NAME:_____ Section:_____ Student Number:_____

Spring 2020 **Chemistry 2500 Midterm #2A** ____/ 60 marks

INSTRUCTIONS:

1) Please read over the test carefully before beginning. You should have 8 pages of questions and a data/periodic table sheet.
2) Unless otherwise stated in the question, explain all of your answers fully. Use diagrams where appropriate. When invoking any argument based on resonance, you must draw all relevant resonance structures.
3) ALL structures must be drawn showing lone pairs, non-zero formal charges and reasonable bond angles – regardless of whether they are expanded, condensed or line-bond. Marks will be deducted for poorly drawn structures.
4) Marks will be deducted for incorrect information added to an otherwise correct answer.
5) If your work is not legible, it will be given a mark of zero.
6) Calculators are not allowed. You are not permitted to have any electronic devices with you during the exam unless authorized by the instructor.
7) You may use a molecular model kit.
8) You have 2 hours to complete this test.

Confidentiality Agreement:

I agree not to discuss (or in any other way divulge) the contents of this exam with (or in the presence of) any student who has not written it until after 5:00 pm Mountain Time on Monday, March 16th, 2020 (the Monday after the official date of the test). I understand that breaking this agreement would constitute academic misconduct, a serious offense with serious consequences. The minimum punishment would be a mark of 0/60 on this exam and removal of the "overwrite midterm mark with final exam mark" option for my grade in this course; the maximum punishment would include expulsion from this university.

Signature: _____ Date: _____

Course: CHEM 2500 (Organic Chemistry I)
Semester: Spring 2020
The University of Lethbridge

Question Breakdown

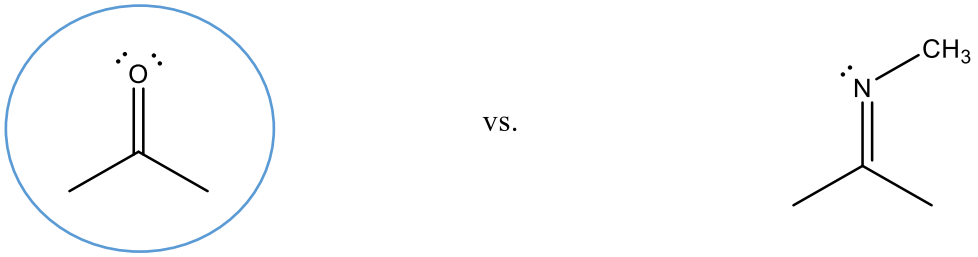
Q1	/ 4
Q2	/ 4
Q3	/ 4
Q4	/ 4
Q5	/ 5
Q6	/ 10
Q7	/ 10
Q8	/ 8
Q9	/ 6
Q10	/ 5

Total	/ 60

NAME:_____ Section:_____ Student Number:_____

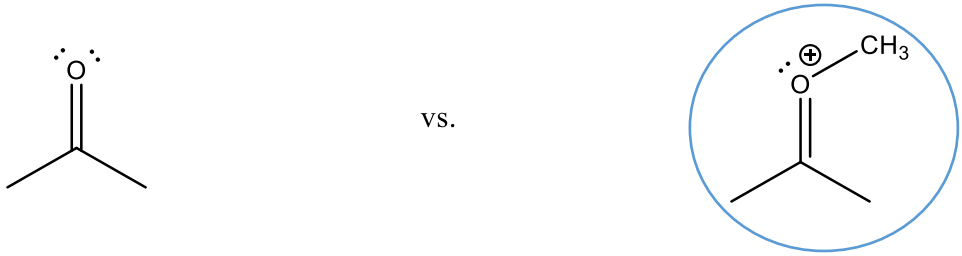
1. For each of the pairs of molecules below, circle the better electrophile and briefly explain your choice. Your explanations must make it clear that you know what the term electrophile means. **[4 marks]**

(a)



Oxygen is more electronegative than nitrogen. As such, the carbon atom attached to oxygen bears a greater partial positive charge than the carbon atom attached to nitrogen. That makes the carbonyl carbon a better electron pair acceptor than the imine carbon.

(b)



The oxygen atom with the positive charge pulls more electron density away from the carbonyl carbon than the neutral oxygen atom does. That makes the carbon atom of the methylated carbonyl group a better electron pair acceptor than the carbon of the neutral carbonyl group.

Several students drew the other resonance structure for the cation in which the pi bonding electrons have shifted onto the oxygen as a lone pair, leaving the carbon atom electron deficient (only 6 electrons instead of a complete octet) and bearing a positive charge. That was an excellent way to illustrate this point.

