NAME _____

ID # _____

ORGANIC CHEMISTRY I (2301)

1:30 pm – 3:30 pm, December 16, 2014

Final Exam

You will be able to pick up your graded Exam 4 from Chemistry department staff in 115 Smith beginning Monday, December 22nd at 10 AM. Exams that are not picked up by the second week of spring semester will be disposed of.

A periodic table, a table of standard reaction conditions, and tables of typical NMR chemical shifts, coupling constants, and IR frequencies are attached to the back of this exam as aids. Otherwise, you are not permitted to use any other materials (including notes, books, or electronic devices of any kind).

When the exam begins, please write your name at the top of the next page.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

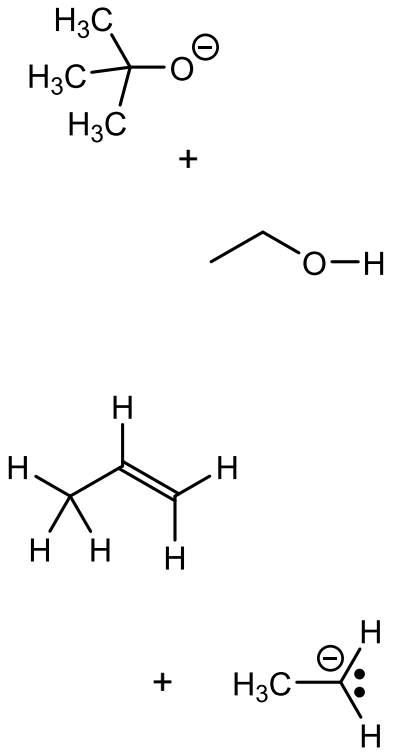
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

NAME _____

Scoring:		
	1. _____ / 12	6. _____ / 23
	2. _____ / 16	7. _____ / 15
	3. _____ / 37	8. _____ / 24
	4. _____ / 16	9. _____ / 15
	5. _____ / 16	10. _____ / 26

Total Score: _____ / 200

1. (12 pts) For each of the sets of molecules below:
   - Using "electron pushing" (with double-barbed arrows), show how the molecules on the left would react in an acid-base reaction to transfer a proton from one to the other.
   - In the box on the right, draw the conjugate acid and base products of each reaction.
   - In the middle, draw an equilibrium arrow that shows whether you feel the acid-base equilibrium would lie on the left or the right.



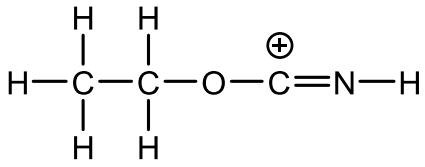
products

or

?

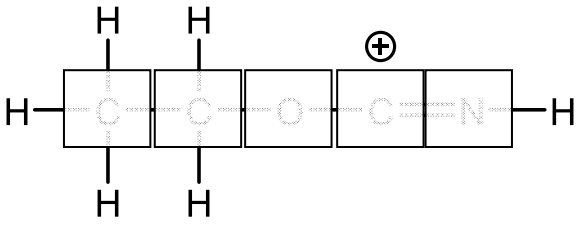
products

2. (16 pts) For the ion drawn at right, in the boxes provided:



- Draw all significant resonance structures. In each structure, draw all atoms, bonds, lone pairs of electrons, and formal charges. Then, circle which resonance structure you think is the most representative, and which is the least. **Circle only one MOST and one LEAST.**
- Draw a Lewis wedge/dashed-bond structure that illustrates the most stable three-dimensional conformation of the molecule. Draw all atoms, bonds, and charges, but omit lone pairs.
- In the boxes provided, write the hybridization state on any atom heavier than hydrogen.

atom hybridizations:



MOST *or* **LEAST** *representative?*

3-dimensional representation

resonance structure

MOST *or* **LEAST** *representative?*

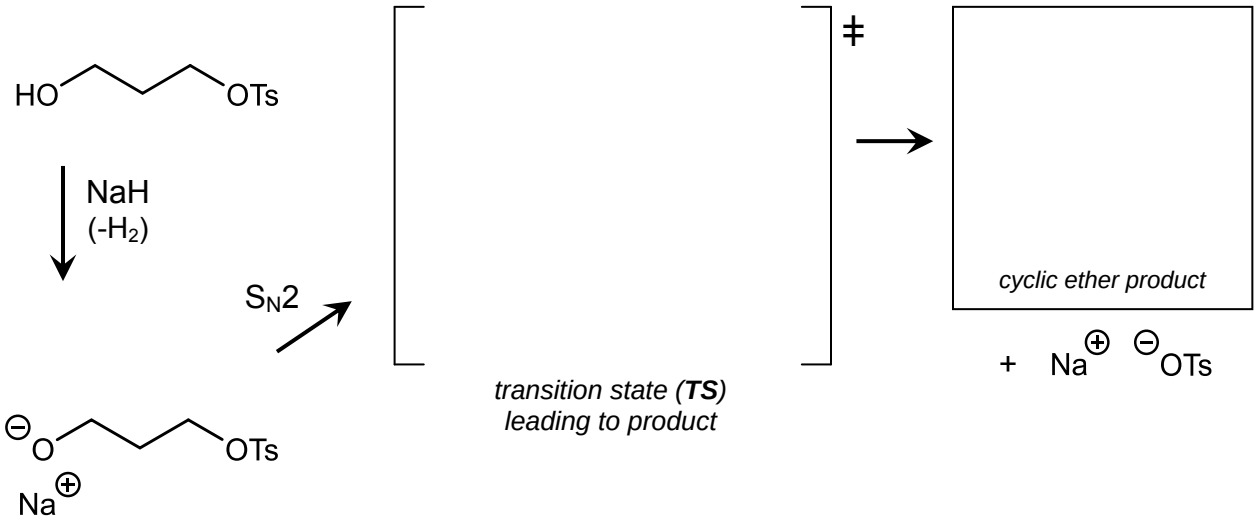
resonance structure

MOST *or* **LEAST** *representative?*

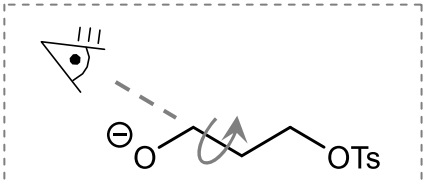
3. (37 pts) Cyclic ethers can often be synthesized by an intramolecular, ring-closing S_N2 reaction. For example, when the alcohol starting material shown on the next page is deprotonated with NaH, the resulting alkoxide reacts with itself to form a cyclic product.

a. **Draw the product** in the empty box on the right. Then, **draw a transition state structure** that illustrates the conformation of the transition state in the S_N2 reaction.

b. Using "electron pushing", draw a mechanism that illustrates how the alkoxide intermediate reacts. I've drawn the alkoxide for you—**just add curved arrows to my alkoxide intermediate structure**.



