8	19
(E)	8	1	4	17



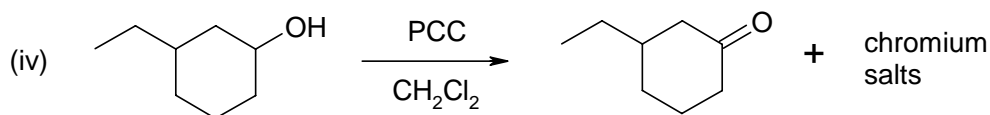
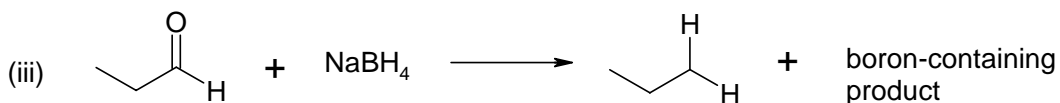
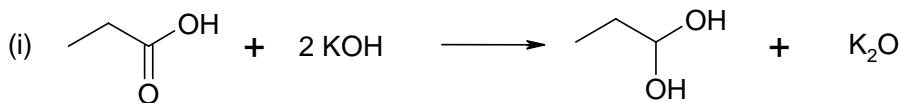
Since the molecule is planar, that tells us that all non-hydrogen atoms (8C + 1N) are  $sp^2$  hybridized. Completing the Lewis structure to show all H atoms will help show the correct  $\sigma$ -bond count.,

4. Which of the following statements is **not true** about pyridinium chlorochromate (PCC)?

- (A) It will oxidize benzyl alcohol to benzaldehyde
- (B) It is an electron acceptor
- (C) It can promote 2 electron oxidation reactions
- (D) It will convert ethanol to acetic acid
- (E) It is soluble in some organic solvents

PCC is a mild oxidizing agent – it will allow one step of 2-electron oxidation to occur (C), but not two oxidations. For example, it will convert a primary alcohol to an aldehyde (A), but not to a carboxylic acid (D). As an oxidizing agent, it gets reduced (B). It is typically used with  $CH_2Cl_2$  solvent.

5. Which of the following reactions is/are **CORRECTLY** formulated?



(A) i, iii

(B) i, ii

(C) ii, iii

(D) **ii, iv**

(E) iv

(i) FALSE – products will be potassium carboxylate salt and water.  
 (ii) Correct (similar to reaction of Na in water).  
 (iii) FALSE – end product will be primary alcohol, not alkane (after acid workup)  
 (iv) Correct. PCC can accomplish one step of oxidation (primary alcohol to aldehyde, or secondary alcohol to ketone).

6. The carbon-oxygen bond length in cyclopropanone is longer than for the same bond in acetone. **This can be explained by:**

(A) The differences in molecular weight between the two molecules.

(B) The differences in electronegativity between carbon and oxygen.

(C) **Bond angle (ring) strain.**

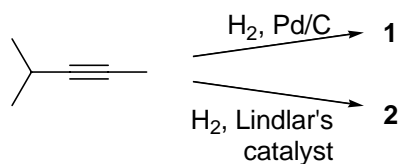
(D) *sp* hybridization at the carbon atom of the carbonyl group.

(E) Both (C) and (D).

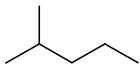
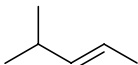
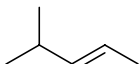
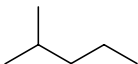
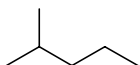
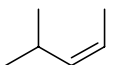
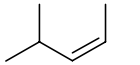
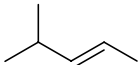
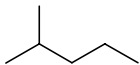
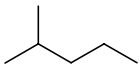
(A) There is little difference.  
 (B) Both molecules have the C=O double bond. (C) – see below.  
 (D) The hybridization is  $sp^2$ .

The cyclopropane ring experiences a great deal of ring strain, with angles close to  $60^\circ$  as compared to the ideal of  $109.5^\circ$  in a chain structure. The effect of the induced ring strain in the small ring structure will be to lengthen the corresponding carbonyl bond.