2. For each of the pairs of molecules below, circle the better nucleophile and briefly explain your choice. Your explanations must make it clear that you know what the term nucleophile means. **[4 marks]**

(a) CH_3OH vs. $CH_3O^{\ominus}$

The negative charge on the oxygen atom in methoxide makes it more electron rich than the oxygen atom in methanol. As such, it is a better electron pair donor.

(b) CH_3OH vs. CH_3NH_2

Nitrogen is less electronegative than oxygen. As such, a neutral nitrogen atom holds onto its electrons less strongly than a neutral oxygen atom, and the amine is a better electron pair donor than the alcohol.

Many students referenced the number of lone pairs in their answers to question 2. The number of lone pairs is irrelevant. A nucleophile is only donating one pair of electrons; what matters is how tightly it's holding onto those electrons.

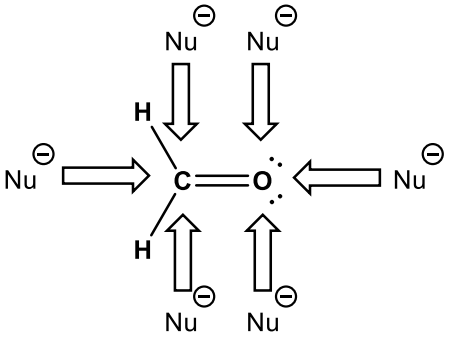
NAME:_____ Section:_____ Student Number:_____

3. **[4 marks]**

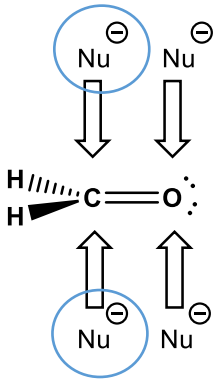
(a) The drawings below show nucleophiles moving toward an aldehyde from different directions. Assuming each nucleophile continues along its current path, circle all of the nucleophiles that would be able to react with the aldehyde when they hit it. *[2 marks]*

Please make the simplifying assumption that the aldehyde is not moving.

Marks will be deducted for incorrect circles.



top view of aldehyde



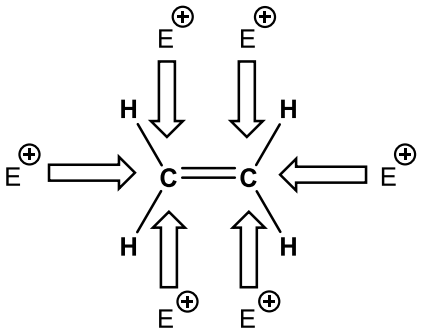
side view of aldehyde

A nucleophile always attacks the carbon of a carbonyl group (never the oxygen).
Because the reacting MO of the carbonyl is the π^* MO (which has its lobes above and below the plane of the molecule), the nucleophile must approach the carbonyl from above or below the plane of the molecule.

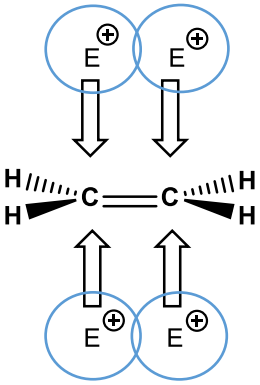
(b) The drawings below show electrophiles moving toward an alkene from different directions. Assuming each electrophile continues along its current path, circle all of the electrophiles that would be able to react with the alkene when they hit it. *[2 marks]*

Please make the simplifying assumption that the alkene is not moving.

Marks will be deducted for incorrect circles.



top view of alkene



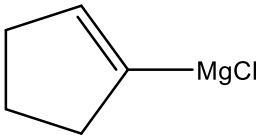
side view of alkene

Because the reacting MO of the alkene is the π MO (which has its lobes above and below the plane of the molecule), the electrophile must approach the alkene from above or below the plane of the molecule.

NAME:_____ Section:_____ Student Number:_____

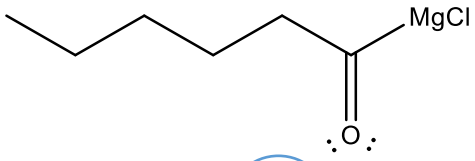
4. Under each potential Grignard reagent, circle "yes" or "no" to indicate whether or not it could be prepared. **[4 marks]**

(a)



yes / no

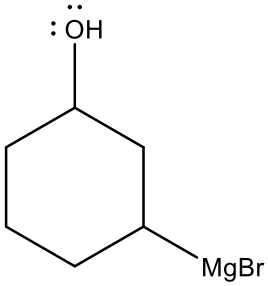
(b)



yes / no

Can't make Grignard in presence of carbonyl.

