

CH 336

Midterm Exam 2

Monday, May 16, 2016

Name KEY

You may use a molecular model kit, but no other notes or material with chemical information. Electronic gadgets (including but not limited to: calculators, phones, MP3 players, smart watches) are prohibited; we may ask you to leave electronic watches at the front of the room or in your backpack for the exam period.

Please ask questions if a question is not clear.

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]	ununnium 110 <b>Uun</b> [271]	ununium 111 <b>Uuu</b> [272]	unubium 112 <b>Uub</b> [277]		ununquadium 114 <b>Uuq</b> [289]						

\* Lanthanide series

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

\*\* Actinide series

Score Table:

Section I \_\_\_\_\_/24

Section II \_\_\_\_\_/30

Section III \_\_\_\_\_/22

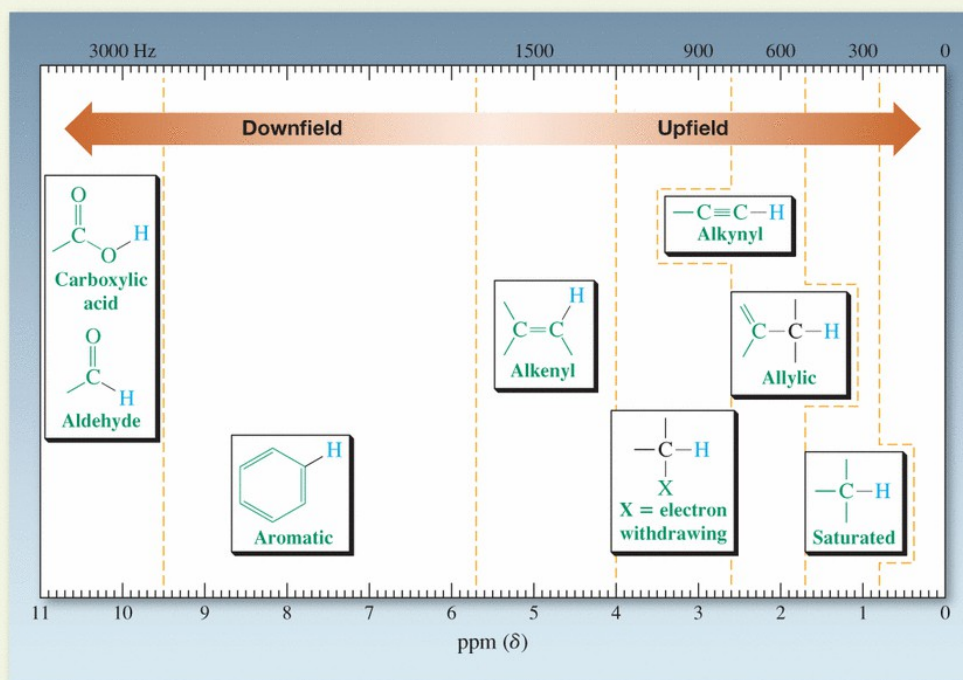
Section IV \_\_\_\_\_/24

Total: \_\_\_\_\_/100

**Table 10-2 Typical Hydrogen Chemical Shifts in Organic Molecules**

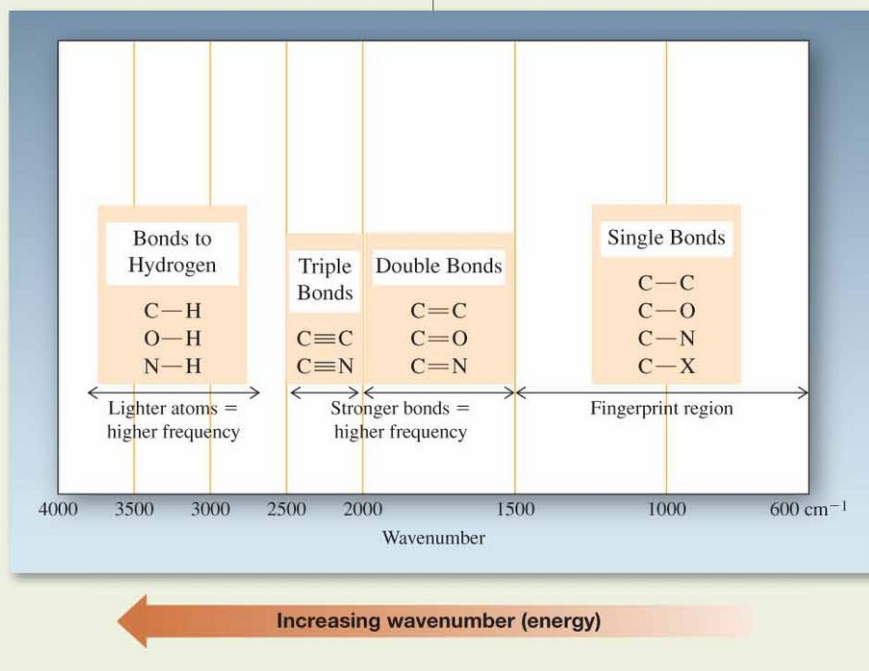
Type of hydrogen <sup>a</sup>	Chemical shift $\delta$ in ppm	
Primary alkyl, $\text{RCH}_3$	0.8–1.0	Alkane and alkane-like hydrogens
Secondary alkyl, $\text{RCH}_2\text{R}'$	1.2–1.4	
Tertiary alkyl, $\text{R}_3\text{CH}$	1.4–1.7	
Allylic (next to a double bond), $\text{R}_2\text{C}=\text{C}(\text{CH}_3)\text{R}'$	1.6–1.9	Hydrogens adjacent to unsaturated functional groups
Benzylic (next to a benzene ring), $\text{ArCH}_2\text{R}$	2.2–2.5	
Ketone, $\text{RCCH}_3$ $\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{CH}_3 \end{array}$	2.1–2.6	
Alkyne, $\text{RC}\equiv\text{CH}$	1.7–3.1	Hydrogens adjacent to electronegative atoms
Chloroalkane, $\text{RCH}_2\text{Cl}$	3.6–3.8	
Bromoalkane, $\text{RCH}_2\text{Br}$	3.4–3.6	
Iodoalkane, $\text{RCH}_2\text{I}$	3.1–3.3	
Ether, $\text{RCH}_2\text{OR}'$	3.3–3.9	
Alcohol, $\text{RCH}_2\text{OH}$	3.3–4.0	