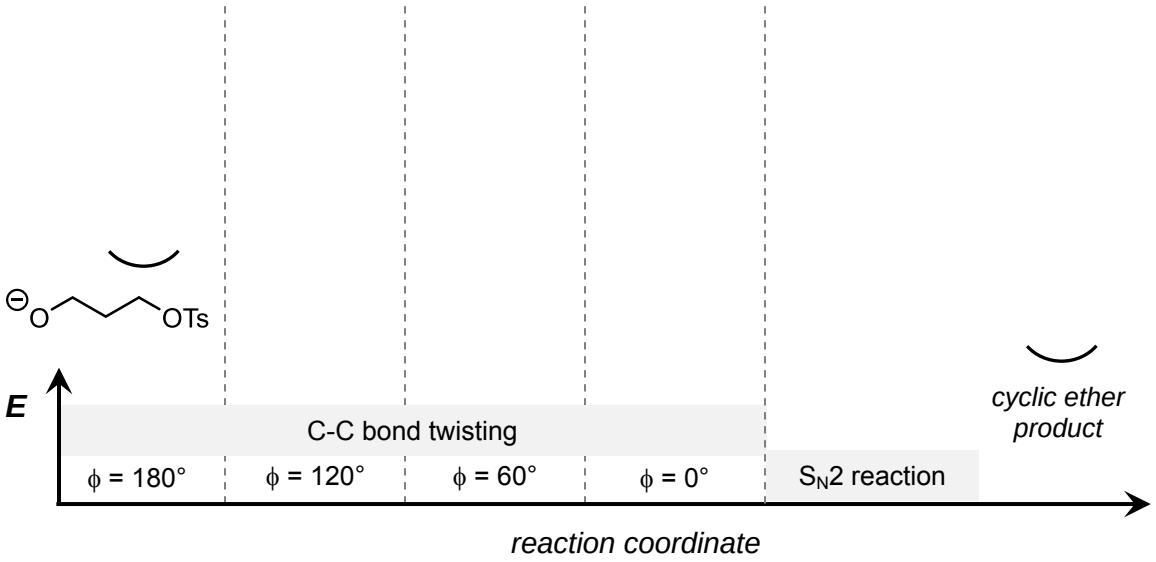
c. The alkoxide intermediate can't react in the conformation drawn on the left; the indicated C-C bond has to twist, so that its dihedral angle changes from $\phi = 180°$ to $\phi = 0°$. In the spaces below, **draw Newman projections** for different conformations of the alkoxide that would be encountered by twisting the C-C bond in 60° steps, using the perspective I've provided. Then, indicate whether each Newman projection represents a ***gauche***, an ***anti***, or an ***eclipsed*** conformer by circling one answer.



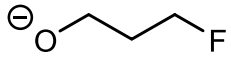
draw this conformation here

$\phi = 180°$	$\phi = 120°$	$\phi = 60°$	$\phi = 0°$
gauche *or* ***anti*** *or* ***eclipsed*** *?*	***gauche*** *or* ***anti*** *or* ***eclipsed*** *?*	***gauche*** *or* ***anti*** *or* ***eclipsed*** *?*	***gauche*** *or* ***anti*** *or* ***eclipsed*** *?*

d. **Draw a potential energy diagram** that shows everything the alkoxide must do to react—including the C-C bond twisting and the S_N2 reaction. I have already drawn energies for the starting material and product; connect them with one, continuous energy curve. *You do not need to draw any molecule structures in this part.* Label the S_N2 transition state ("**TS**") on your curve.



e. What if the functional group on the right was a fluoride instead of a tosylate? Would

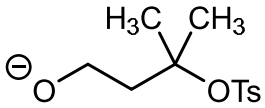


react **FASTER** than **SLOWER** than *or* at the **SAME RATE** as

?

(Circle one answer.)

f. What if the right-hand carbon also bore two methyl groups? Would

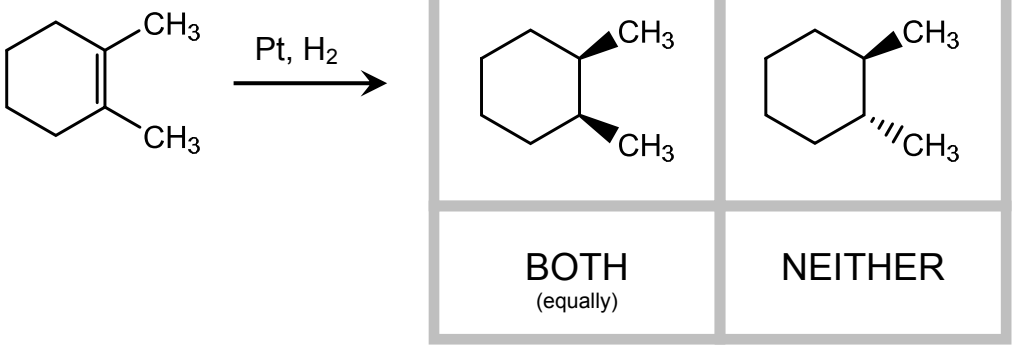


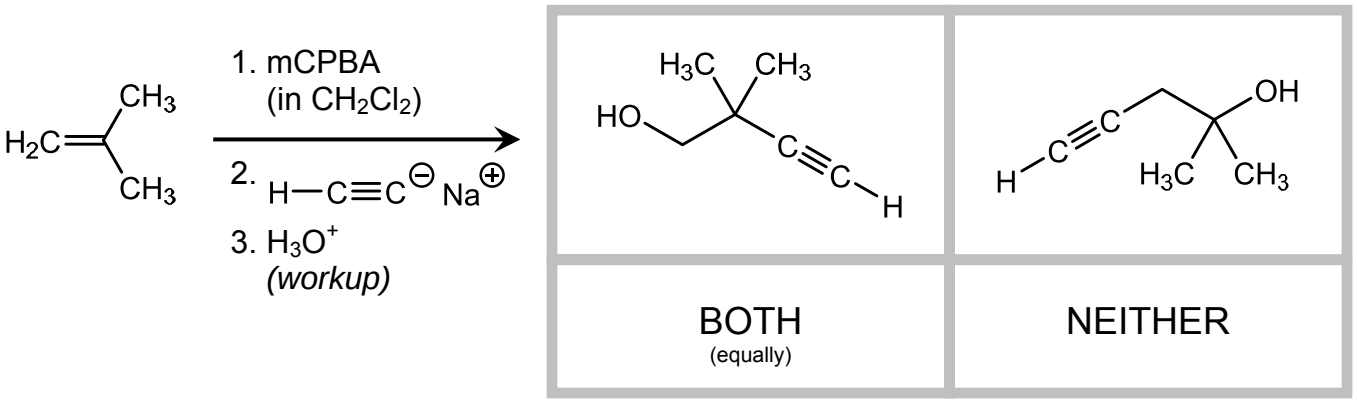
react **FASTER** than **SLOWER** than *or* at the **SAME RATE** as

