

CHEM 3331, Professor M. Walczak, Spring 2015
Third hour exam, 7.00 PM, April 14th, 2015

Printed Name: _____

Student ID: _____

Recitation TA: _____

Recitation Day and Time: _____

Signature: _____

1. _____ / 11

2. _____ / 32

3. _____ / 15

4. _____ / 15

5. _____ / 15

6. _____ / 12

Total: _____ / 100

This is a closed-book exam. You are not allowed to use molecular models, lecture notes, personal class notes, textbooks, and electronic copies of the above materials on mobile devices. Use the backs of the pages for scratch notes.

Honor Code: All students of the University of Colorado at Boulder are responsible for knowing and adhering to the academic integrity policy of this institution. Violations of this policy may include: cheating, plagiarism, aid of academic dishonesty, fabrication, lying, bribery, and threatening behavior. Students who are found to be in violation of the academic integrity policy will be subject to both academic sanctions from the faculty member and non-academic sanctions (including but not limited to university probation, suspension, or expulsion).

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selecnium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 * *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * * * *	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [269]	meitnerium 109 Mt [269]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbinium 112 Uub [277]	ununquadium 114 Uuq [289]										

* Lanthanide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

** Actinide series

1.

(a) Unlike LiAlH_4 , the following reagent - $\text{HAl}[\text{OC}(\text{CH}_3)_3]_3$ - selectively reduces acyl halides to aldehydes. The reason(s) for the reduced activity of this reagent is/are (3 points):

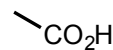
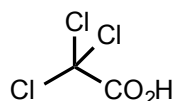
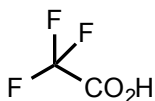
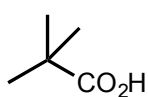
(a) the hydride ion is less nucleophilic;

(b) it is sterically hindered;

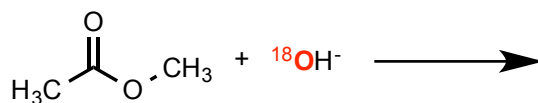
(c) both (a) and (b) are correct;

(e) both (a) and (b) are incorrect.

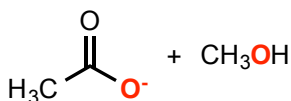
(b) Identify the most acidic compound (3 points).



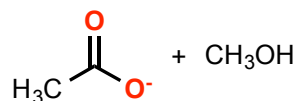
(c) Methyl acetate (shown below) was reacted with a hydroxide anion labeled with a heavy isotope of oxygen (oxygen-18, shown in red). Based on your understanding of the saponification reaction, predict the location of the labeled oxygen atom in the products (5 points).



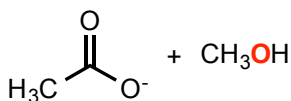
(a)



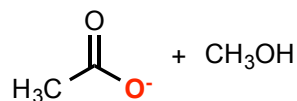
(b)



(c)

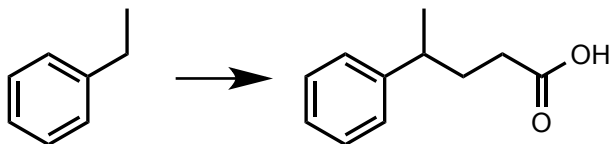


(d)

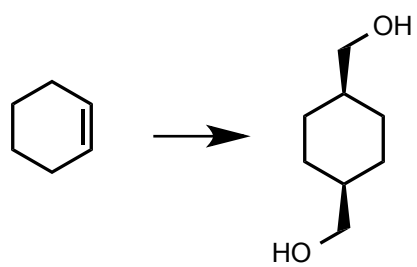


2. Provide a reasonable synthesis of the following two compounds using provided starting materials. More than one step may be required to complete the synthesis. The products are racemic but pay close attention to relative stereochemistry (32 points).

