

Name

Student Number

03-59-3310/3315

Midterm 1

27/02/19 (60 min)

Fill out your name on each page. Make sure all pages are handed in at the end.

**Hint: There are questions of varying difficulty. Read through the exam and answer the easy ones first!**

The distribution of marks for the questions is approximate, and may change. You may use the back of any page for additional space or rough work.

Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18	
1 H 1.0078																		2 He 4.0026
3 Li 6.938	4 Be 9.012											5 B 10.806	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 28.085	15 P 30.974	16 S 32.059	17 Cl 35.45	18 Ar 39.948	
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.922	34 Se 78.971	35 Br 79.904	36 Kr 83.798	
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.95	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 1.008	
55 Cs 132.91	56 Ba 137.33		72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	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 -	85 At -	86 Rn -	
87 Fr -	88 Ra -		104 Rf -	105 Db -	106 Sg -	107 Bh -	108 Hs -	109 Mt -	110 Ds -	111 Rg -	112 Cn -	113 Nh -	114 Fl -	115 Mc -	116 Lv -	117 Ts -	118 Og -	
			57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 144.91	62 Sm 150.36	63 Eu 151.96	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 173.05	71 Lu 174.97	
			89 Ac -	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np -	94 Pu -	95 Am -	96 Cm -	97 Bk -	98 Cf -	99 Es -	100 Fm -	101 Md -	102 No -	103 Lr -	

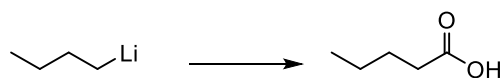
Name: \_\_\_\_\_

1. Quick fire round! [2 marks] each, unless otherwise stated

a) Which halide will form a Grignard reagent faster, 1-chloropropane or 1-iodopropane? BRIEFLY explain why.

b) Name a method for making an organometallic reagent, OTHER than a Grignard. [1 mark]

c) What reagent(s) would you use for this transformation?



d) BRIEFLY describe the characteristics of a “hard” nucleophile

e) Suggest a reagent for the reduction of a carboxylic acid to a primary alcohol. [1 mark]

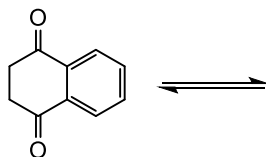
f) In the Felkin-Anh model, the major conformer (conformational isomer) of the substrate is the one that reacts. [1 mark]

TRUE or FALSE

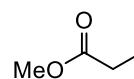
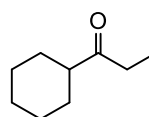
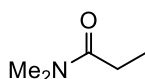
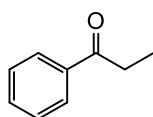
g) The largest coefficient in the HOMO of an enolate is on which atom?

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- h) Draw all the enol forms of the following molecule. Which do you expect to be the major tautomer that this molecule exists in? BRIEFLY explain why.

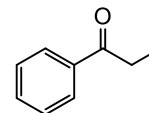


- i) Rank the following enolisable compounds in order of DECREASING acidity (*i.e.* increasing  $pK_a$ )



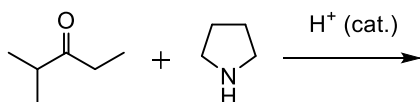
- j) The *thermodynamic product* of a reaction is the lowest energy product of a reaction. BRIEFLY explain what a kinetic product is and why it forms.

- k) The following ketone can form either a *cis* or a *trans* enolate, depending on the conditions/reagents chosen. What conditions/reagents would you use to selectively form the *trans* enolate?



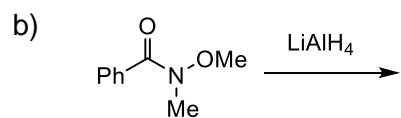
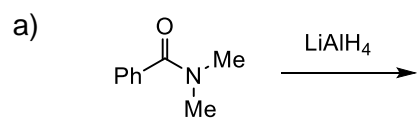
- l) What are TWO possible problems with alkylation of a standard enolate?