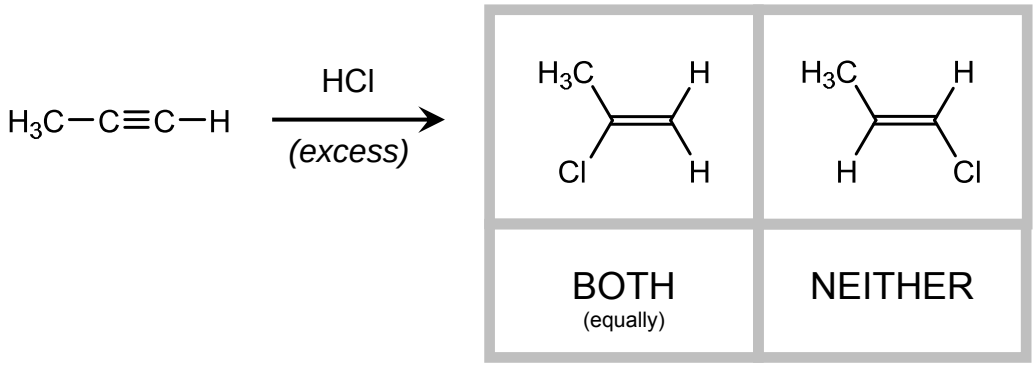
?

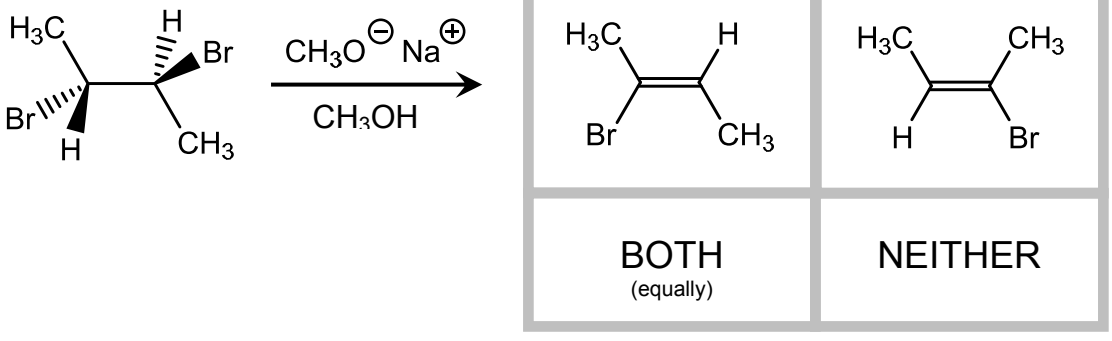
(Circle one answer.)

4. (16 pts) Each of the reactions on the next page is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced <u>equally</u>, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