Terminal alkene, $\text{R}_2\text{C}=\text{CH}_2$	4.6–5.0	Alkene hydrogens
Internal alkene, $\text{R}_2\text{C}=\text{CH}-\text{R}'$	5.2–5.7	
Aromatic, $\text{ArH}$	6.0–9.5	
Aldehyde, $\text{RCH}=\text{O}$ $\begin{array}{c} \text{O} \\    \\ \text{R}-\text{C}-\text{H} \end{array}$	9.5–9.9	
Alcoholic hydroxy, $\text{ROH}$	0.5–5.0	(variable)
Thiol, $\text{RSH}$	0.5–5.0	(variable)
Amine, $\text{RNH}_2$	0.5–5.0	(variable)

<sup>a</sup>R, R', alkyl groups; Ar, aromatic group (not argon).



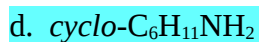
**Table 11-4** Characteristic Infrared Stretching Wavenumber Ranges of Organic Molecules

Bond or Functional Group	$\tilde{\nu}$ (cm <sup>-1</sup> )	Bond or Functional Group	$\tilde{\nu}$ (cm <sup>-1</sup> )
RO—H (alcohols)	3200–3650	RC≡N (nitriles)	2220–2260
$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCO—H} \end{array}$ (carboxylic acids)	2500–3300	$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{RCH, RCR}' \end{array}$ (aldehydes, ketones)	1690–1750
R <sub>2</sub> N—H (amines)	3250–3500	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOR}' \end{array}$ (esters)	1735–1750
RC≡C—H (alkynes)	3260–3330	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCOH} \end{array}$ (carboxylic acids)	1710–1760
$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$ (alkenes)	3050–3150	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$ (alkenes)	1620–1680
$\begin{array}{c}   \\ \text{—C—H} \\   \end{array}$ (alkanes)	2840–3000	$\begin{array}{c}   \\ \text{RC—OR}' \\   \end{array}$ (alcohols, ethers)	1000–1260
RC≡CH (alkynes)	2100–2260		

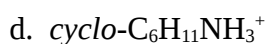
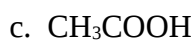
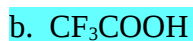
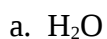


Section I (4 points each) Select the best answer among the possibilities given and circle it.

