

# Chemistry 3371: Organic Chemistry

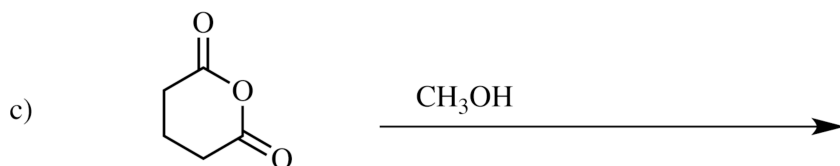
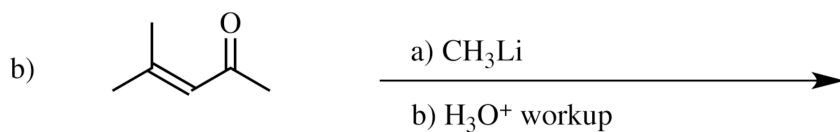
*Instructor: Hubert Yin/TA: Adam Csakai*

Tuesday: Apr. 12 @ 7:00 - 9:00 PM /3<sup>rd</sup> Exam

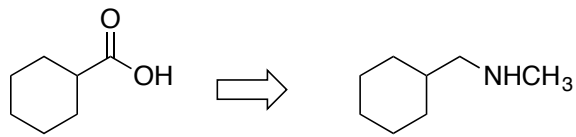
Name: \_\_\_\_\_ (please print, 1 pt)

Page	Possible Points	Score
1	<u>1</u>	_____
2	<u>12</u>	_____
3	<u>8</u>	_____
4	<u>8</u>	_____
5	<u>8</u>	_____
6	<u>15</u>	_____
7	<u>10</u>	_____
8	<u>8</u>	_____
9	<u>10</u>	_____
10	<u>10</u>	_____
11	<u>10</u>	_____
12	<u>Appendix: Periodic Table, common NMR, IR absorption</u>	_____
TOTAL	<u>100</u>	_____

1. Give the **single major product** of each of the following reactions, carefully showing stereochemistry if appropriate. If a racemate is formed, show only one enantiomer, and label it "rac". Assume chiral starting materials are single pure enantiomers (3 pts each)

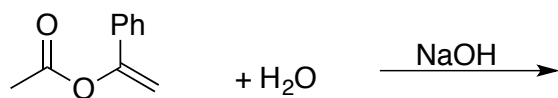


2. (8 pts) Outline a synthesis of (cyclohexylmethyl)methylamine from cyclohexanecarboxylic acid.

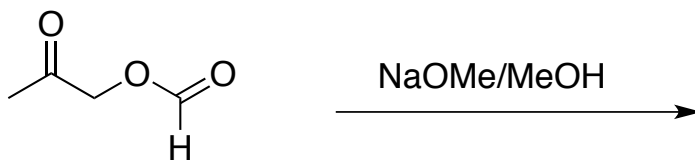


3. (8 pts) Complete the reactions by giving the principal organic products (assume an acidic workup). Provide curved arrows to indicate the electron flow.

a)

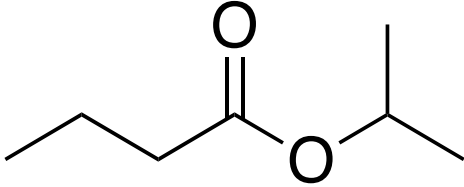


b)

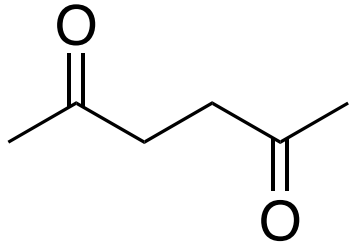


4. (8 pts) Draw and circle hydrogen atoms in each compound have a  $pK_a \leq 25$

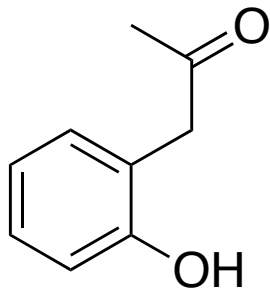
a)