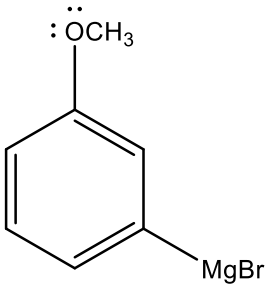
(c)



yes / no

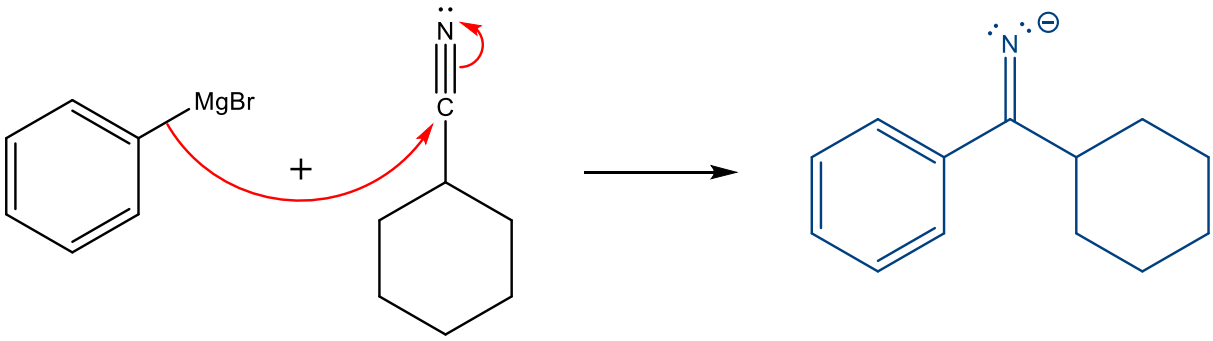
Can't make Grignard in presence of acidic hydrogen (OH).

(d)

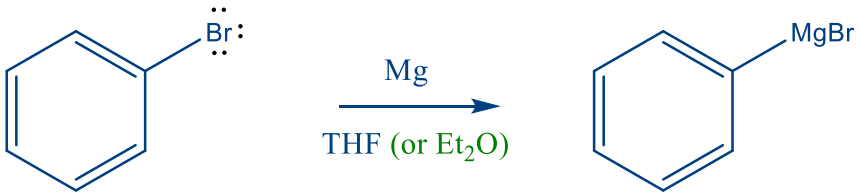


yes / no

5. Consider the reaction below: **[5 marks]**



(a) Briefly describe how you would prepare the Grignard reagent shown above. Your answer should be a reaction equation including all essential information. *[3 marks]*



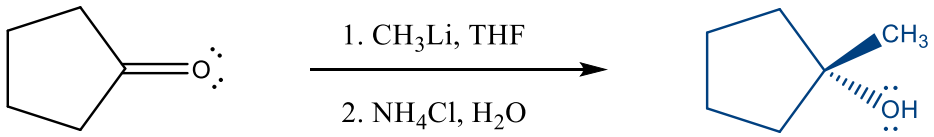
(b) Complete the diagram for this reaction by adding curved arrows to show electron movement and drawing the product. Do **NOT** assume any work-up steps that are not shown. *[2 marks]*

Answer directly on the diagram above.

NAME:_____ Section:_____ Student Number:_____

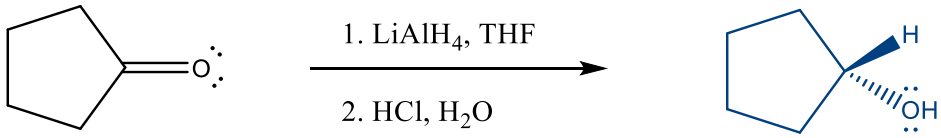
6. Draw the major organic product of each of the following reactions. Clearly show any relevant stereochemistry. If a mixture of enantiomers is formed, write "racemic" next to the product. *These are all reactions in which a nucleophile attacks an electrophilic carbonyl (chapter 7).* **[10 marks]**

(a)