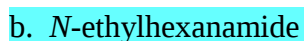
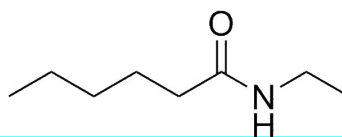
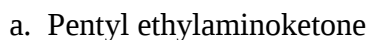
1. Select the strongest Brønsted base.



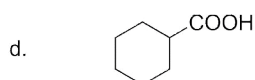
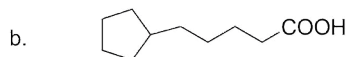
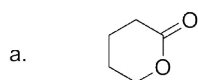
2. Select the strongest Brønsted acid.



3. Select the best name for the following compound:



4. Select the structure whose name is cyclopentanecarboxylic acid.



5. Select the structure best fitting the following spectroscopic data:

Molecular formula  $C_{10}H_{12}O_2$

IR: 1741, 1280, 1111, 747  $cm^{-1}$ .

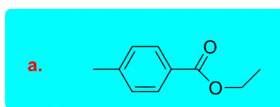
$^1H$  NMR: 7.77 2H d,  $J = 8$  Hz

7.13 2H d,  $J = 8$  Hz

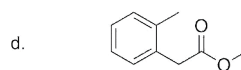
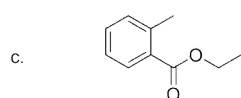
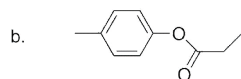
4.20 2H q,  $J = 7$  Hz

2.40 3H s

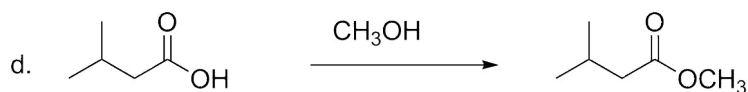
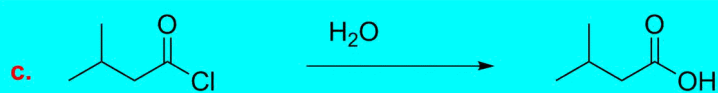
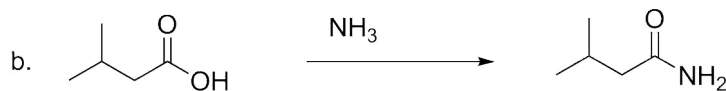
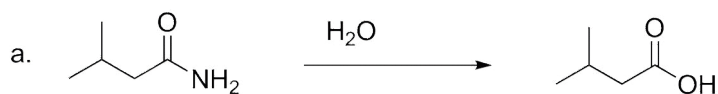
1.10 3H t,  $J = 7$  Hz