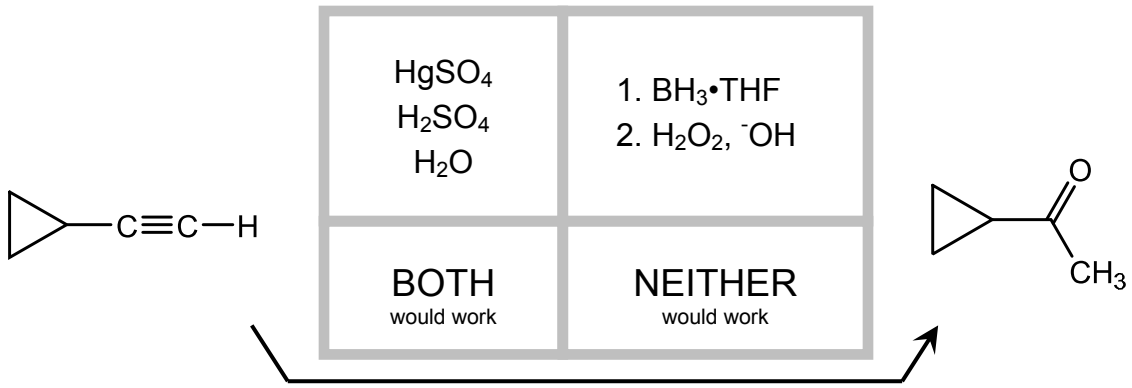


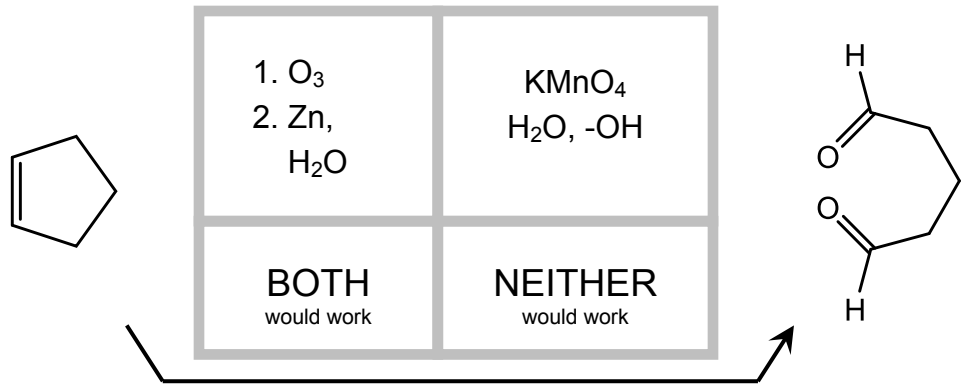


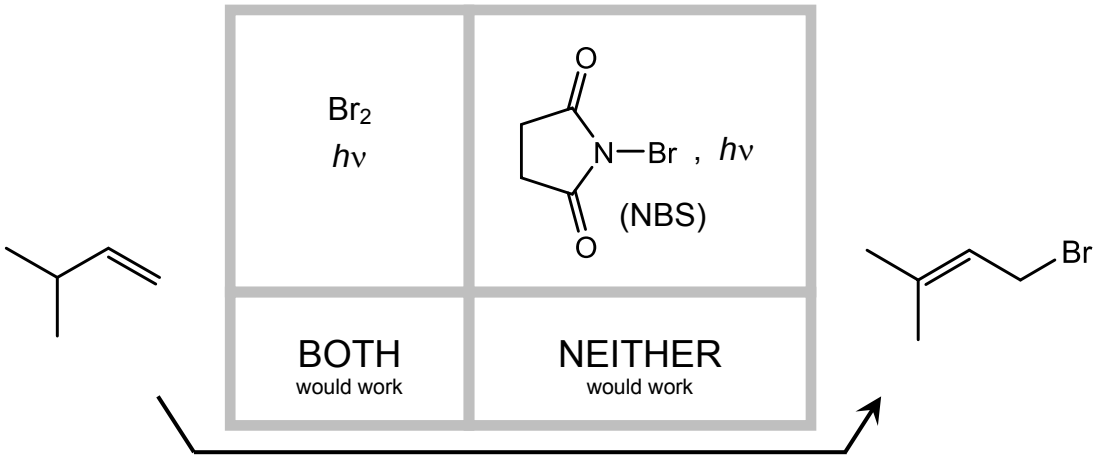


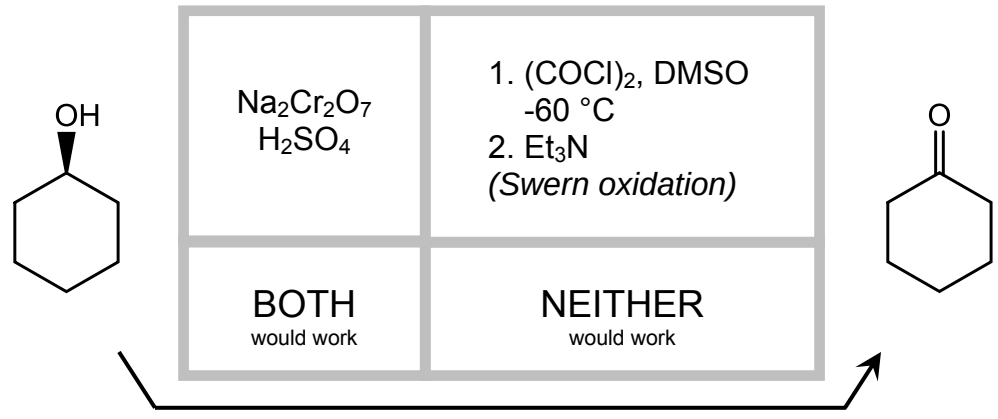


5. (16 pts) Each of the reactions on the next page is drawn with two possible reaction conditions. If only one of the two reaction conditions would generate the given molecule as the major product, circle those conditions. If both sets of conditions would accomplish the reaction, circle "BOTH". If neither set of reaction conditions would succeed, circle "NEITHER". **Circle one answer only.**

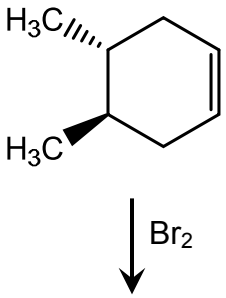

HgSO4
H2SO4
H2O
1. BH3•THF
2. H2O2, -OH
BOTH
would work
NEITHER
would work
C≡C—H
O
CH3


1. O3
2. Zn,
H2O
KMnO4
H2O, -OH
BOTH
would work
NEITHER
would work
H
O
O
H


Br2
hν
O
N—Br , hν
(NBS)
O
BOTH
would work
NEITHER
would work
Br

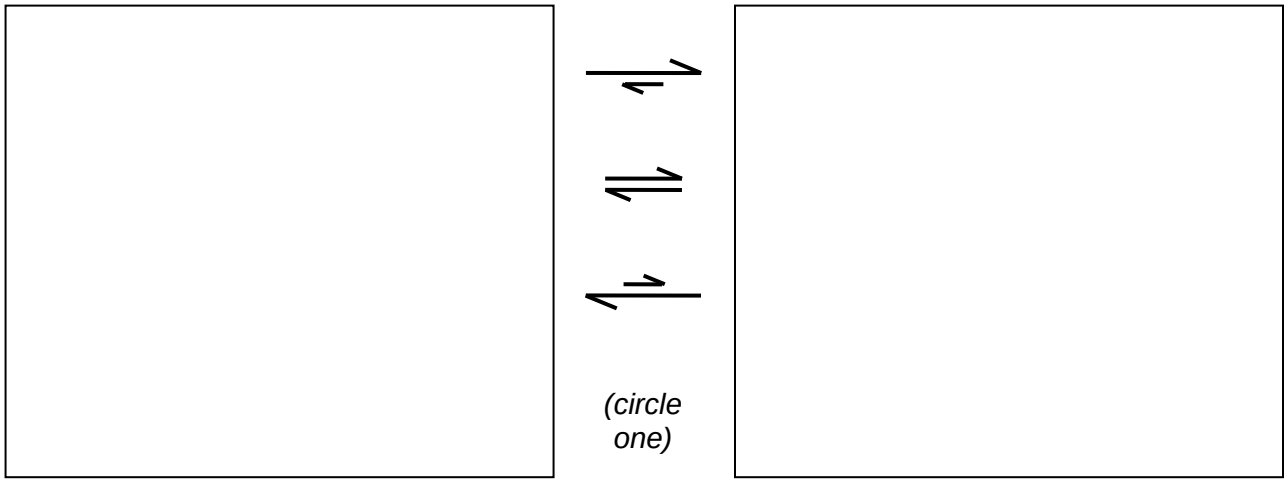

Na2Cr2O7
H2SO4
1. (COCl)2, DMSO
-60 °C
2. Et3N
(Swern oxidation)
BOTH
would work
NEITHER
would work
OH
O

6. (23 pts) The *trans*-dimethylcyclohexene starting material shown at right reacts with Br_2 to yield just one preferred product.

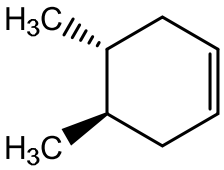


   a. **Draw the preferred product** as a pair of equilibrating cyclohexane chair conformers. Draw all non-hydrogen substituents, but feel free to omit H atoms.

   b. Which conformer is more stable? Indicate which chair is more stable, or that they are equally stable, by circling one of the three equilibrium arrows between them.