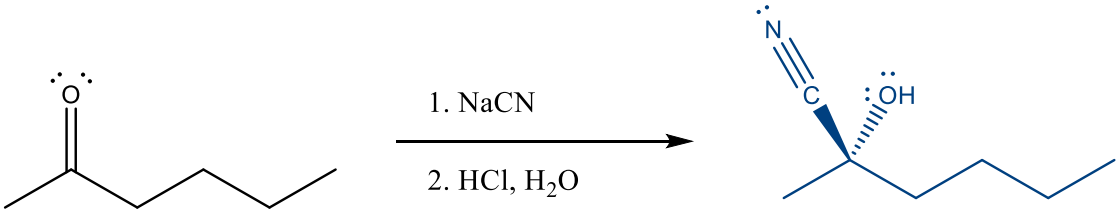
product not chiral

(b)



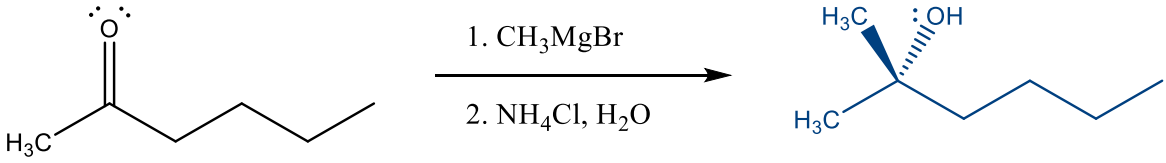
product not chiral

(c)



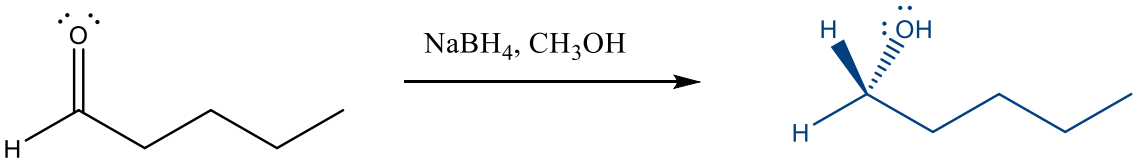
racemic

(d)



product not chiral

(e)

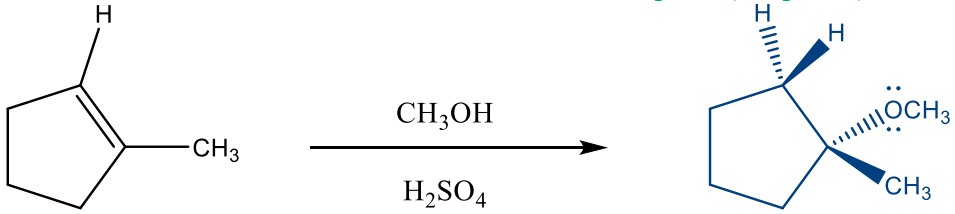


product not chiral

NAME:_____ Section:_____ Student Number:_____

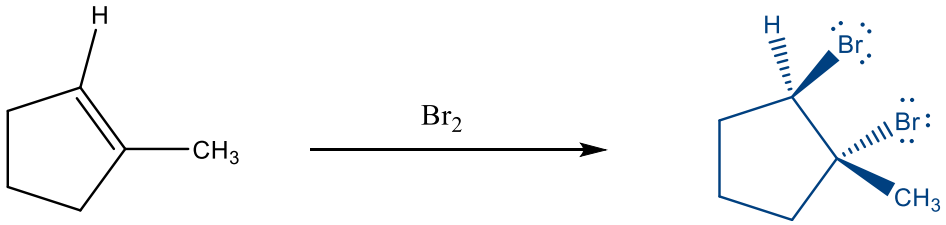
7. Draw the major organic product of each of the following reactions. Clearly show any relevant stereochemistry. If a mixture of enantiomers is formed, write "racemic" next to the product. *These are all reactions in which an alkene acts as a nucleophile (chapter 8).* **[10 marks]**

(a)



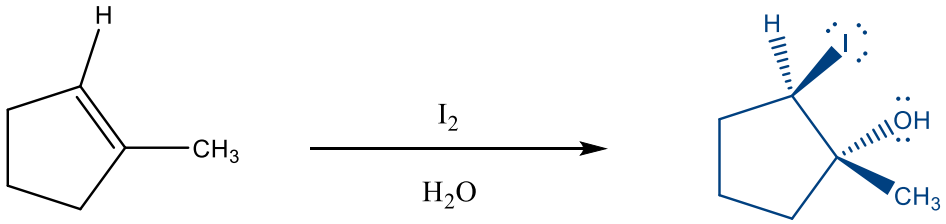
Markovnikov addition; product not chiral

(b)