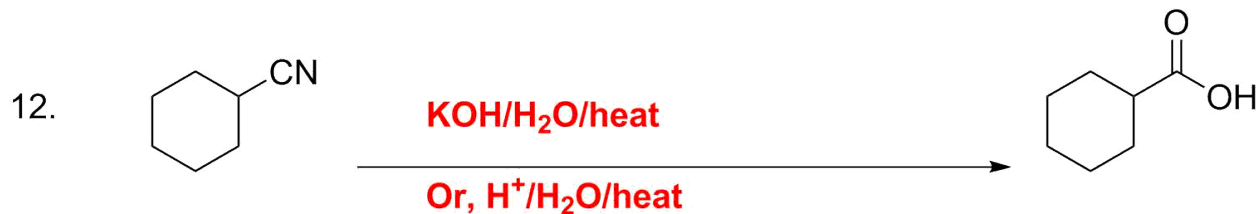
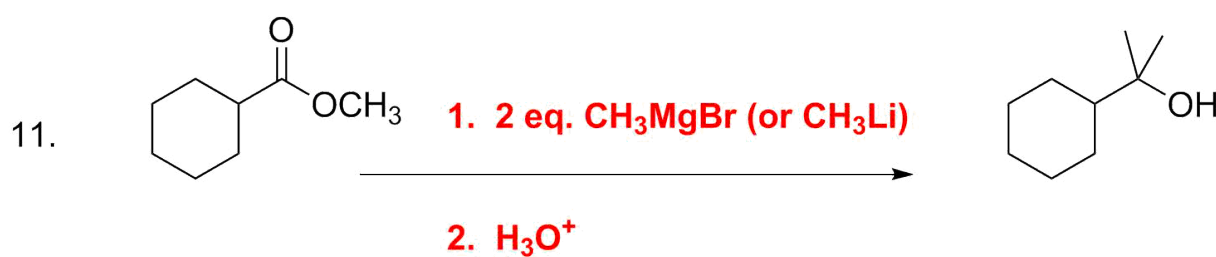
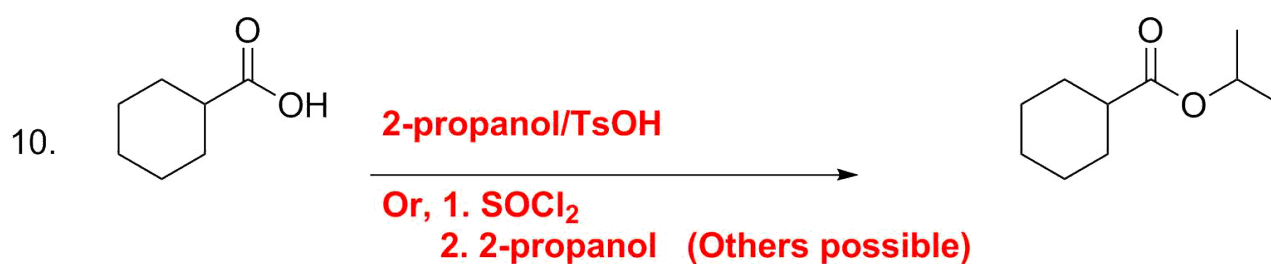
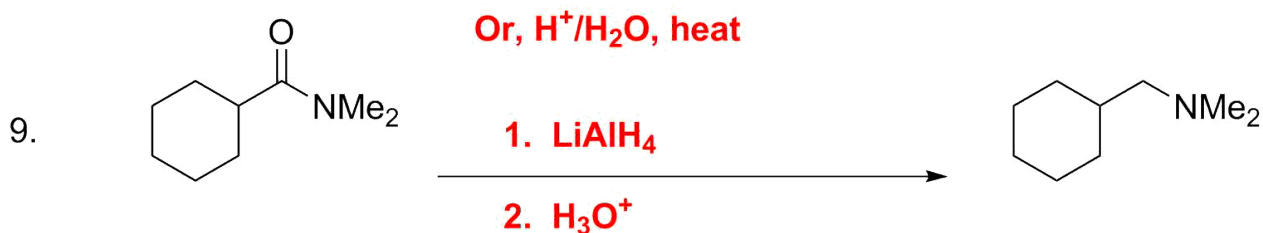
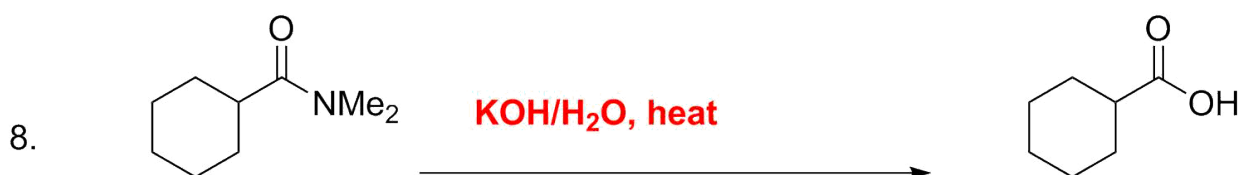
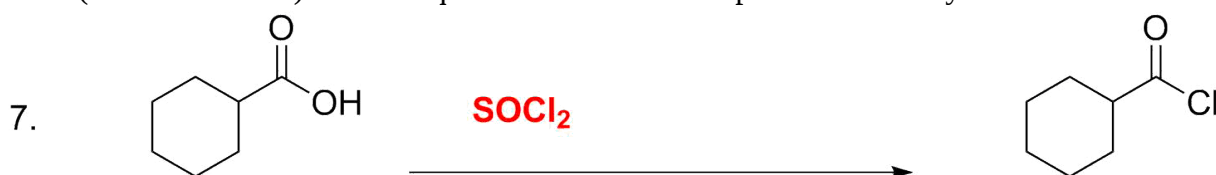
(IR = ester; q at 4.2 must be on  $CH_2-CH_3$  bonded to O; aromatic pair of d indicates para substitution)