7. What would the **products** be of the following **hydrogenation reactions**?

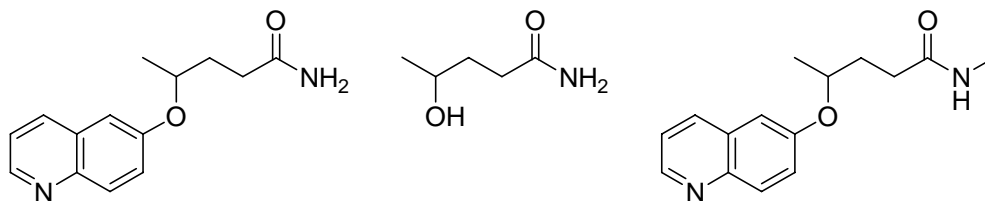


Compound 1    Compound 2

- (A)  
- (B)  
- (C)  
- (D)  
- (E)  

Reaction 1 will fully saturate the triple bond.  
(Product = alkane).  
Reaction 2 will selectively and partially  
saturate the triple bond. (Product = Z-alkene).

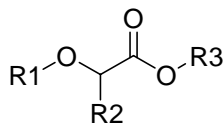
8. The following structures represent members of a combinatorial library of compounds. **How many sites of diversity** are represented here?



- (A) 0  
(B) 1  
(C) 2  
(D) 3  
(E) 4

The sites of diversity are as follows:  
(1) The amide nitrogen atom (H or methyl attached).  
(2) The oxygen of the alcohol group (alcohol or ring system attached).

9. A combinatorial library consists of 56 members. R1 = (every mono- and dibromoalkyl group with 1 or 2 carbons), and R2 = (H, OH). **How many different substituents at R3** are present in the library?



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

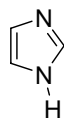
# substituents at R3 = 56 / (# at R1)(# at R2)  
# at R2 = 2 (H, OH)  
# at R3 = 7 (CH<sub>2</sub>Br, CHBr<sub>2</sub>, CBr<sub>2</sub>CH<sub>3</sub>,  
CHBrCH<sub>2</sub>Br, CH<sub>2</sub>CHBr<sub>2</sub>, CHBrCH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>Br)  
∴ # substituents at R3 = 56 / (2)(7) = 56/14 = 4

10. Chemical biology can be used to investigate biological phenomena and to find new candidates for the treatment of disease. **Key components** of a chemical biology program **include**:

- (A) Libraries of molecules  
(B) High throughput screening  
(C) Aromatic compounds  
(D) Homovanillyl alcohol  
(E) Both A and B

Refer to class notes. The specific example of an analogue for homovanillyl alcohol did involve the HVA compound, which was aromatic, however the general field of chemical biology is not restricted to these specifics. The field involves, however, tools such as high throughput screening in order to assay activity of large libraries of molecules.

11. Imidazole (shown below) is found in the amino acid histidine. Under normal conditions imidazole does not undergo an addition reaction with bromine.

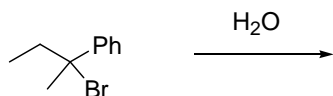


Which of the following statements is **TRUE** about imidazole?

- (A) It is aromatic.
- (B) The bond angles at all carbon atoms are  $109^\circ$ .
- (C) One nitrogen atom is  $sp^2$  hybridized and the other is  $sp^3$  hybridized.
- (D) Imidazole should be a reactive electrophile.
- (E) All answers are correct.

The information given is that imidazole does not undergo an addition reaction with bromine – in other words it does not react like an alkene. Thus its reactivity is special, like that of an aromatic. Answer (A) is TRUE. Given the idea that the molecule is aromatic, we can say then that the molecule is planar, and thus all non-hydrogen atoms are  $sp^2$  hybridized (bond angles not  $109^\circ$ ). Answers (B) and (C) are FALSE. Answer (D) cannot also be correct.