- m) Draw the enamine that you would expect to be the major product in this reaction:



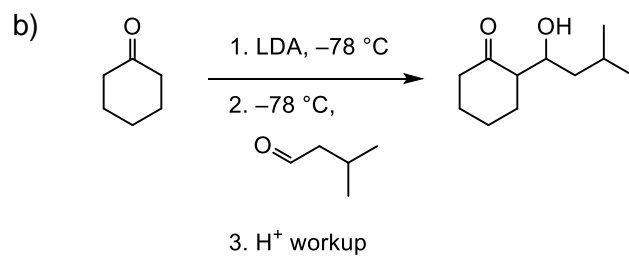
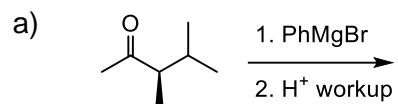
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2. When these two amides are subjected to  $\text{LiAlH}_4$ , two different products are formed. Predict the product of each reaction and draw a mechanism for its formation. [5 marks each]  
**Explain the difference in reactivity!**



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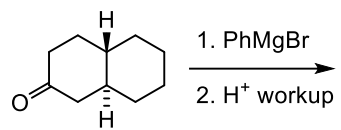
3. Hopefully you saw this one coming... [5 marks each]  
Predict the stereochemistry of the products of the following reactions with the aid of a mechanism and appropriate 3D conformations *etc.*



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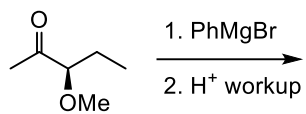
c) Answer **EITHER i) or ii)**

i)



**OR**

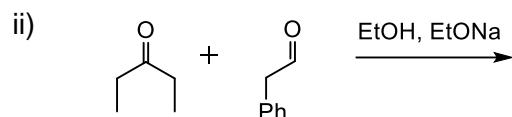
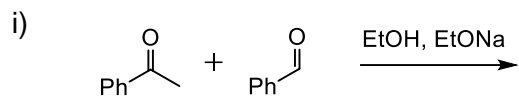
ii)



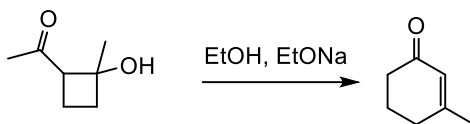
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4.

a) Predict the product formed in each of the following reactions, each of which only yield one major product. Mechanisms not required (just this once). Explain the selectivity/control (if there is any). [5 marks]



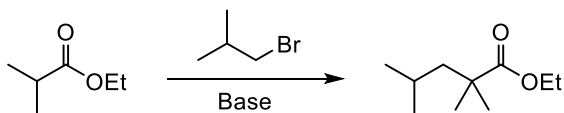
b) Provide a mechanism for this reaction. Explain the driving force(s) for the reaction. [5 marks]



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

5.

a) Consider this reaction:

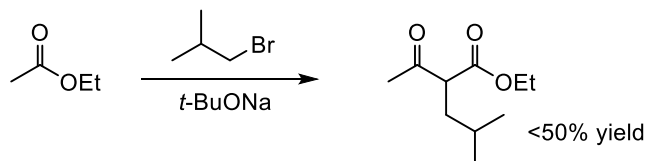


When the base is sodium *tert*-butoxide ( $t\text{-BuO}^-$ ) the desired product is formed.

However, when the base is sodium ethoxide ( $\text{EtO}^-$ ), none of the desired product is formed. Why? What product is formed instead? [3 marks]

b) When ethyl acetate is used as the substrate with *tert*-butoxide as the base, the alkylation does not proceed as planned and forms a mixture of products.

Propose a mechanism that explains the formation of this product from the reaction (note: this is not the only product formed!): [7 marks]

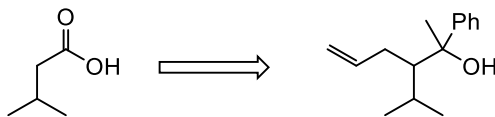




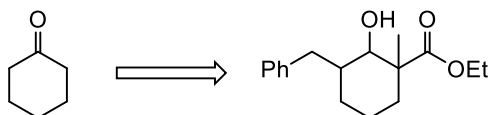
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6. Propose syntheses of **ONE** of the following molecules from the given starting materials.  
[10 marks]

a)



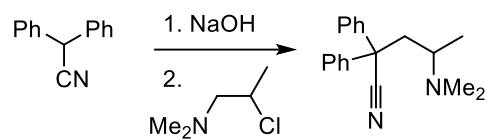
b)



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

**Bonus question!**

When we were discussing the synthesis of methadone, I showed you the following enolate-like alkylation:



Draw a mechanism that explains the regioselectivity of the product formed