6. Select the reaction below that would proceed to completion most readily (without application of heat or additional reagents).

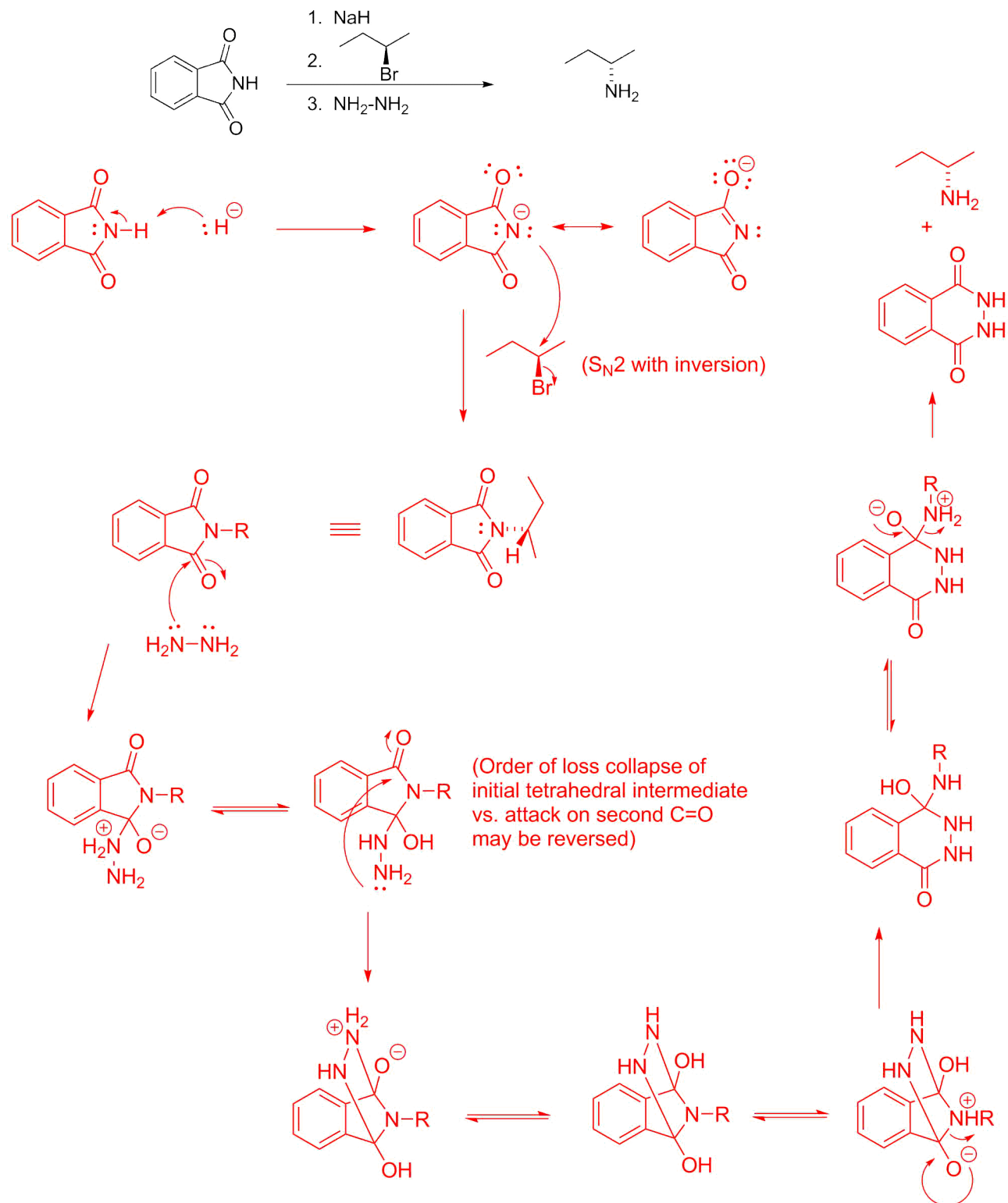


Section II. (5 points each) Draw (above the arrow) the reagents/conditions required for each of the following reactions. If you need sequential application of different reagents, indicate the numerical order (1. ...2. ...3. etc.) Include aqueous acid as a last step when necessary.



Section III. (22 points)

13. Write a mechanism for each step in the following transformation. Use electron-pushing arrows correctly, designate lone pairs where necessary, and make sure charges are correctly shown. If resonance is a stabilizing influence for any structure, show appropriate resonance forms. (Hint: write out the reaction occurring in each step first.) Continue on the back of the page if you need more space.

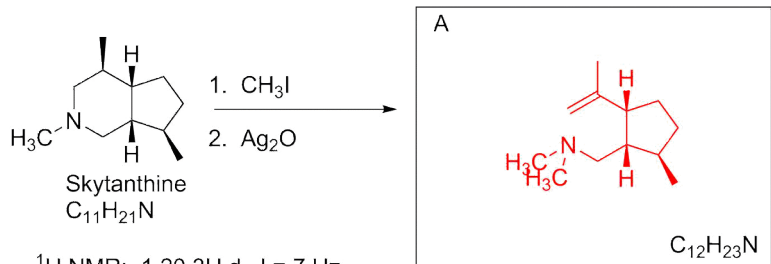




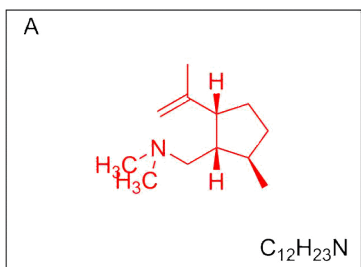
Section IV. (24 points: 3 points per structure; 3 points per rationale)