12. Which of the following statements about the reaction shown below is **TRUE**:



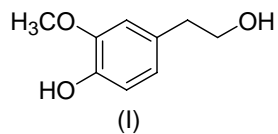
- (A) It should proceed via an  $S_N1$  mechanism.
- (B) It will result in the formation of a secondary alcohol.
- (C) The rate of the reaction will depend on both electrophile and nucleophile.
- (D) Reaction will result in a single organic product showing an inversion of configuration.
- (E) The reaction is likely zeroth order.

(A) is TRUE – a tertiary halide will undergo an  $S_N1$  reaction with water. A tertiary alcohol will result, thus (B) is FALSE. (C) is FALSE for  $S_N1$  (rate depends on [nucleophile] only). (D) is FALSE – we will see a mix of retention and inversion. (E) is also FALSE, as the reaction is first-order.

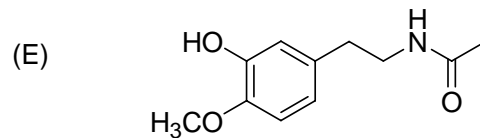
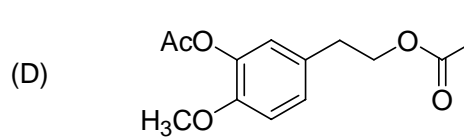
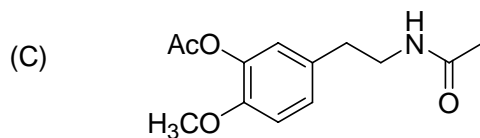
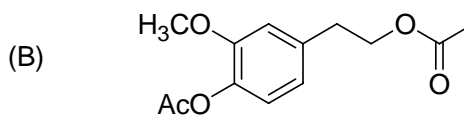
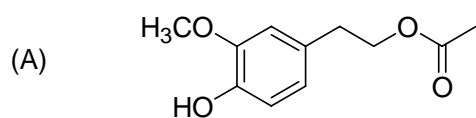
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13. Treatment of homovanillyl alcohol (I) with an excess of acetyl chloride will



produce **which of the following compounds?**

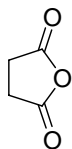


**ANS = B**

Excess acetyl chloride means we can expect to acetylate any possible site, thus both alcohol groups will be acetylated. Answer (B) shows this result.



14. The reaction of succinic anhydride (shown below) with methylamine, followed by



workup with dilute HCl, will produce **what functional groups?**

- (A) Ester and an acid
- (B) Ester and alkene
- (C) Amide and carboxylic acid
- (D) Two amides
- (E) Two carboxylic acids

The hydrolysis that occurs will open the ring in this case, as the anhydride is broken apart. The amine will attack to produce an amide, while the acid workup will protonate the opened up oxygen atom that remains, to generate a carboxylic acid.

15. Which of the following rate equations is/are **third order overall**?

(i) $v_0 = k[A]^3$	(ii) $v_0 = k[B]^3[C][D]^{-1}$
(iii) $v_0 = k[A]^3[B]$	(iv) $v_0 = k[A][B]^2$

Not responsible for this question

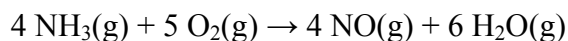
- (A) i, ii, iii
- (B) i, ii, iv
- (C) i
- (D) ii
- (E) i, iv

Overall order = sum of all individual reaction orders.

- (i) Third order.
- (ii) Third order.
- (iii) Fourth order.
- (iv) Third order.

16. In the following reaction,  $\Delta[O_2]/\Delta t = -0.45 \text{ M/s}$  over the first 10 s of the reaction.

What is the **average reaction rate in that time?**



Not responsible for this question

- (A) 0.09 M/s
- (B)  $0.09 \text{ s}^{-1}$
- (C) -0.45 M/s
- (D) 0.45 M/s
- (E) 0.85 M/s

Average rate can be expressed as loss of any reactant or appearance of any product, including stoichiometry.