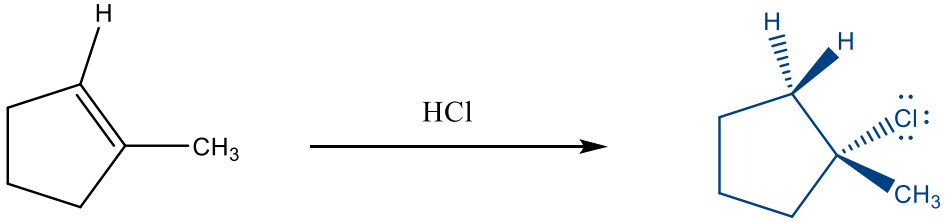
anti addition therefore Br atoms must be trans to each other racemic

(c)



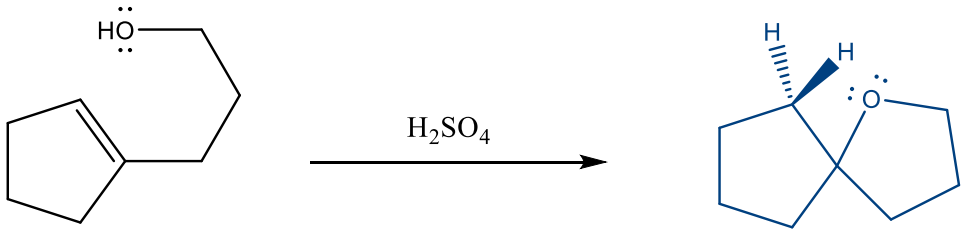
*Markovnikov addition *and* anti addition* racemic

(d)



Markovnikov addition; product not chiral

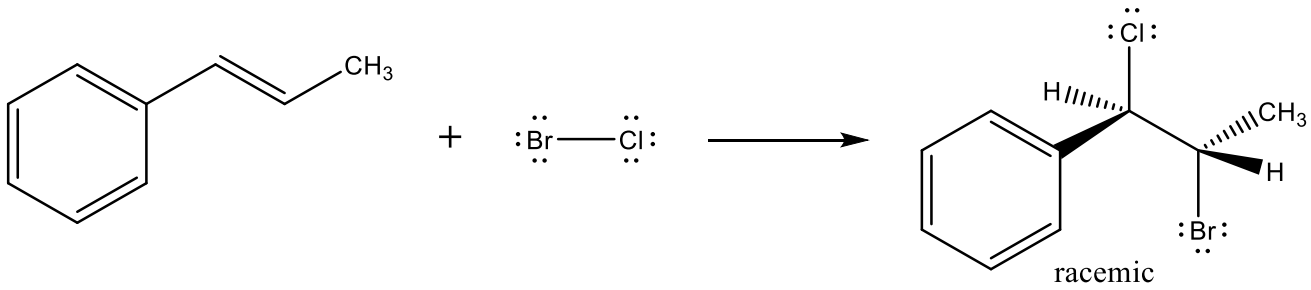
(e)



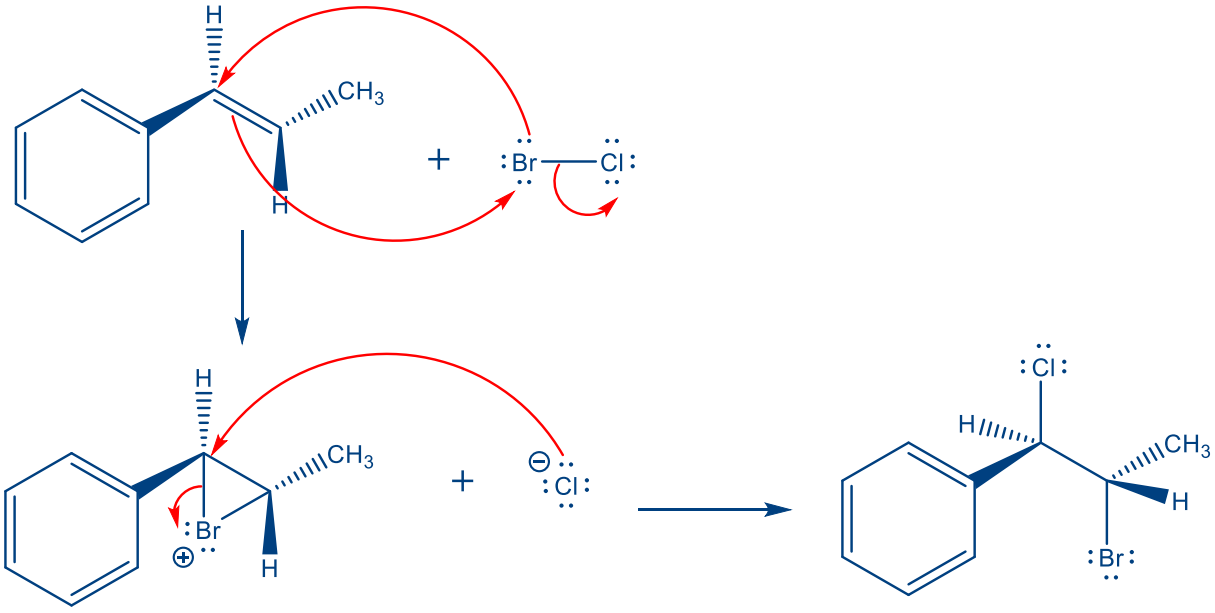
Markovnikov addition; product not chiral