14. Historically, degradation of an unknown to a compound with a known structure has been a method of identifying new compounds. The following sequence of reactions was applied to the alkaloid skytanthine, isolated from a Chilean plant that makes a range of bioactive compounds. Partial NMR data is given for each compound in the sequence; IR spectra with frequencies (in  $\text{cm}^{-1}$ ) of strong peaks noted are on the following page.

Identify each structure represented by an empty box (A-D). For each, provide a rationale for structure based on either chemistry or IR/NMR data for the new compound created. (If you cannot provide a complete structure, show as much as you can figure out for partial credit.)



$^1\text{H}$  NMR: 1.20 3H d,  $J = 7$  Hz  
 1.33 3H d,  $J = 7$  Hz  
 2.32 3H, s  
 1.3-2.7, 12H, m  
 $^{13}\text{C}$  NMR: 57.8, 53.5, 47.6  
 47.4, 46.0, 42.3, 35.6  
 32.7, 24.5, 18.6, 16.2

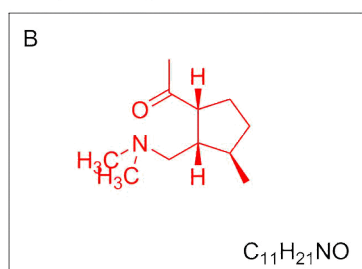


$^{13}\text{C}$  NMR now has peaks at 108.5 and 141.9 ppm.