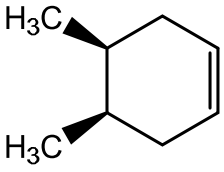


   c. Is the starting material **CHIRAL** or **ACHIRAL** ? *(Circle one.)*



   d. On the structure on the right, **label each chiral center** with its appropriate Cahn-Ingold-Prelog designation [(*R*) or (*S*)]. Make it clear which atom in the drawing you are labeling.

   e. What about the *cis*-dimethylcyclohexene at right—is this



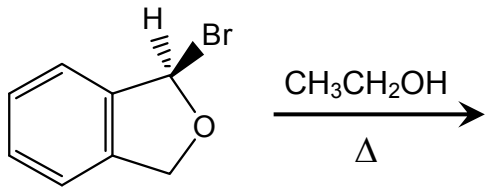
   CHIRAL or **ACHIRAL** ? *(Circle one.)*

   Once again, **label each chiral center** with its appropriate (*R*) or (*S*) designation.

   f. Are the *cis*- and *trans*-dimethylcyclohexenes above

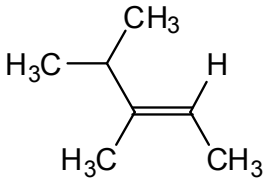
   ENANTIOMERS , **DIASTEREOMERS** , or **THE SAME MOLECULE** ?

7. (15 pts) For each of the reactions below, **fill in the empty box corresponding to the major product**. Wherever appropriate, illustrate stereochemistry in your drawings (using wedge and dashed bonds). If multiple enantiomers or diastereomers are produced, indicate this in the answer box (e.g., by writing "+ enantiomer", etc.)



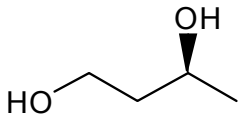
CH_3CH_2OH

Δ



BH_3

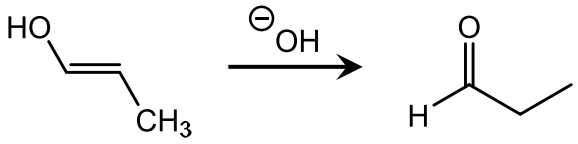
(no second step!)



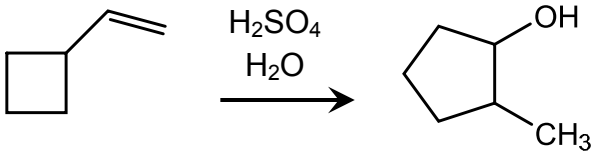
$Na_2Cr_2O_7$

H_2SO_4

8. (24 pts) **Draw a mechanism** (using "electron pushing") for each reaction or series of reactions shown on the next page. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "H-A" as a generic acid.)

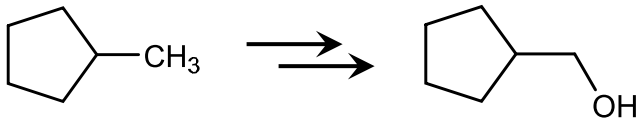


Mechanism:

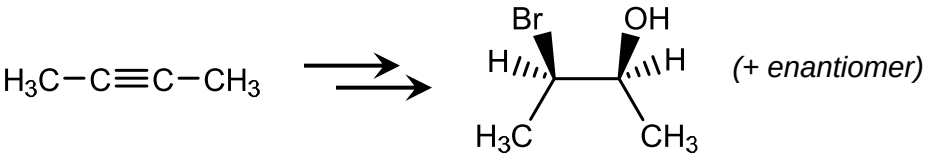


Mechanism:

9. (15 pts) For each set of starting materials and products shown below, **propose a multistep synthesis**. In addition to the molecules shown, you can use any reagents and reactions we've learned about in class. You might discover multiple answers to each problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



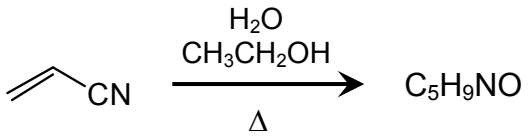
Multistep synthesis:



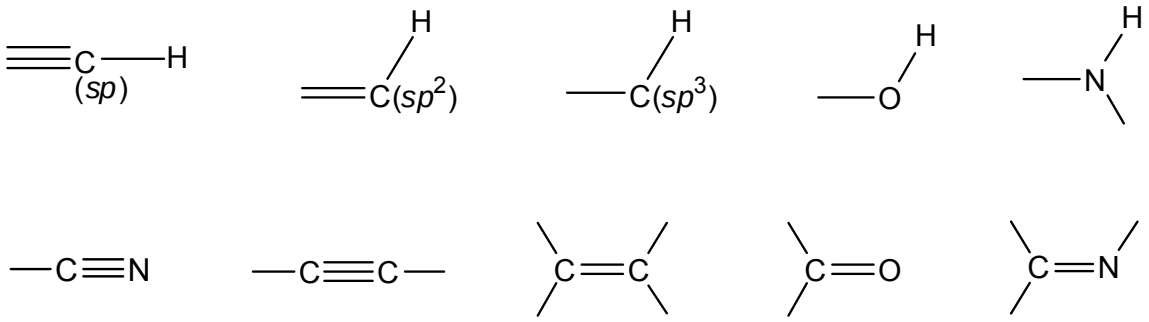
(+ enantiomer)

Multistep synthesis:

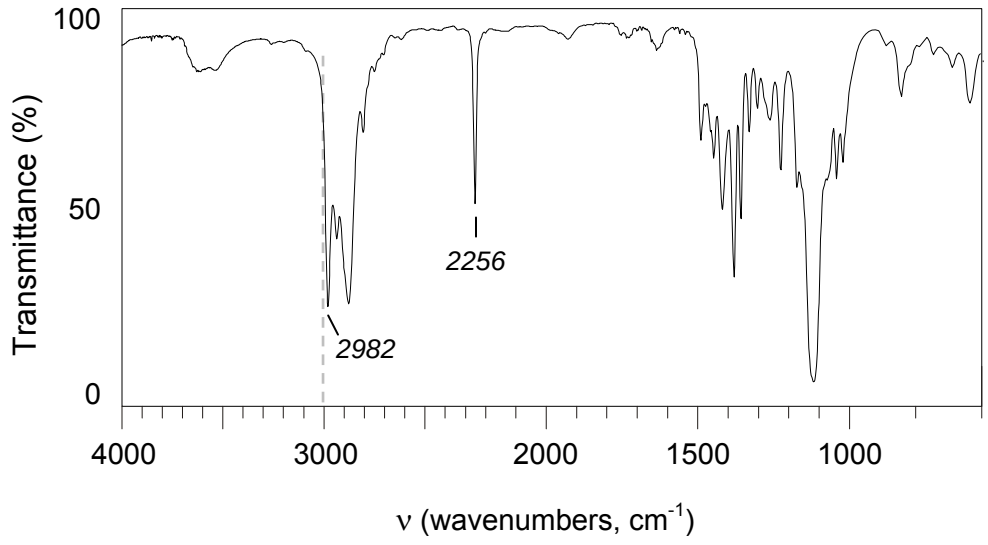
10. (26 pts) Acrylonitrile, the starting material on the right, can be polymerized into polyacrylonitrile (a component of plastic consumer goods) by heating it in solvent, but heating acrylonitrile in a mixture of ethanol and water generates a small molecule product instead. This product was isolated and characterized by NMR and IR spectroscopy and mass spectrometry; the spectra of this product are shown on the next two pages. High-resolution mass spectrometry determined an exact mass of 99.06840 amu for the highest-mass (parent, $\mathbf{M}^+$) peak in the MS spectrum, which corresponds to a molecular formula of **C_5H_9NO**.