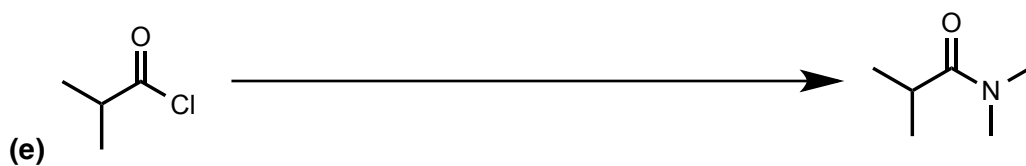
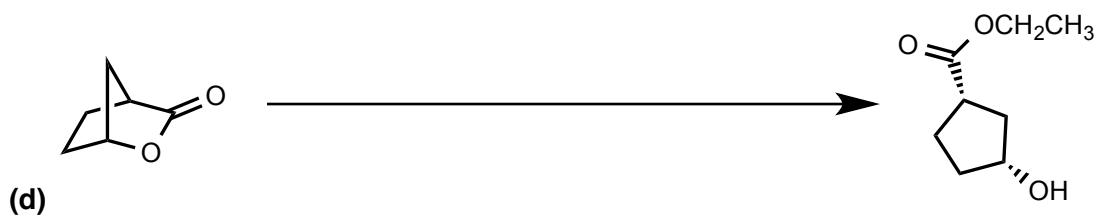
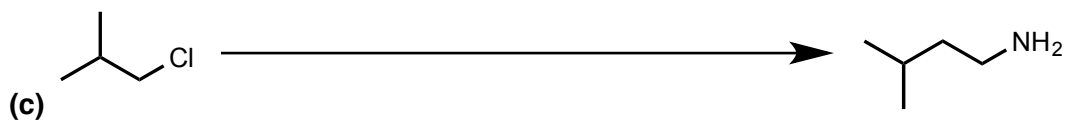
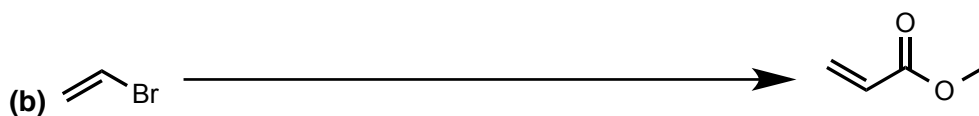
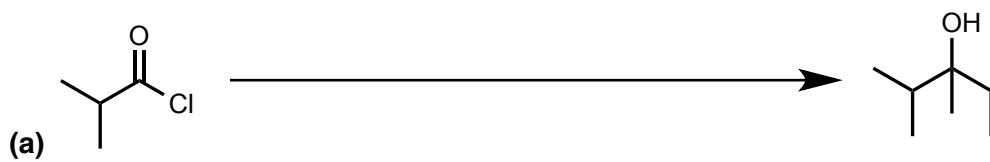
(a)



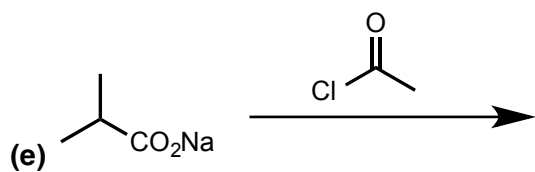
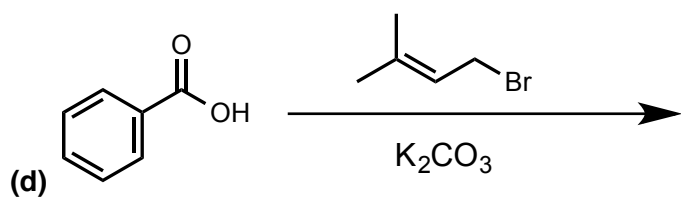
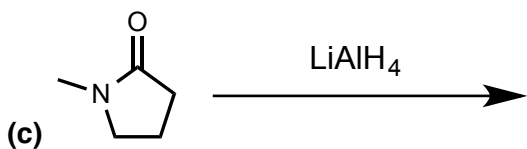
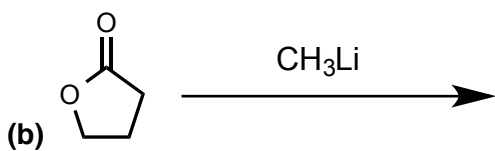
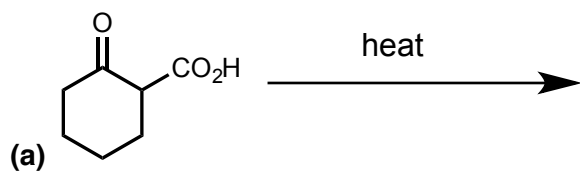
(b)