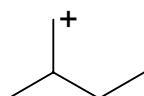
$$\text{Here, Rate} = -\frac{1}{5} \frac{\Delta[O_2]}{\Delta t} = -\frac{1}{4} \frac{\Delta[NH_3]}{\Delta t} = +\frac{1}{4} \frac{\Delta[NO]}{\Delta t} = +\frac{1}{6} \frac{\Delta[H_2O]}{\Delta t}$$

$$\text{Thus Rate} = -\frac{1}{5} \frac{\Delta[O_2]}{\Delta t} \text{ or Rate}(5) = -\Delta[O_2]/\Delta t = -0.45 \text{ M/s}$$

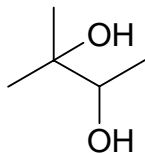
$$\text{Rate} = (-0.45 \text{ M/s}) / 5 = 0.09 \text{ M/s}$$

Questions 24 to 30 are worth three (3) marks each.

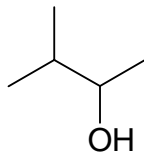
24. In the hydration of 2-methyl-2-butene in the presence of dilute acid, which of the following species (in no particular order) would be the **expected intermediate(s)** and **product(s)** of this reaction?



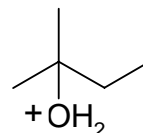
(i)



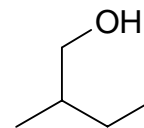
(ii)



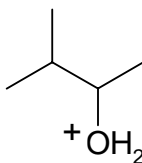
(iii)



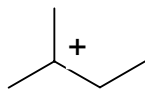
(iv)



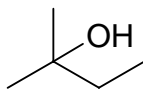
(v)



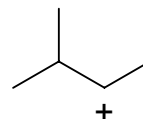
(vi)



(vii)



(viii)



(ix)

(A) i, v

(B) ii, iv, vii

(C) iii, vi, ix

(D) iv, vii, viii

(E) iii, iv, vi, vii, viii, ix

This addition reaction will follow Markovnikov's rule (make the most stable carbocation). The reaction proceeds such that the expected intermediates are first addition of a proton to yield a carbocation (vii), followed by addition of water to yield a protonated alcohol (iv), then deprotonation yields the final alcohol product (viii).

**25.** The high throughput screening assay described in the course notes depends on several assumptions for it to be valid. **Which of the following assumptions must be true** for the high throughput assay to be a valid test of HVA-like activities?

- (i) That all insects use HVA to control memories.
- (ii) That HVA does not directly suppress cAMP production independent of its effect on [dopamine] in the cells.
- (iii) That suppression of bad memories is the main function of HVA, and not a side effect.
- (iv) That neural cells in culture respond in the same way as they do in the bee.
- (v) That the HVA-like test compounds be aromatic.

(A) i, v

(B) ii

(C) i, iii

(D) iii, iv

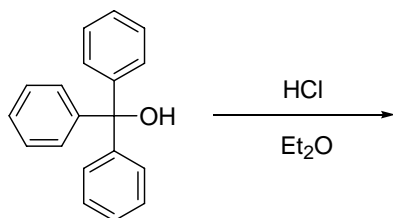
(E) ii, iv

Refer to class notes.

The assay relies upon bee neural cells to reproduce the physiological phenomenon, so (iv) must be TRUE. The assay also assumes that the effect of the HVA is to suppress cAMP production *because* it suppresses the concentration of dopamine, so (ii) is TRUE.

The assay is focused on bee neural cells, so (A) is not relevant. Whether the effect is principal or a side effect is not what the assay is probing, so (C) is not necessarily true. The key structural features for activity are not known, so (E) does not have to be true.

26. Consider the reaction shown below where triphenylmethanol is dissolved in ether containing HCl (ethereal HCl). Which of the following statements about the reaction is **TRUE**?