NAME:_____ Section:_____ Student Number:_____

8. Consider the reaction below: **[8 marks]**



(a) Draw a mechanism for this reaction. *[3 marks]*



(b) Explain the regioselectivity of this reaction. In other words, why does each halogen atom wind up attached to the particular carbon atom shown? *[3 marks]*

The electrophile is Br-Cl. Bromine is less electronegative than chlorine, so it's the positive end of the electrophile. As such, the alkene attacks the bromine atom, kicking out chloride as a leaving group.

The chloride then acts as a nucleophile, and nucleophiles attack bromonium ions at the more positive carbon atom (i.e. the one corresponding to the better of the two carbocations which can be drawn as resonance structures of the bromonium). In this case both carbon atoms are secondary; however, the carbon next to the benzene ring would give a resonance-stabilized carbocation so it is the carbon atom which is attacked by the chloride nucleophile.

(c) Explain the stereospecificity of this reaction. In other words, why is only one diastereomer of product formed? *[2 marks]*

This is an anti addition, meaning that the chlorine and bromine atom add to opposite faces of the alkene. This is a result of the bromonium ion intermediate. The chloride ion can only attack the bromonium ion on the opposite face to the bromine atom.

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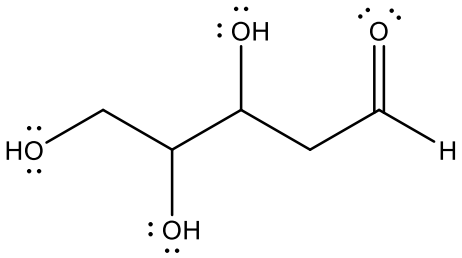
9. The linear form of deoxyribose is shown below. **[6 marks]**