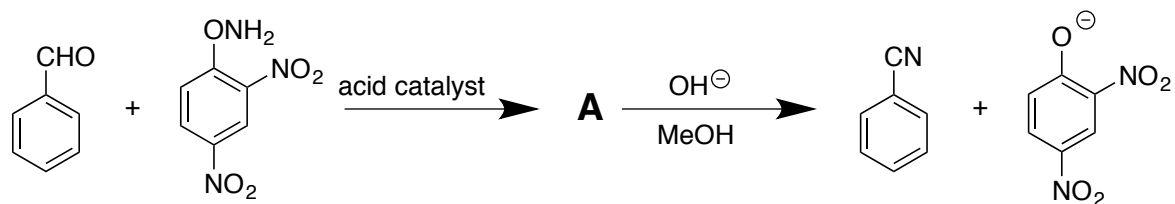
b)



c)

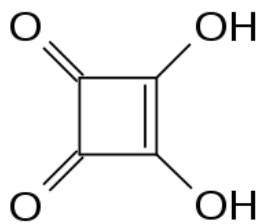


5. (15 pts) The sequence shown below illustrates a method for the preparation of nitriles from aldehydes. Identify compound A and give a curved-arrow mechanism for the conversion of A to the products.



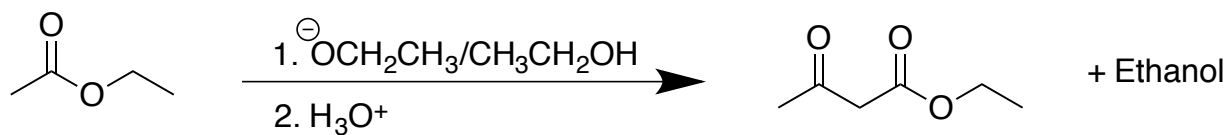
6. (10 pts) Synthesize 2,4-dimethylhexan-3-one from four carbon alcohols.

7. (8 pts) Squaric acid has pKa values of about 1 and 3.5. Draw the reactions corresponding to the two successive ionization of squaric acid and label each with the appropriate pKa value.



**Squaric acid**

8. (10 pts) The Claisen condensation converts two molecules of an ester into a  $\beta$ -keto ester. The reaction starts with the ester in an alkoxide/alcohol solution and is worked up with acid to form the neutral  $\beta$ -keto ester product. Show the curved arrow mechanism for the Claisen condensation of ethyl ethanoate treated ethoxide ion. In each step, draw only the species that react in that step. If an enolate resonance form is possible, draw only the carbanionic form. Always omit ethanol byproducts.



9. (10 pts) Give the structures of the aldol addition products expected from the base-catalyzed reaction of acetaldehyde and propionaldehyde. Assume all products are racemates.

10. (10 pts) Give the structure of the compound  $C_7H_5O_2Cl$  that has an IR absorption at  $1685\text{ cm}^{-1}$  as well as a strong, broad O-H absorption, and the following proton NMR spectrum:  $\delta = 7.56$  (2H, leaning d,  $J = 10\text{ Hz}$ );  $\delta = 8.00$  (2H, leaning d,  $J = 10\text{ Hz}$ );  $\delta = 8.27$  (1H, broad s, exchanges with  $D_2O$ ).