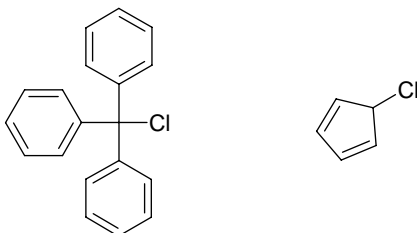


- (A) The reaction will likely proceed via an S<sub>N</sub>1 mechanism.
- (B) The reaction will likely proceed via an S<sub>N</sub>2 mechanism.
- (C) One of the products of the reaction will be triphenylmethane.
- (D) The reaction involves only one transition state.
- (E) The product of the reaction will contain a non-conjugated alkene.

The reactant is a tertiary alcohol, so any substitution will be S<sub>N</sub>1. In the presence of acid the OH group will be protonated, and can then leave as water, generating a carbocation. The remaining Cl<sup>-</sup> ion will then attack the cation to produce a tertiary chloride.

(A) is TRUE, and (B) is therefore FALSE. (C) and (E) are also FALSE – an alkane will not be produced. (D) is FALSE, as 2 steps are involved, thus 2 transition states.

27. When triphenylmethylchloride (shown below) is treated with  $\text{Ag(I)}$  ions in water, the reaction proceeds quickly to the corresponding tertiary alcohol and  $\text{AgCl}_{(s)}$ . The silver ion acts by combining with and precipitating  $\text{Cl}^-$  formed in the reaction. When 5-chloro-1,3-cyclopentadiene (shown below) is reacted with  $\text{Ag(I)}$  ions in water, the reaction is much slower. **The slower reaction rate can be explained by:**



- (A) The differences in molecular weight between the electrophiles.  
(B) The formation of an intermediate that is not aromatic.  
(C) Le Chatelier's principle.  
(D) The need for an inversion of configuration.  
(E) The reversibility of the reaction.

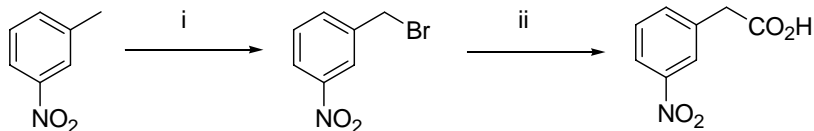
The reactions in question are substitution reactions. The presence of  $\text{Ag(I)}$  ions promotes the formation of cations, indicating an  $\text{S}_{\text{N}}1$  mechanism. The rate-determining step of the  $\text{S}_{\text{N}}1$  mechanism is the formation of the carbocation.

Thus, answers (C) and (E) do not apply, as the rate-determining step is not at equilibrium. Answer (D) does not apply, as with  $\text{S}_{\text{N}}1$  we will have a mixture of inversion and retention of configuration.

Answer (A) does not apply, as molecular weight itself does not determine carbocation stability. Rather, the carbocation stability can be determined by thinking about structure.

The chlorocyclopentadiene reagent will form a carbocation that is antiaromatic ( $4 \pi$  electrons). Since we know that formation of an aromatic is favoured, it follows by analogy that formation of an antiaromatic species is disfavoured. Of the available choices, this one provides the best explanation.

**28.** Fill in the **correct combination of reagents** to accomplish the following synthesis.



- (A) i)  $\text{H}_2$ , Pd/C                      ii)  $\text{HCl(aq)}$   
(B) i)  $\text{Br}_2$ , light                      ii) PCC,  $\text{CH}_2\text{Cl}_2$   
(C) i)  $\text{Br}_2$ , heat                      ii) AcOH then HCl  
(D) i)  $\text{Br}_2$ , light                      ii) Mg followed by  $\text{CO}_2(\text{s})$  then HCl  
(E) i) HBr                      ii) Mg followed by  $\text{CO}_2(\text{s})$  then HCl