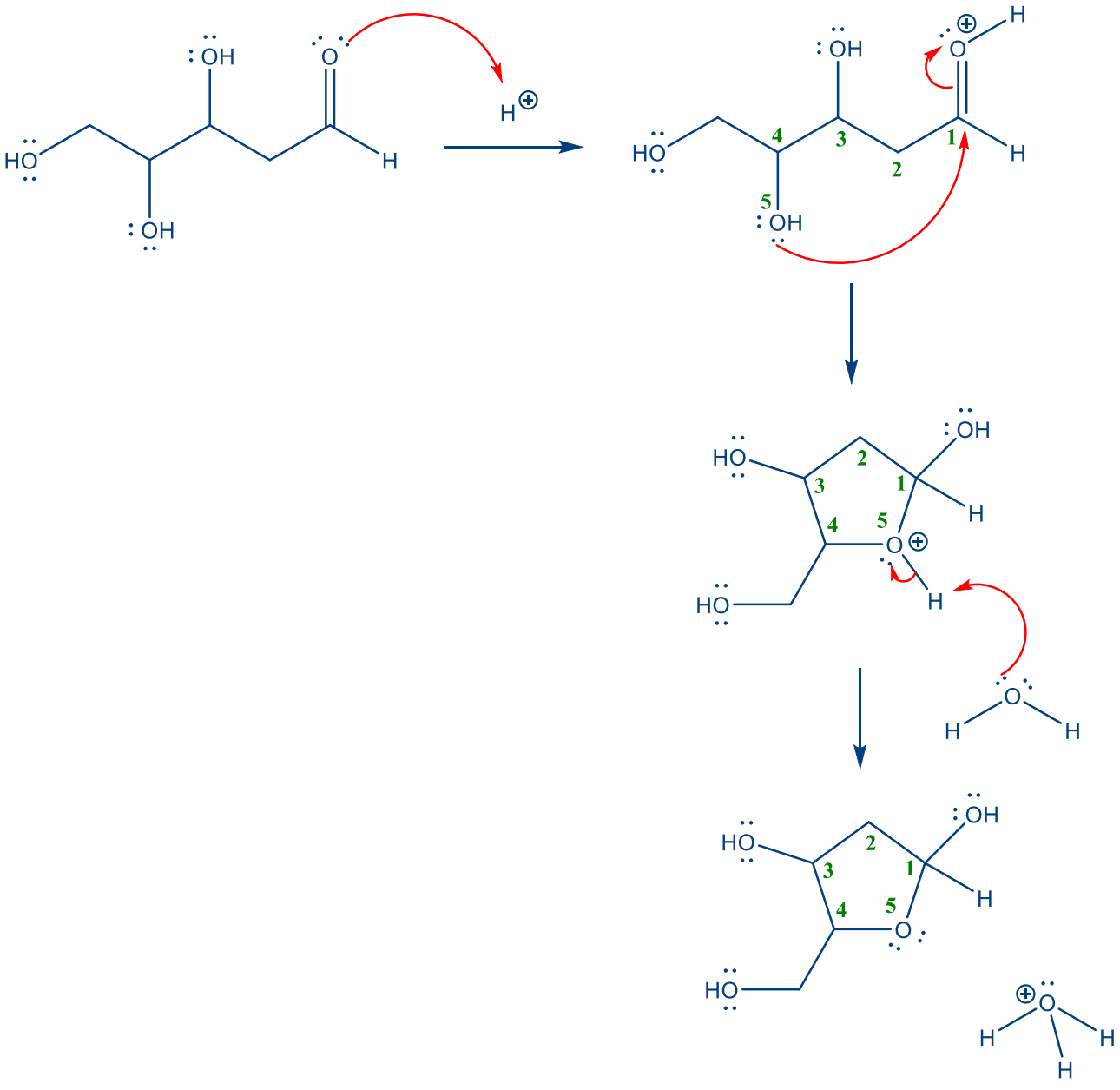
Deoxyribose exists primarily in the furanose form (hemiacetal with 5-atom ring).

Draw a mechanism showing the acid-catalyzed reaction in which linear deoxyribose is converted to the furanose form.

You may assume the presence of as much H_3O^+ and H_2O as your mechanism requires.

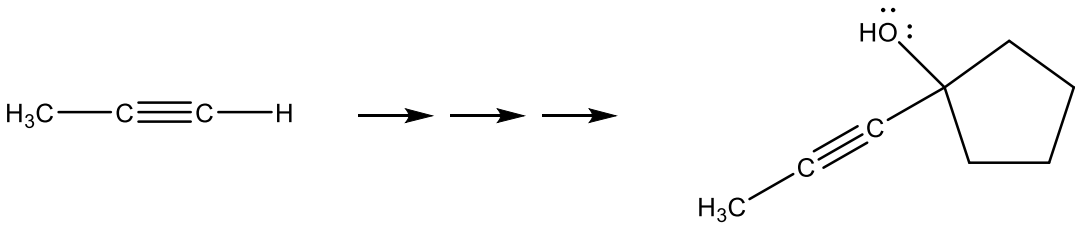
You do NOT need to show stereochemistry.

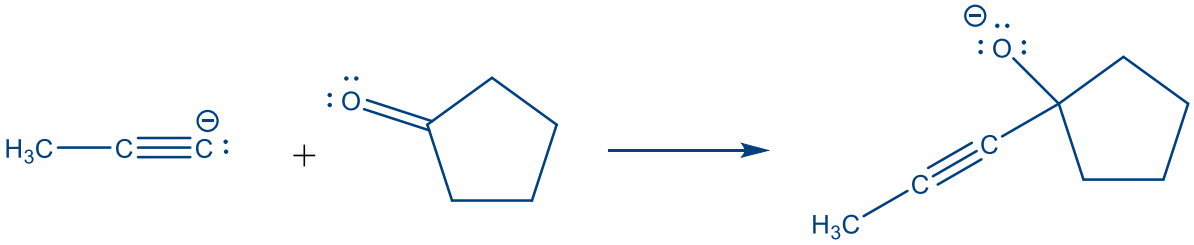
A hemiacetal contains a carbon atom with both -OH and -OR attached.