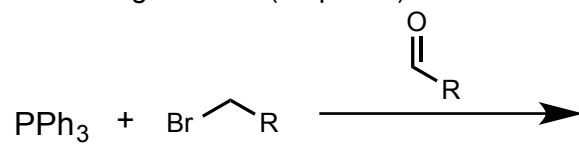
3. Complete the following syntheses using any reagents you need. You do not have to show the synthesis of the reagents you use, but you must use the starting material indicated. All chiral products are racemic mixtures (3 points each, 15 points total).



4. Provide the products of the following reactions (all reactions have an appropriate aqueous work up). If no reaction would occur, write NR. Ignore stereochemistry in the products (3 points each, 15 points total).



5. Draw a plausible mechanism of the Wittig reaction (15 points).

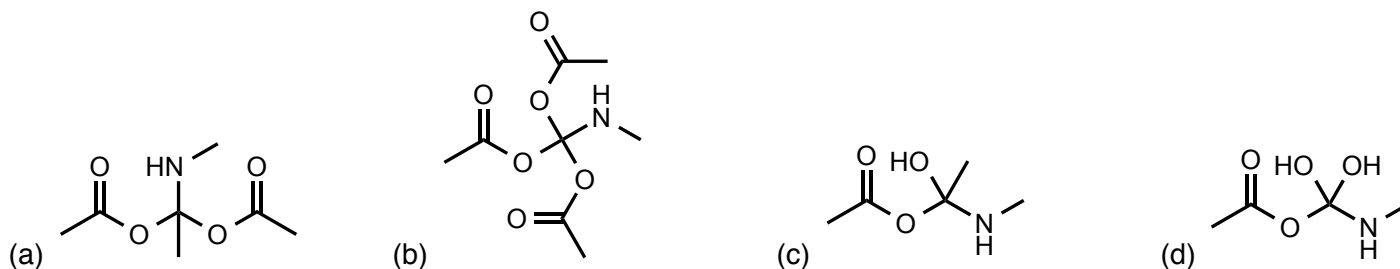
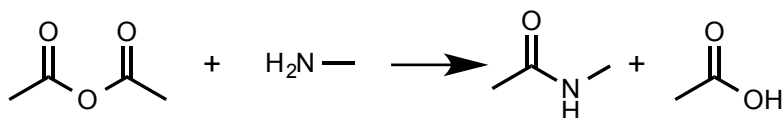


6. In the following questions, please circle only the correct answer (3 points each, 12 points total):

(a) Among the following choices, which group is the least reactive in a reaction with LiAlH_4 ?

- (a) $-\text{CO}_2\text{H}$ (b) $-\text{CN}$ (c) $-\text{CO}_2\text{CH}_3$ (d) $-\text{CO}_2\text{CH}_2\text{CH}_3$ (e) $-\text{COCl}$

(b) Which structure represents a tetrahedral intermediate involved in acylation of methylamine with acetic anhydride?



(c) In acylation reaction of an alcohol with acyl chloride, tertiary amine (Et_3N) or pyridine are added. Which statement about these additives is *incorrect*?

- (a) they act as a Lewis base; (b) they deprotonate the alcohol to form an alkoxide;
(d) they scavenge HCl ; (e) they can be used as a solvent.

(d) Which statement about transesterification reaction is correct?

- (a) only stoichiometric amounts of acid can be used; (b) can be catalyzed by a base;
(c) works only with aliphatic alcohols; (d) can occur under acidic or basic conditions.