a. Based on the features in the IR spectrum below, what functional groups would you expect the unknown molecule to have? **Circle all answers that apply.**



IR Spectrum:

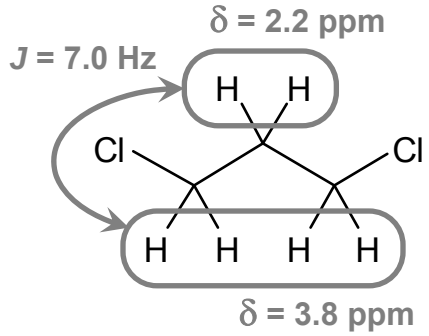


b. **What is the structure of the product**? In the box on the next page, draw the molecule's structure, <u>including all hydrogens</u>. Then, considering the ^{1}H NMR spectrum,

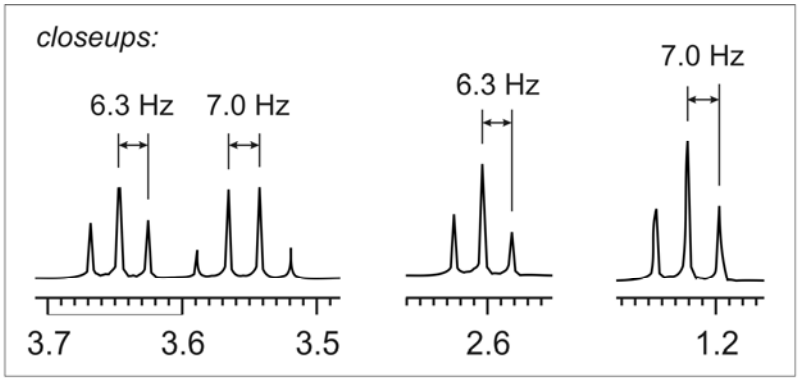
- Circle each group of equivalent H's;
- Assign a ^{1}H chemical shift (δ) to each circled group, within 0.05 ppm;
- Connect any pair of coupled, inequivalent groups of H's with a double-headed arrow, and then label that arrow with the corresponding coupling constant (*J*).

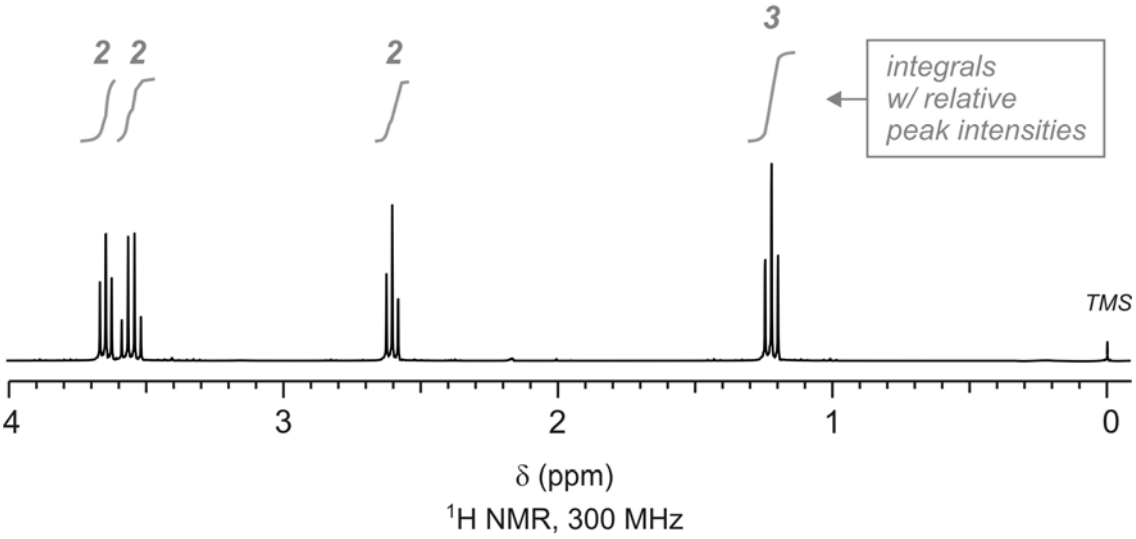
the product
(C_5H_9NO)

Format for answer to (c):