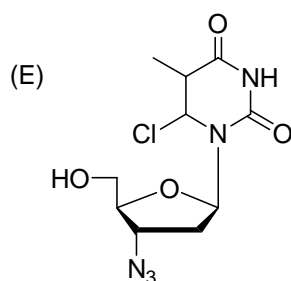
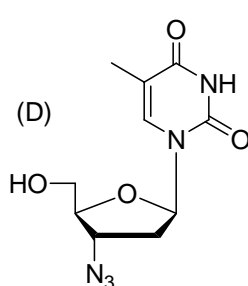
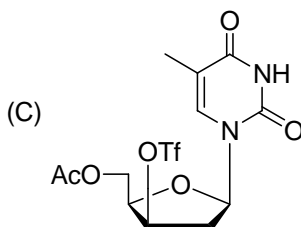
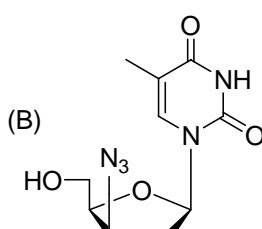
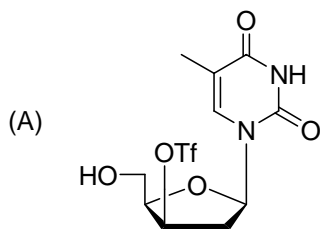
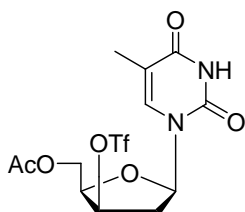
The first reaction requires introduction of Br at an alkyl substituent. The radical halogenation reaction is required:  $\text{Br}_2$  in the presence of light or heat. This eliminates answers (A) and (E).

The second reaction requires formation of a C-C bond. Our sole strategy for this is the use of a Grignard reagent. This eliminates answers (A), (B) and (C).

**29.** Sodium azide ( $\text{NaN}_3$ ) is a good nucleophile that tends to react by an  $\text{S}_{\text{N}}2$  process.

When the nucleotide shown below is treated with sodium azide, followed by a further reaction in  $\text{HCl}(\text{aq})$ , with heat, **the product will be:**

(where  $\text{OTf} = \text{OSO}_2\text{CF}_3$ , triflate)



**ANS = D**

The first reaction is an  $\text{S}_{\text{N}}2$  mechanism, so the product will show inversion of stereochemistry. This eliminates answers (A), (B) and (C).

The second reaction will hydrolyze the acetyl ester, but do no further reaction (e.g.,  $\text{HCl}$  will not add to the double bond in the upper ring, as the ring is aromatic. If the ring were not aromatic, then  $\text{HCl}$  addition could occur, but it would still follow Markovnikov's rule, which is not shown in (E).

The correct answer is (D).

Name: \_\_\_\_\_

Student number: \_\_\_\_\_

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

**A periodic table is provided on the next page.**

STP = 273.15 K, 1 atm

$R = 8.3145 \text{ J/K}\cdot\text{mol} = 0.08206 \text{ L}\cdot\text{atm/K}\cdot\text{mol}$

1 atm = 760 mm Hg = 101.325 kPa

$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ kPa}\cdot\text{L} = 1 \text{ Pa}\cdot\text{m}^3$

$1 \text{ cm}^3 = 1 \text{ mL}$

$F = 96485 \text{ C/mol}$

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

$0^\circ\text{C} = 273.15 \text{ K}$

$1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ \AA}$

$1 \text{ g} = 10^3 \text{ mg}$

average rate = $-\frac{1}{a} \frac{\Delta[A]}{\Delta t} = \dots = \frac{1}{g} \frac{\Delta[G]}{\Delta t} \dots$	$v = \lim_{t \rightarrow 0} \frac{1}{g} \frac{\Delta[G]}{\Delta t} = \frac{1}{g} \frac{d[G]}{dt}$
$v_0 = k[A]^m[B]^n$	$\ln \frac{[A]_t}{[A]_0} = -kt$
$[A]_t = [A]_0 \cdot e^{-kt}$	$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$
$[A]_t = [A]_0 - kt$	$v_0 = k[A]^2 \text{ or } k[A][B]$