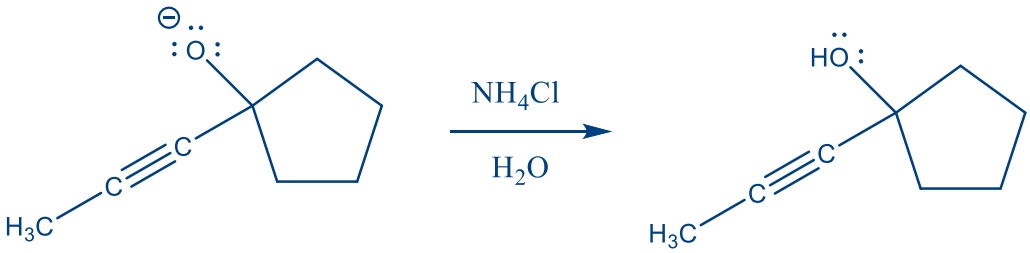


NAME:_____ Section:_____ Student Number:_____

10. Show how the alcohol below can be prepared starting with propyne (also shown below). *Your answer should be a series of reaction equations. Please show the product of each step. You do **not** need to include mechanisms; however, there will be no penalty for adding them if they help you think.* **[5 marks]**







The three arrows were not intended to communicate that three steps were required; they simply meant that multiple steps were required. It was a coincidence that the synthesis could be written as three steps.

The pKa of the terminal alkyne is approximately 25, so you have to choose a base that is strong enough to deprotonate it. Good choices included NaH, $NaNH_2$, any Grignard reagent or any alkyllithium reagent. Hydroxides and alkoxides are not strong enough bases.

Any mildly acidic aqueous solution was acceptable for the work-up. $NH_4Cl_{(aq)}$ is simply one example.

NAME:_____ Section:_____ Student Number:_____

Some Useful Data

Principal Functional Group Priority List

Carboxylic acid
Sulfonic acid
Ester
Acid chloride
Amide
Nitrile
Aldehyde
Ketone
Alcohol
Thiol
Amine

Chem 1000 Standard Periodic Table

1																	18
1.0079 **H** 1	2											13	14	15	16	17	4.0026 **He** 2
6.941 **Li** 3	9.0122 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.0067 **N** 7	15.9994 **O** 8	18.9984 **F** 9	20.1797 **Ne** 10
22.9898 **Na** 11	24.3050 **Mg** 12	3	4	5	6	7	8	9	10	11	12	26.9815 **Al** 13	28.0855 **Si** 14	30.9738 **P** 15	32.066 **S** 16	35.4527 **Cl** 17	39.948 **Ar** 18
39.0983 **K** 19	40.078 **Ca** 20	44.9559 **Sc** 21	47.88 **Ti** 22	50.9415 **V** 23	51.9961 **Cr** 24	54.9380 **Mn** 25	55.847 **Fe** 26	58.9332 **Co** 27	58.693 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.9216 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
85.4678 **Rb** 37	87.62 **Sr** 38	88.9059 **Y** 39	91.224 **Zr** 40	92.9064 **Nb** 41	95.94 **Mo** 42	(98) **Tc** 43	101.07 **Ru** 44	102.906 **Rh** 45	106.42 **Pd** 46	107.868 **Ag** 47	112.411 **Cd** 48	114.82 **In** 49	118.710 **Sn** 50	121.757 **Sb** 51	127.60 **Te** 52	126.905 **I** 53	131.29 **Xe** 54
132.905 **Cs** 55	137.327 **Ba** 56	**La-Lu**	178.49 **Hf** 72	180.948 **Ta** 73	183.85 **W** 74	186.207 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.967 **Au** 79	200.59 **Hg** 80	204.383 **Tl** 81	207.19 **Pb** 82	208.980 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
(223) **Fr** 87	226.025 **Ra** 88	**Ac-Lr**	(265) **Rf** 104	(268) **Db** 105	(271) **Sg** 106	(270) **Bh** 107	(277) **Hs** 108	(276) **Mt** 109	(281) **Ds** 110	(280) **Rg** 111	(285) **Cn** 112	(284) **Nh** 113	(289) **Fl** 114	(288) **Mc** 115	(293) **Lv** 116	(294) **Ts** 117	(294) **Og** 118

138.906 **La** 57	140.115 **Ce** 58	140.908 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.965 **Eu** 63	157.25 **Gd** 64	158.925 **Tb** 65	162.50 **Dy** 66	164.930 **Ho** 67	167.26 **Er** 68	168.934 **Tm** 69	173.04 **Yb** 70	174.967 **Lu** 71
227.028 **Ac** 89	232.038 **Th** 90	231.036 **Pa** 91	238.029 **U** 92	237.048 **Np** 93	(240) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(262) **Lr** 103

Developed by Prof. R. T. Boeré (updated 2016)