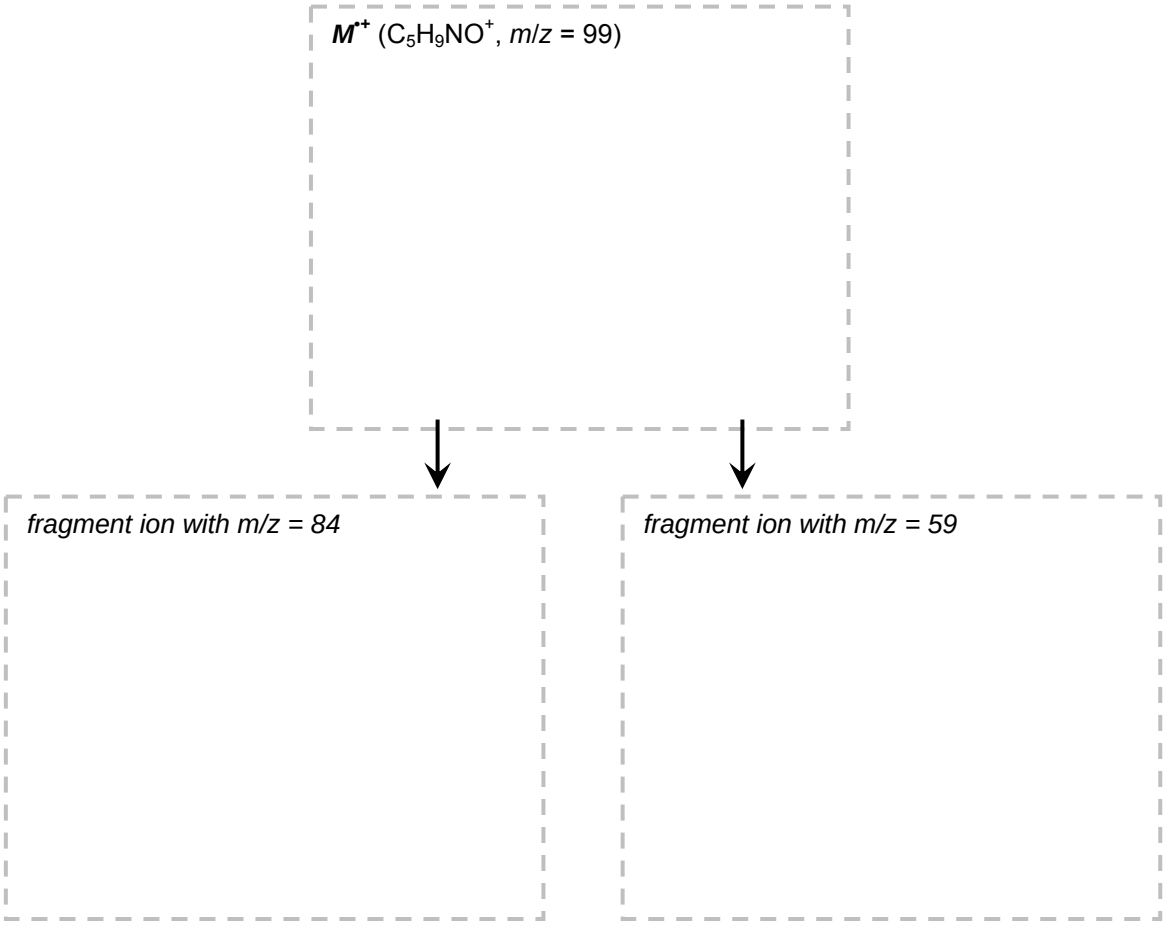


^{1}H NMR Spectrum:

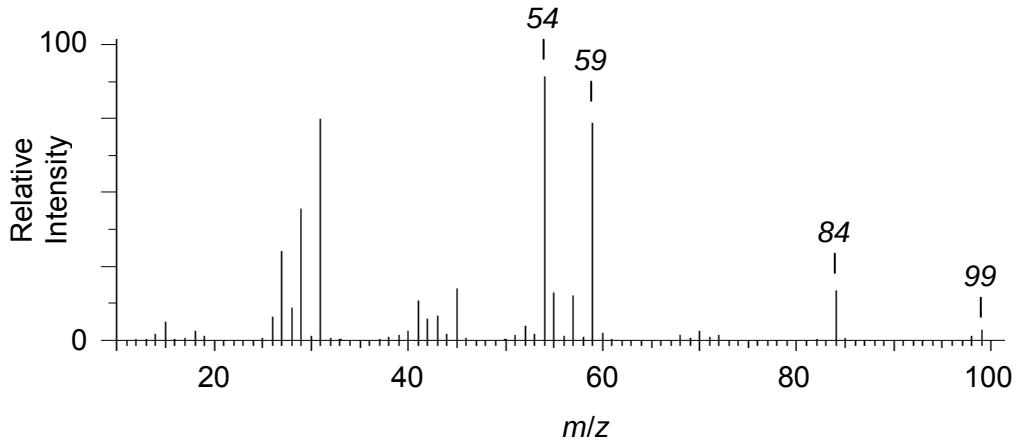




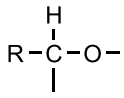
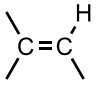
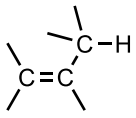
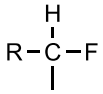
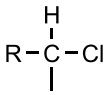
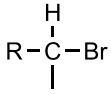
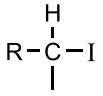
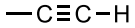
c. In an electron-ionization (EI) mass spectrometry experiment, parent ions often fragment into daughter ions that give information about the parent's molecular structure. In the EI mass spectrum below, the parent mass peak at m/z = 99 corresponds to a radical cation ($\mathbf{M}^{\bullet+}$) that fragments into ions with mass 84 and 59. In the boxes below, draw the structures of these ions. *You do not need to do electron pushing to answer this question—just draw the cations.* On all ion structures, make sure to specifically illustrate where the formal charge lies.

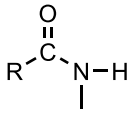
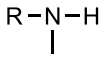
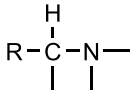
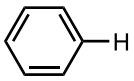
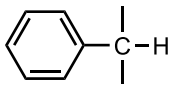
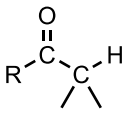
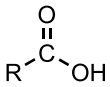
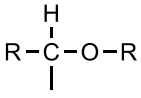


Mass Spectrum:

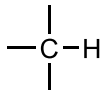
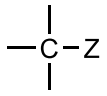
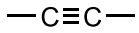
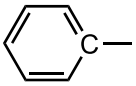


^{1}H NMR Chemical Shifts

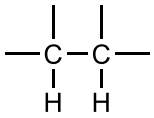
Compound Type	Chemical Shift (ppm)
Alcohol	
	1-5
	3.4-4.0
Aldehyde	
	9-10
Alkane	0.9-2.0
RCH_3	~0.9
R_2CH_2	~1.3
R_3CH	~1.7
Alkene	
 sp^2 C-H	4.5-6.0
 allylic sp^3 C-H	1.5-2.5
Alkyl Halide	
	4.0-4.5
	3.0-4.0
	2.7-4.0
	2.2-4.0
Alkyne	
	~2.5

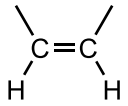
Compound Type	Chemical Shift (ppm)
Amide	
	7.5-8.5
Amine	
	0.5-5.0
	2.3-3.0
Aromatic compound	
 sp^2 C-H	6.5-8
 benzylic sp^3 C-H	1.5-2.5
Carbonyl compound	
 sp^3 C-H on the α carbon	2.0-2.5
Carboxylic acid	
	10-12
Ether	
	3.4-4.0

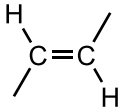
^{13}C NMR Chemical Shifts

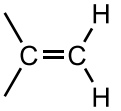
Carbon Type	Structure	Chemical Shift (ppm)
Alkyl, sp^3 hybridized C		5-45
Alkyl, sp^3 hybridized C bonded to N, O, or X	 Z = N, O, X	30-80
Alkynyl, *sp* hybridized C		65-100
Alkenyl, sp^2 hybridized C		100-140
Aryl, sp^2 hybridized C		120-150
Carbonyl C		160-210