## Appendix

hydrogen 1 <b>H</b> 1.0079																				helium 2 <b>He</b> 4.0026
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122											boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180			
sodium 11 <b>Na</b> 22.990	magnesium 12 <b>Mg</b> 24.305											aluminum 13 <b>Al</b> 26.982	silicon 14 <b>Si</b> 28.086	phosphorus 15 <b>P</b> 30.974	sulfur 16 <b>S</b> 32.065	chlorine 17 <b>Cl</b> 35.453	argon 18 <b>Ar</b> 39.948			
potassium 19 <b>K</b> 39.098	calcium 20 <b>Ca</b> 40.078	scandium 21 <b>Sc</b> 44.956	titanium 22 <b>Ti</b> 47.867	vanadium 23 <b>V</b> 50.942	chromium 24 <b>Cr</b> 51.996	manganese 25 <b>Mn</b> 54.938	iron 26 <b>Fe</b> 55.845	cobalt 27 <b>Co</b> 58.933	nickel 28 <b>Ni</b> 58.693	copper 29 <b>Cu</b> 63.546	zinc 30 <b>Zn</b> 65.39	gallium 31 <b>Ga</b> 69.723	germanium 32 <b>Ge</b> 72.61	arsenic 33 <b>As</b> 74.922	selenium 34 <b>Se</b> 78.96	bromine 35 <b>Br</b> 79.904	krypton 36 <b>Kr</b> 83.80			
rubidium 37 <b>Rb</b> 85.468	strontium 38 <b>Sr</b> 87.62	yttrium 39 <b>Y</b> 88.906	zirconium 40 <b>Zr</b> 91.224	niobium 41 <b>Nb</b> 92.906	molybdenum 42 <b>Mo</b> 95.94	technetium 43 <b>Tc</b> [98]	ruthenium 44 <b>Ru</b> 101.07	rhodium 45 <b>Rh</b> 102.91	palladium 46 <b>Pd</b> 106.42	silver 47 <b>Ag</b> 107.87	cadmium 48 <b>Cd</b> 112.41	indium 49 <b>In</b> 114.82	tin 50 <b>Sn</b> 118.71	antimony 51 <b>Sb</b> 121.76	tellurium 52 <b>Te</b> 127.60	iodine 53 <b>I</b> 126.90	xenon 54 <b>Xe</b> 131.29			
cesium 55 <b>Cs</b> 132.91	barium 56 <b>Ba</b> 137.33	* 57-70	lutetium 71 <b>Lu</b> 174.97	hafnium 72 <b>Hf</b> 178.49	tantalum 73 <b>Ta</b> 180.95	tungsten 74 <b>W</b> 183.84	rhenium 75 <b>Re</b> 186.21	osmium 76 <b>Os</b> 190.23	iridium 77 <b>Ir</b> 192.22	platinum 78 <b>Pt</b> 195.08	gold 79 <b>Au</b> 196.97	mercury 80 <b>Hg</b> 200.59	thallium 81 <b>Tl</b> 204.38	lead 82 <b>Pb</b> 207.2	bismuth 83 <b>Bi</b> 208.98	polonium 84 <b>Po</b> [209]	astatine 85 <b>At</b> [210]	radon 86 <b>Rn</b> [222]		
francium 87 <b>Fr</b> [223]	radium 88 <b>Ra</b> [226]	* * 89-102	lawrencium 103 <b>Lr</b> [262]	rutherfordium 104 <b>Rf</b> [261]	dubnium 105 <b>Db</b> [262]	seaborgium 106 <b>Sg</b> [266]	bohrium 107 <b>Bh</b> [264]	hassium 108 <b>Hs</b> [269]	meitnerium 109 <b>Mt</b> [268]	ununnitium 110 <b>Uun</b> [271]	unununium 111 <b>Uuu</b> [272]	ununbium 112 <b>Uub</b> [277]		ununquadium 114 <b>Uuq</b> [289]						

Group	Chemical shift, ppm
	0.7-1.5
	4.6-5.7
	varies with solvent and with acidity of O-H
	1.7-2.5
	6.5-8.5

Group	Chemical shift, ppm
	9-11
	7.5-9.5
	0.5-1.5
	2.5-3.5

**TABLE 12.1** Regions of the Infrared Spectrum

Wavenumber range, cm <sup>-1</sup>	Type of absorptions	Name of region
3400-2800	O—H, N—H, C—H stretching	Functional group
2250-2100	C≡N, C≡C stretching	
1850-1600	C=O, C=N, C=C stretching	
1600-1000	C—C, C—O, C—N stretching; various bending absorptions	Fingerprint
1000-600	C—H bending	C—H bending