Rationale: Hofmann elimination;  $\text{C}=\text{C}$  peaks in  $^{13}\text{C}$  NMR. (IR shows weak  $\text{C}=\text{C}$  stretch, and vinyl  $\text{C}-\text{H}$  at  $3144\text{ cm}^{-1}$ )

$\text{O}_3$ ,  $\text{Me}_2\text{S}$  workup

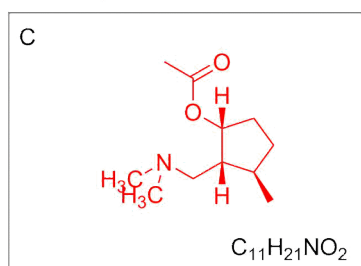
1 eq. HCHO plus



$^1\text{H}$  NMR methyl signals are now 1.02 3H d,  $J = 7$  Hz; 1.95 3H s; and 2.31 6H s.

Rationale: Ozonolysis of  $\text{C}=\text{C}$  leaves ketone. IR at  $1715\text{ cm}^{-1}$  confirms. 6H methyl is the amine; singlet at 1.95 is the methyl ketone; one doublet is left upfield.

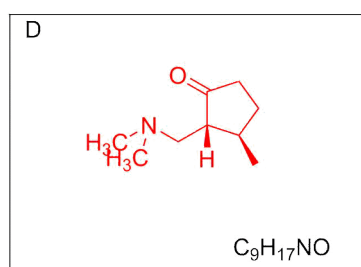
mCPBA, NaOH



There is a  $^1\text{H}$  NMR peak at 5.02 ppm that is a ddd ( $J = 6, 5, 3$  Hz) and  $^{13}\text{C}$  NMR peaks at 170 and 87.8 ppm.

Rationale: Baeyer-Villiger makes an acetate. The ddd is on a carbon bonded to oxygen. New  $^{13}\text{C}$  peak at 170 is the  $\text{C}=\text{O}$ ; the one at 87.8 is bound to oxygen.