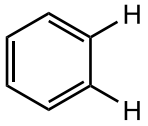
Typical ^{1}H-^{1}H Coupling Constants (*J*)

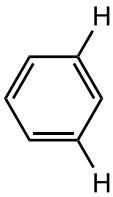
 (free rotation) ~7 Hz

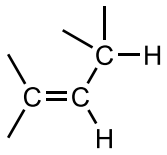
 (cis) 5-10 Hz

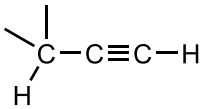
 (trans) 11-18 Hz

 (geminal) 0-3 Hz

 (ortho) ~8 Hz

 (meta) ~2 Hz

 (allylic) ~6 Hz

 (propargyl) ~2 Hz

IR Absorption Frequencies

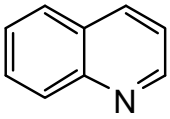
Bond	Functional group	Wavenumber (cm^{-1})	Comment
O – H			
	• ROH	3600–3200	broad, strong
	• RCOOH	3500–2500	very broad, strong
N – H			
	• RNH_2	3500–3300	two peaks
	• R_2NH	3500–3300	one peak
	• $RCONH_2$, RCONHR	3400–3200	one or two peaks; N – H bending also observed at 1640 cm^{-1}
C – H			
	• C_{sp} – H	3300	sharp, often strong
	• C_{sp^2} – H	3150–3000	medium
	• C_{sp^3} – H	3000–2850	strong
	• C_{sp^2} – H of RCHO	2830–2700	one or two peaks
C ≡ C		2250	medium
C ≡ N		2250	medium
C = O			strong
	• RCOCl	1800	
	• $(RCO)_2O$	1800, 1760	two peaks
	• RCOOR	1745–1735	increasing $\tilde{\nu}$ with decreasing ring size
	• RCHO	1730	
	• R_2CO	1715	increasing $\tilde{\nu}$ with decreasing ring size
	• R_2CO, conjugated	1680	
	• RCOOH	1710	
	• $RCONH_2$, RCONHR, $RCONR_2$	1680–1630	increasing $\tilde{\nu}$ with decreasing ring size
C = C			
	• Alkene	1650	medium
	• Arene	1600, 1500	medium
C = N		1650	medium

Final Exam Chart of Reaction Conditions

$Pt/H_2(g)$

$NaNH_2$

$Pd, BaSO_4$
$H_2(g)$



(quinoline)

(Lindlar's catalyst)

$Na_2Cr_2O_7$
H_2SO_4

PBr_3

1. $KMnO_4$
   KOH, Δ
2. H_3O^+

1. BH_3•THF
2. H_2O_2, OH^-

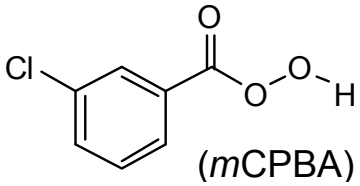
1. O_3
2. $(CH_3)_2S$
   or Zn, H_2O

Na
NH_3

$HgSO_4$
H_2SO_4
H_2O

1. $(COCl)_2$
   DMSO
   -60 °C
2. Et_3N
   (Swern oxidation)

H_2SO_4
H_2O



(*m*CPBA)

$KMnO_4$
(cold, dilute)
H_2O, OH^-

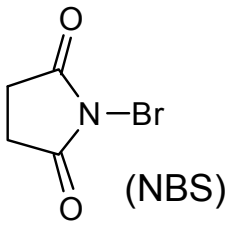
$SOCl_2$
pyridine

TsCl
pyridine

*m*CPBA
H_2O

1. O_3
2. H_2O

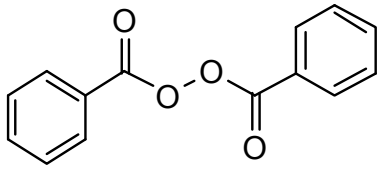
Cl_2 *or* Br_2,
$h\nu$



(NBS)

$h\nu$ *or* AIBN

HBr



(benzoyl peroxide)

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01	2 2A																2 **He** Helium 4.00
2	3 **Li** Lithium 6.94	4 **Be** Beryllium 9.01											5 **B** Boron 10.81	6 **C** Carbon 12.01	7 **N** Nitrogen 14.01	8 **O** Oxygen 16.00	9 **F** Fluorine 19.00	10 **Ne** Neon 20.18
3	11 **Na** Sodium 22.99	12 **Mg** Magnesium 24.31	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 **Al** Aluminum 26.98	14 **Si** Silicon 28.09	15 **P** Phosphorus 30.97	16 **S** Sulfur 32.07	17 **Cl** Chlorine 35.45	18 **Ar** Argon 39.95
4	19 **K** Potassium 39.10	20 **Ca** Calcium 40.08	21 **Sc** Scandium 44.96	22 **Ti** Titanium 47.87	23 **V** Vanadium 50.94	24 **Cr** Chromium 52.00	25 **Mn** Manganese 54.94	26 **Fe** Iron 55.85	27 **Co** Cobalt 58.93	28 **Ni** Nickel 58.69	29 **Cu** Copper 63.55	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.72	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92	34 **Se** Selenium 78.96	35 **Br** Bromine 79.90	36 **Kr** Krypton 83.80
5	37 **Rb** Rubidium 85.47	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.91	40 **Zr** Zirconium 91.22	41 **Nb** Niobium 92.91	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.91	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.87	48 **Cd** Cadmium 112.41	49 **In** Indium 114.82	50 **Sn** Tin 118.71	51 **Sb** Antimony 121.76	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90	54 **Xe** Xenon 131.29
6	55 **Cs** Cesium 132.91	56 **Ba** Barium 137.33	57 **La** Lanthanum 138.91	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.95	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.21	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.22	78 **Pt** Platinum 195.08	79 **Au** Gold 196.97	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.38	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
7	87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (269)	109 **Mt** Meitnerium (268)									

58 **Ce** Cerium 140.12	59 **Pr** Praseodymium 140.91	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.96	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.93	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.97
90 **Th** Thorium 232.04	91 **Pa** Protactinium 231.04	92 **U** Uranium 238.03	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Key

11 — Atomic number
Na — Element symbol
Sodium — Element name
22.99 — Average atomic mass*

* If this number is in parentheses, then it refers to the atomic mass of the most stable isotope.