1. KOH,  $\text{H}_2\text{O}$ ,  $\Delta$   
2. Jones' reagent

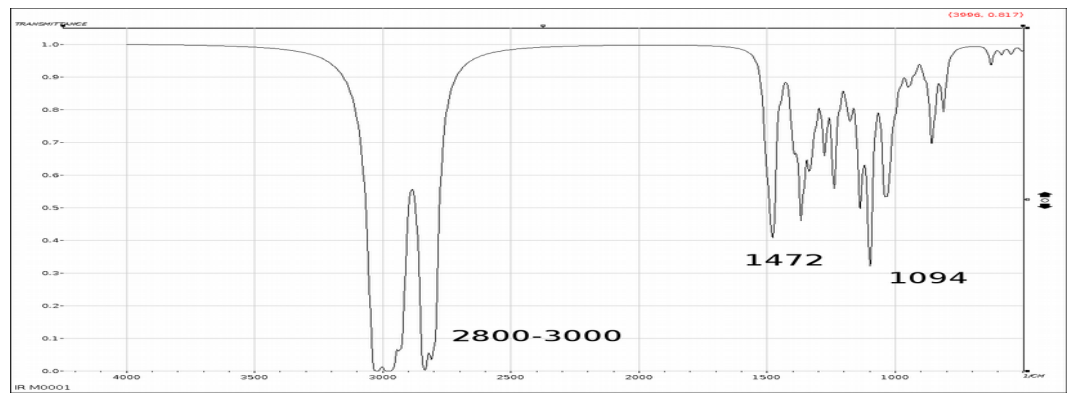


$^{13}\text{C}$  NMR: 219, 59.7, 49.5, 42.6, 41.3, 38.6, 32.4, 20.0

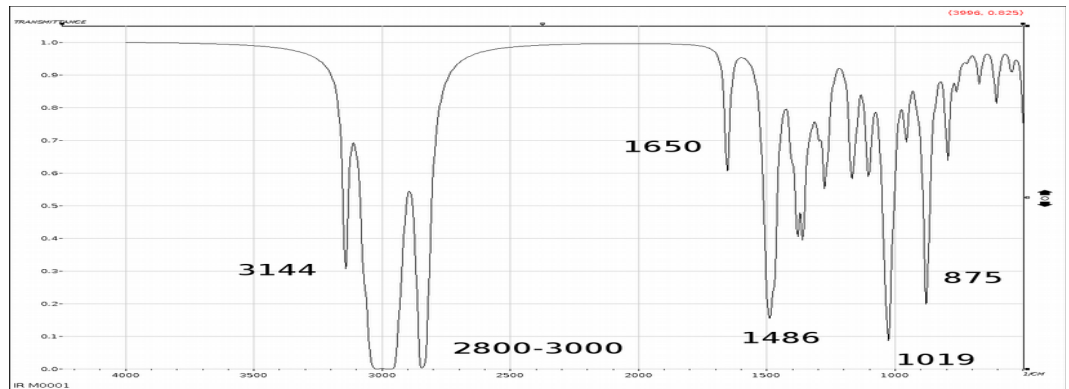
$^1\text{H}$  NMR methyl signals: 1.10 3H d,  $J = 7$  Hz; 2.22 6H, s

Rationale: Hydrolysis of the acetate followed by oxidation to the ketone.  $\text{C}=\text{O}$  seen in IR ( $1730\text{ cm}^{-1}$ ) and  $^{13}\text{C}$  NMR (219 ppm).

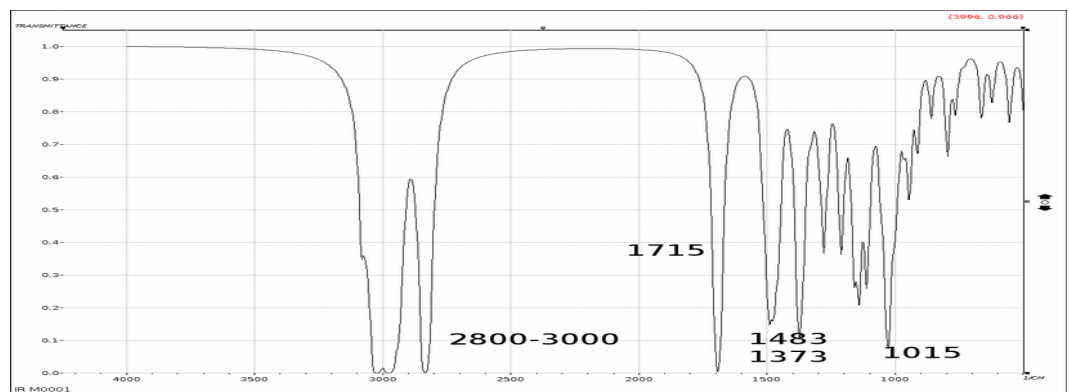
IR of skytanthine:



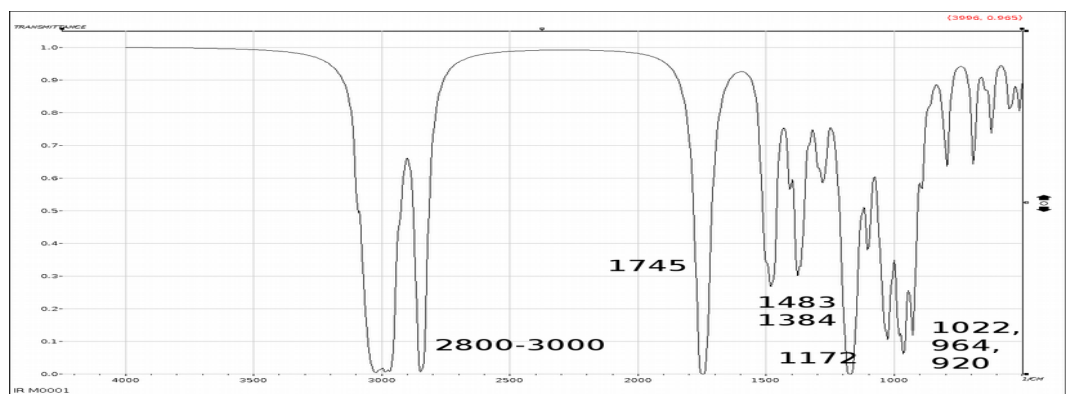
IR of A:



IR of B:



IR of C:



IR of D:

