NAME ________________________

ID # ________________________

ORGANIC CHEMISTRY II (2302)

1:30 pm – 3:30 pm, May 12, 2016

Final Exam

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Tuesday, May 17th at 11 AM. Exams that are not picked up within two weeks will be disposed of.

Tables of amino acid and nucleic acid structures, a chart of reaction conditions, and a periodic table are attached to the back of this exam as an aid. 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.

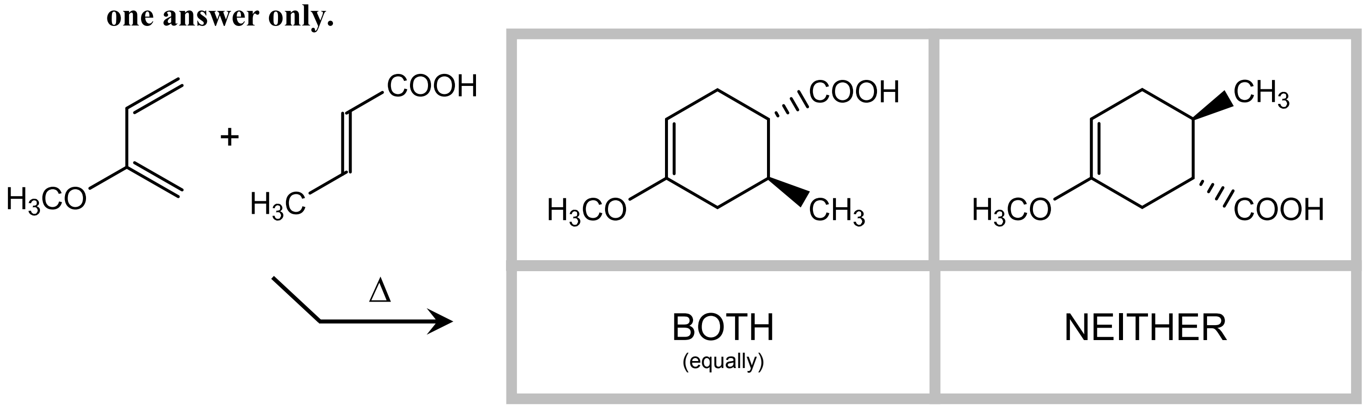
Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

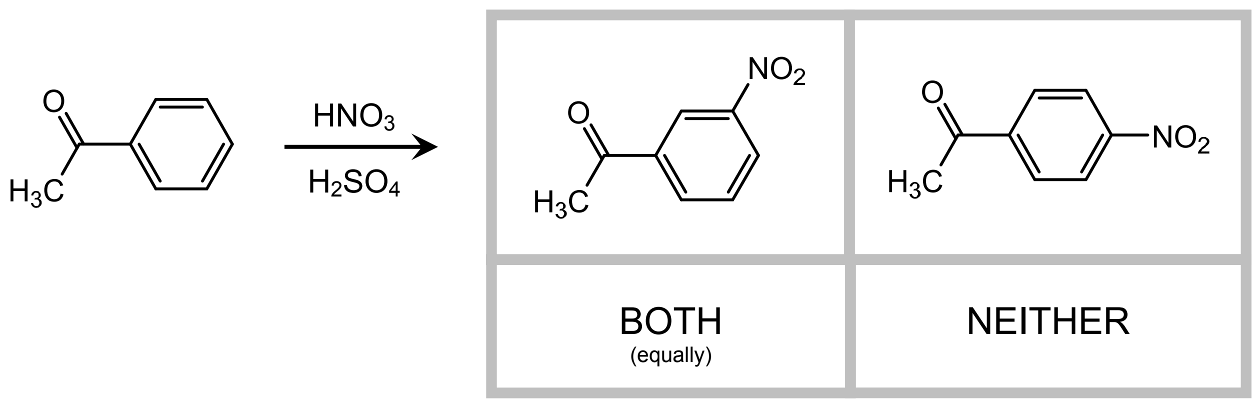
NAME ___________________________

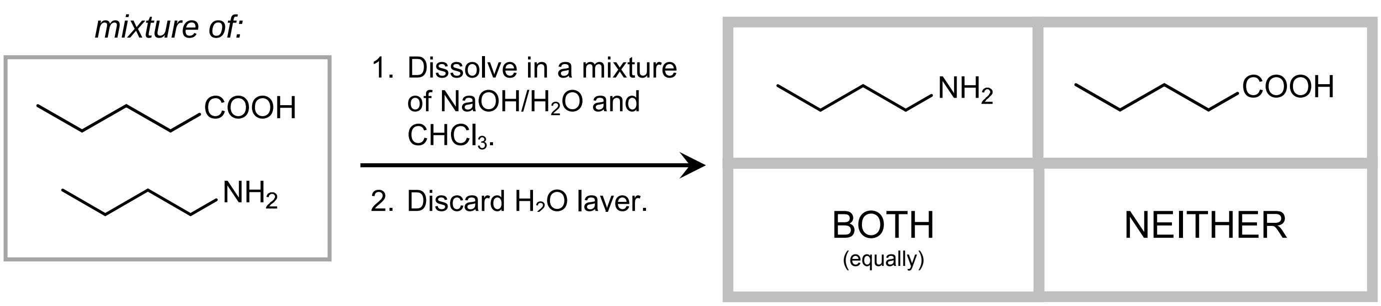
Scoring:		
	1. _________ / 32	6. _________ / 38
	2. _________ / 17	7. _________ / 32
	3. _________ / 6	8. _________ / 11
	4. _________ / 16	9. ________ / 8
	5. _________ / 20	10. ________ / 20

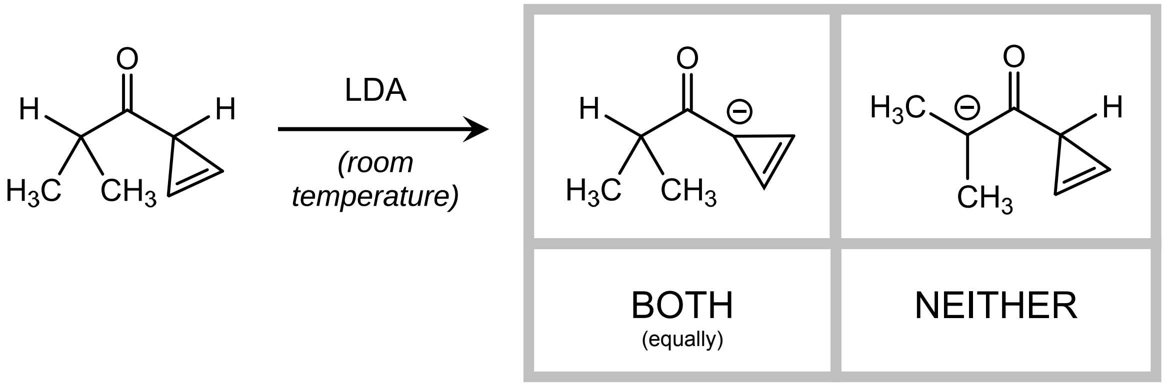
Total Score: _________ / 200

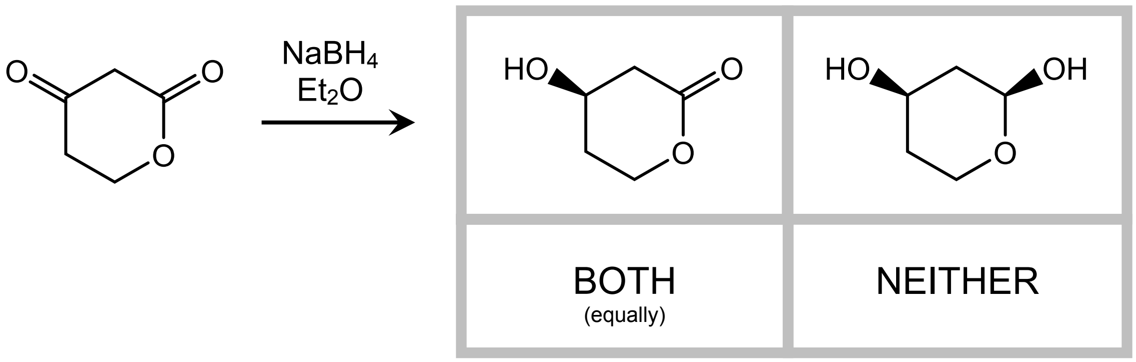
1. (32 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

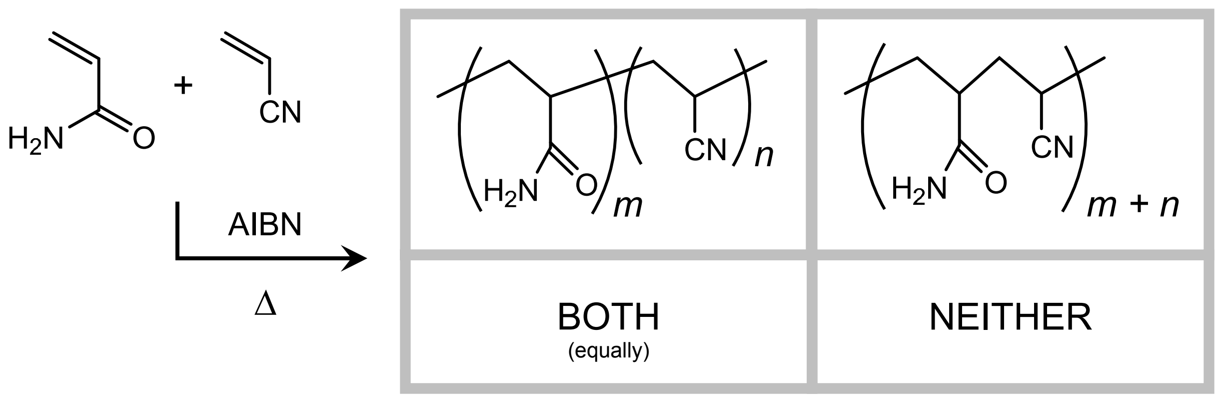


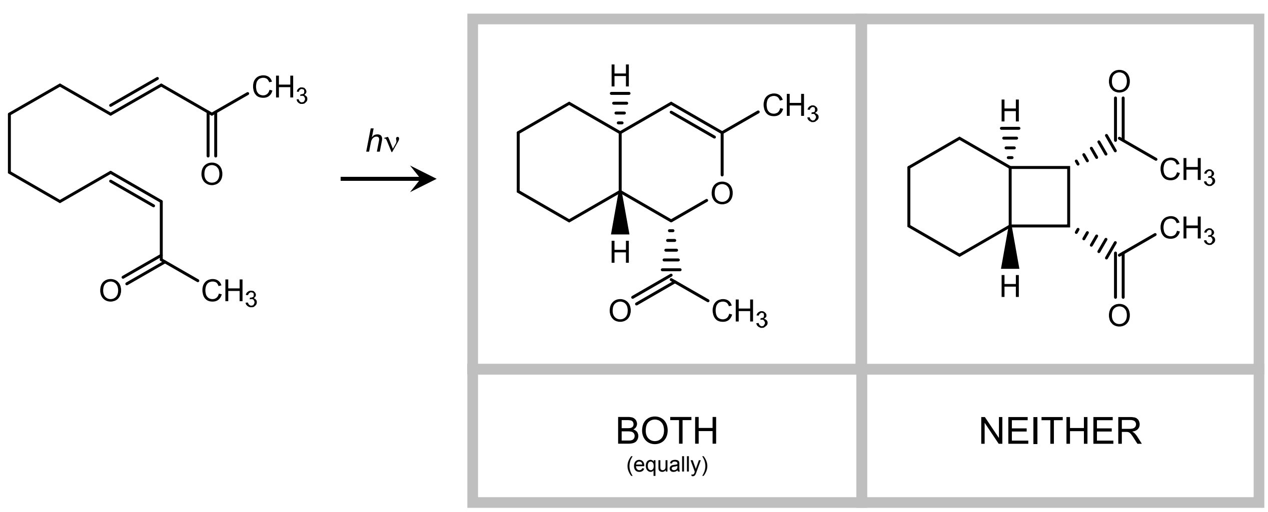


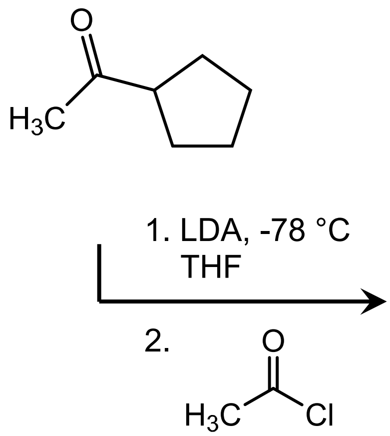


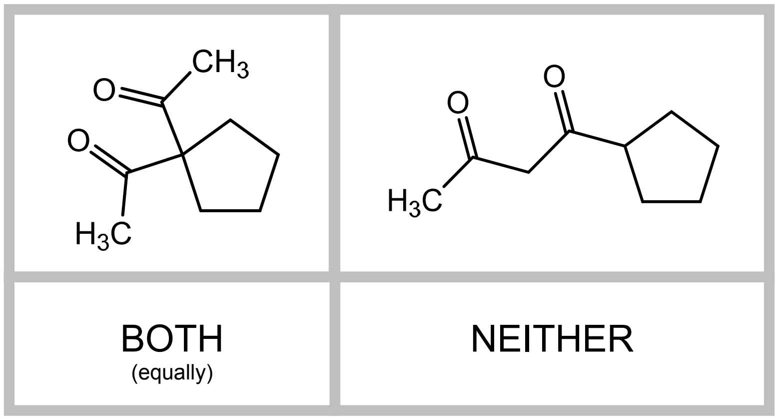

LDA
(room temperature)
BOTH
(equally)
NEITHER


NaBH4
Et2O
BOTH
(equally)
NEITHER


AIBN
Δ
m
n
m + n
BOTH
(equally)
NEITHER


hν
BOTH
(equally)
NEITHER

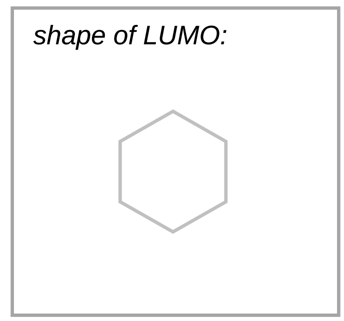


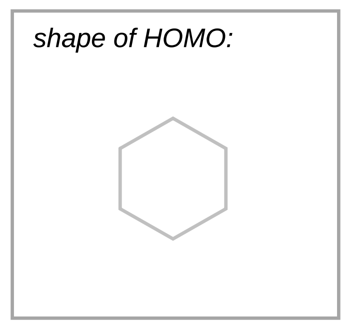


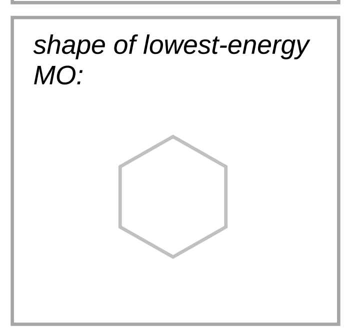
2. (17 pts) Benzene is a prototypical aromatic molecule. Benzene's aromaticity has sometimes been explained s by using a molecular orbital diagram.

   a. On the energy diagram below, **draw a molecular orbital (MO) diagram** for the conjugated π orbitals in benzene.
      - Draw all orbital energy levels as horizontal lines;
      - Fill your orbitals with the appropriate number of electrons.

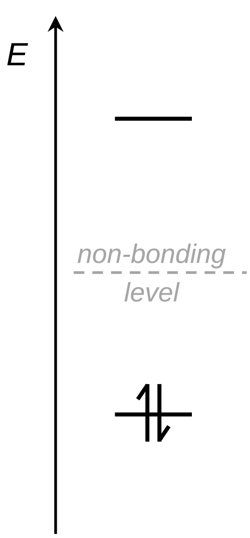
   b. In the boxes on the right, draw the shapes of benzene's LUMO, HOMO, and lowest-energy molecular orbital as combinations of atomic orbital lobes, viewed from the top of the molecule. If there is more than one LUMO, HOMO or lowest-energy orbital, just draw one. I have drawn the framework of benzene in each box; draw each orbital right on top of that.

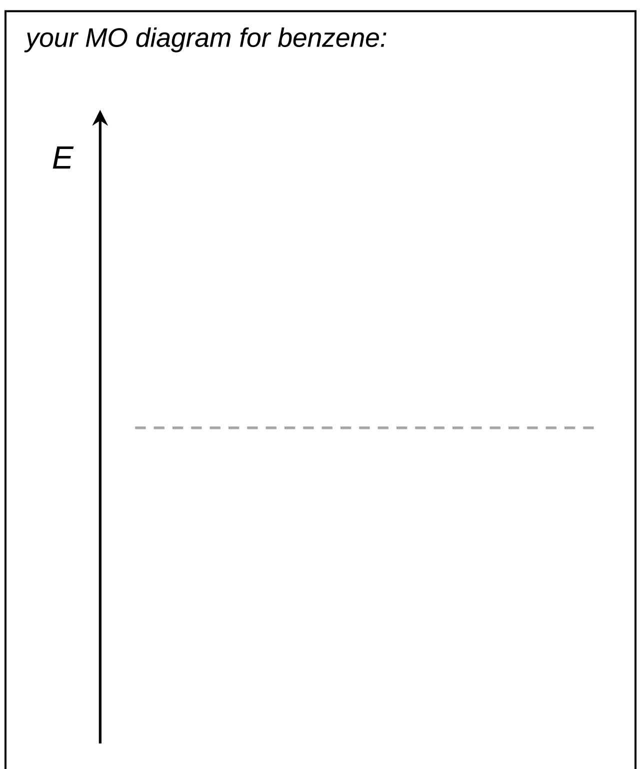


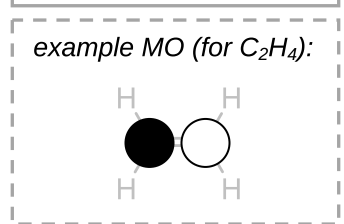




example of an MO diagram (for C_2H_4):

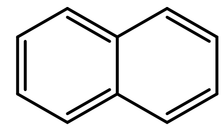






c. On your MO diagram on the previous page, draw a vertical arrow to illustrate an electronic transition that could be observed as an absorption peak in the UV/vis spectrum of benzene. Label the arrow "λ".

d. How would you expect the optical absorbance of benzene to compare to that of naphthalene (shown at right)? Would you expect



naphthalene

λ_{max}(naphthalene) to be **>** , **<** , *or* **=** λ_{max}(benzene)? *(Circle one.)*

e. Double bond hydrogenation is always exothermic—or, put another way, ΔH_{hyd} is always negative. The Lewis structure of benzene is drawn with three double bonds, and exhaustive hydrogenation of benzene would involve three consecutive additions of H_2. How does ΔH_{hyd}[benzene] compare to hydrogenation of a three typical alkenes, like ethylene? Is

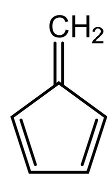
ΔH_{hyd}[benzene] **>** , **<** , *or* **=** 3 x ΔH_{hyd}[ethylene]? *(Circle one.)*

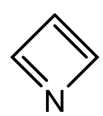
3. (6 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.

AROMATIC

ANTI-AROMATIC

NEITHER



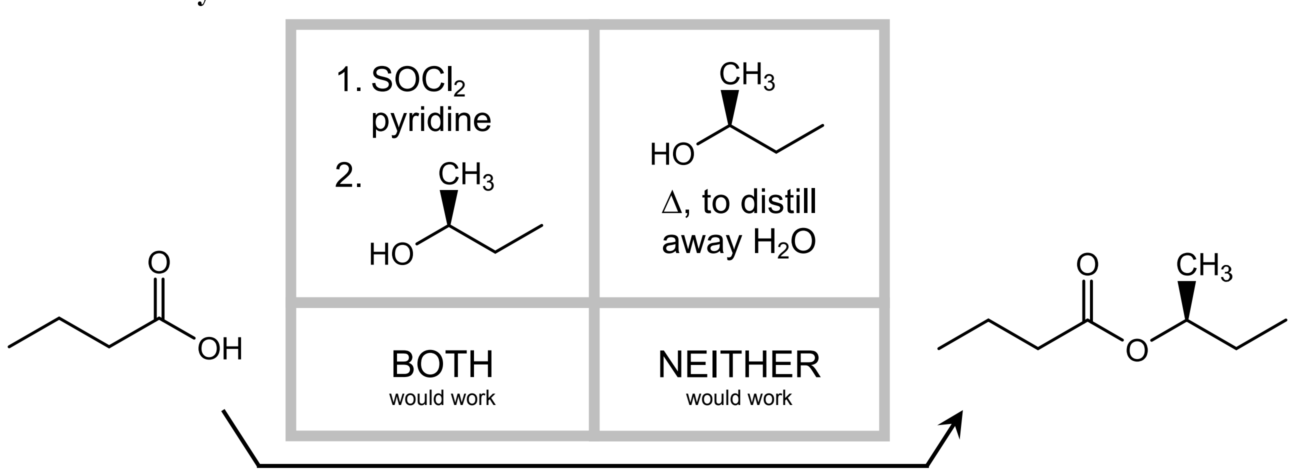


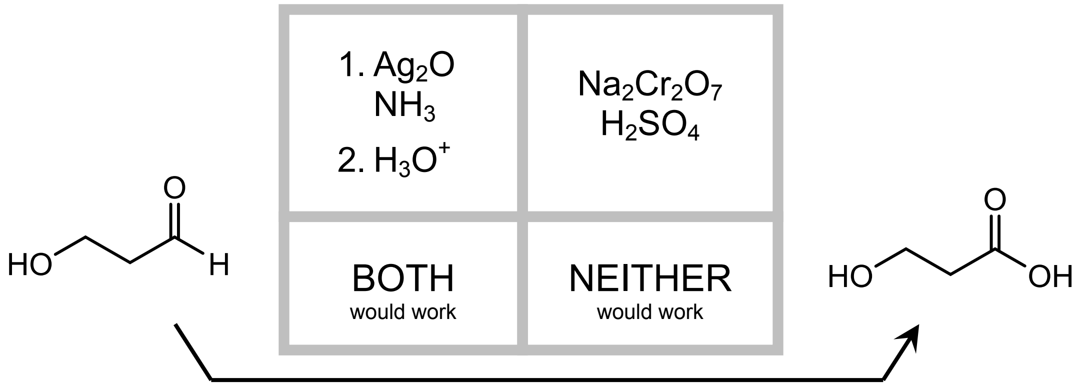
AROMATIC

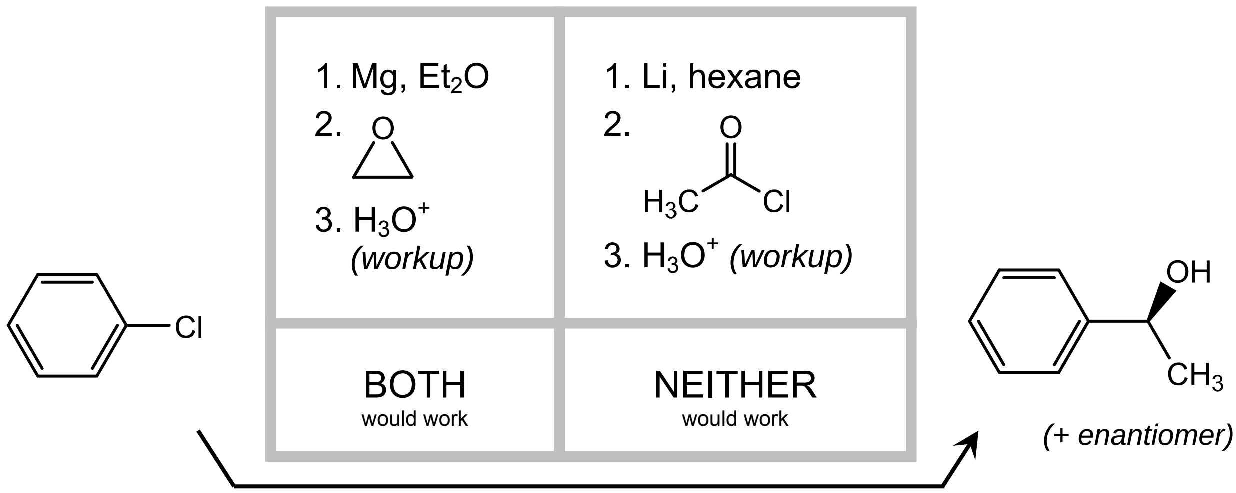
ANTI-AROMATIC

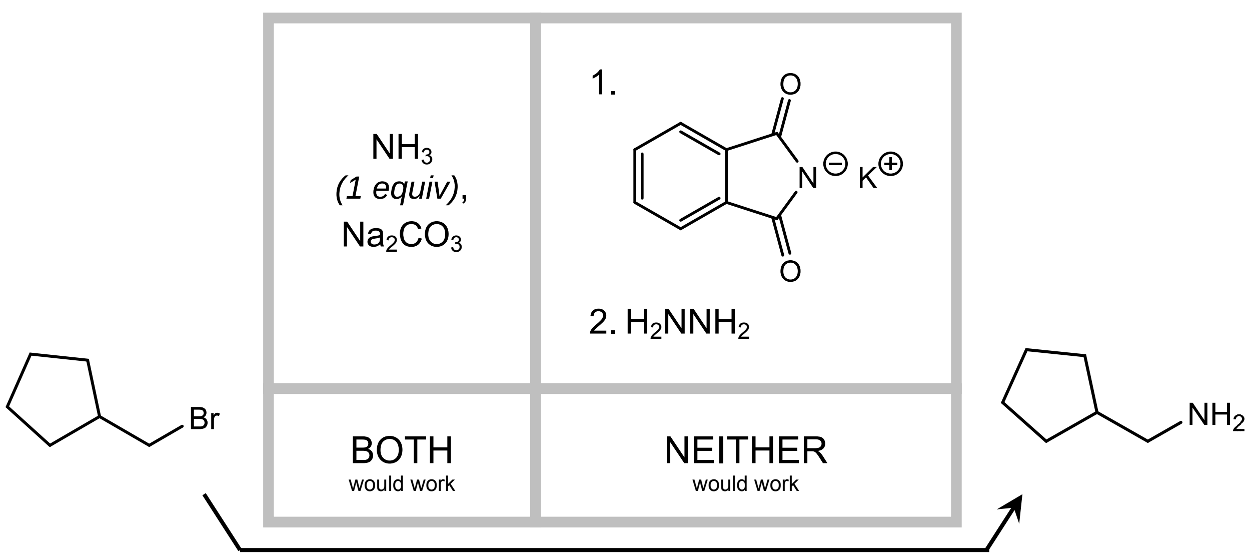
NEITHER

4. (16 pts) Each of the reactions below 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.**

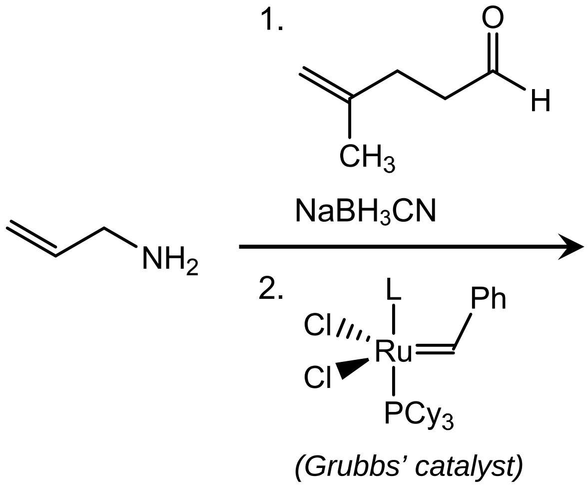


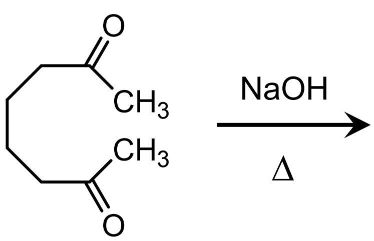


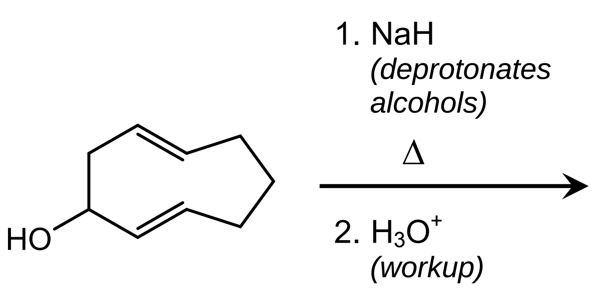


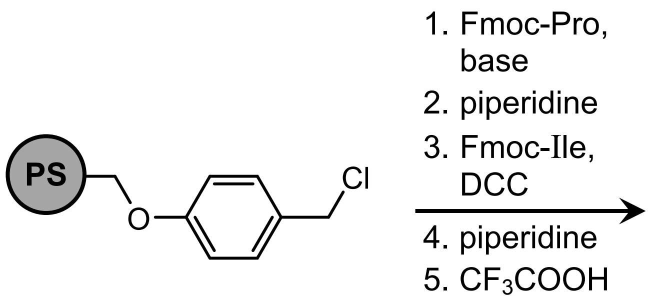


5. (20 pts) For each of the reactions below, fill in the empty box corresponding to reagents or product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".


1.
O
H
CH3
NaBH3CN
NH2
2.
L
Ph
Cl
Ru
Cl
PCy3
(Grubbs' catalyst)

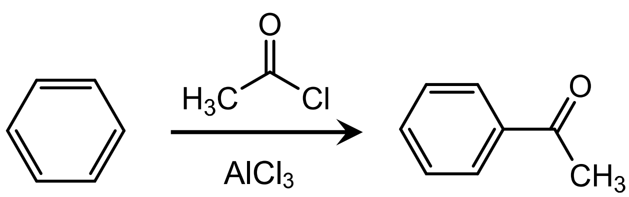

O
CH3
CH3
O
NaOH
Δ


1. NaH
(deprotonates
alcohols)
Δ
HO
2. H3O+
(workup)

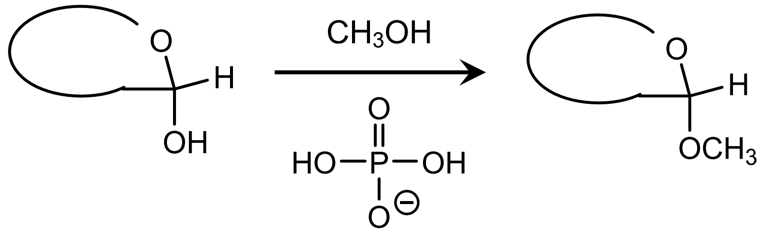


*do **not** use abbreviations*

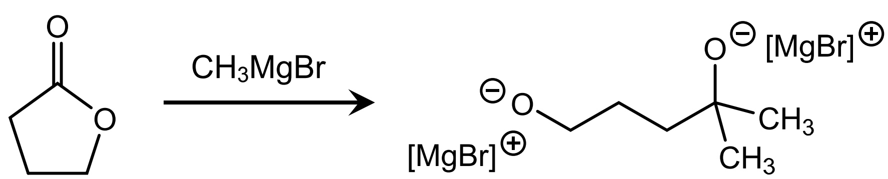
6. (38 pts) **Draw a mechanism** (using "electron pushing") for each of the reactions shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step, or by taking shortcuts. Use only the molecules shown in the problem.



Mechanism:

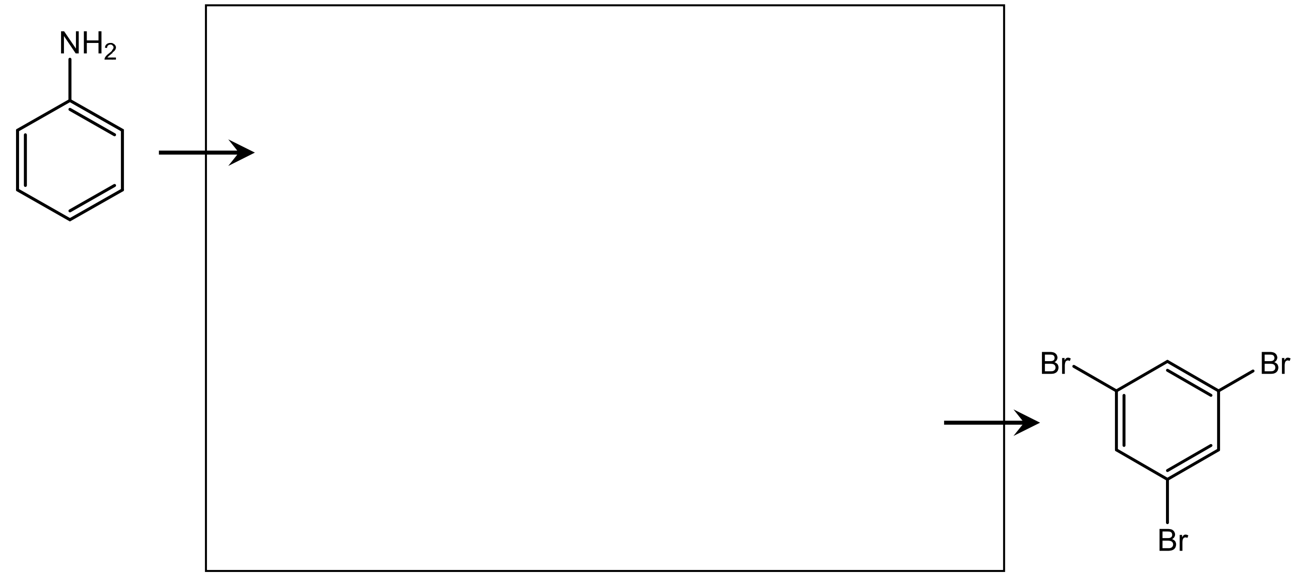


Mechanism:

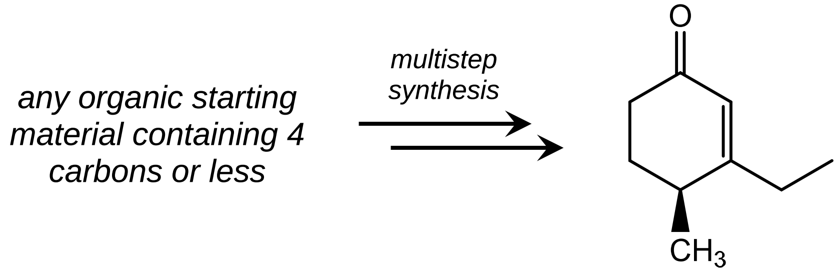


Mechanism:

7. (32 pts) Each of the syntheses shown below can be accomplished in a few steps. For each synthesis, fill in the empty boxes with any appropriate reagents (or sets of reagents) and synthetic intermediates.

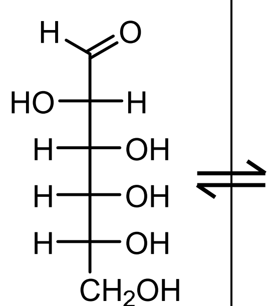


On the next page:



8. (11 pts) The acyclic structure of D-altrose, an epimer of glucose, is shown below as a Fischer projection.

   a. Acyclic D-altrose equilibrates with a cyclic, 6-membered-ring, α-anomer altropyranose form. Draw the cyclic α-anomer as a chair conformer in the box at right.



cyclic α-D-altropyranose
(chair conformer)

   b. What is the timescale of this equilibrium? Does it take place spontaneously over

      minutes? **weeks?** *or* **decades?** *(Circle one.)*

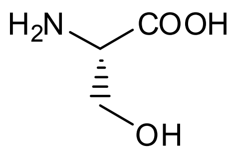
   c. The equilibrium above is responsible for **mutarotation**—the process by which α and β anomers in a monosaccharide equilibrate with each other. By comparison, how quickly do disaccharide, C1 glycosides of altrose undergo mutarotation? Do altrose glycosides exchange α and β anomers

      faster , **slower** , *or* **at the same rate**

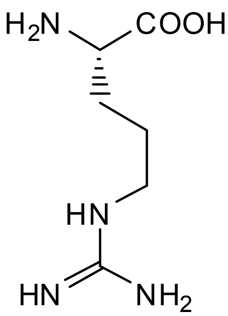
   compared to monosaccharides? *(Circle one.)*

9. (8 pts)

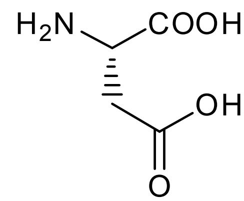
a. Sort the three amino acids serine (Ser), arginine (Arg), and aspartic acid (Asp) in order of increasing isoelectric point (pI). Write their three-letter abbreviations in the appropriate boxes below.



serine (Ser)



arginine (Arg)



aspartic acid (Asp)

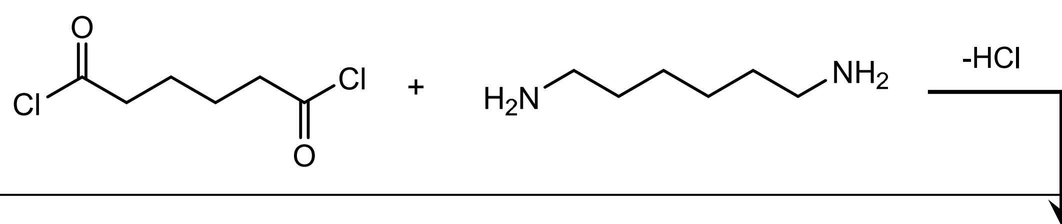
lowest pI [ ] [ ] [ ] **highest pI**

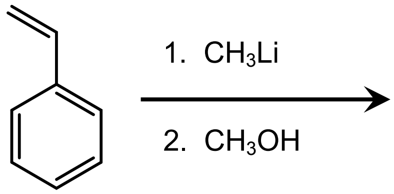
b. If these three amino acids were analyzed by ion exchange chromatography, using an anionic column subjected to a solvent gradient of gradually increasing pH, what would be the order of elution of these three amino acids?

elutes first [ ] [ ] [ ] **elutes last**

10. (20 pts)

a. For each of the polymer syntheses proposed below, draw the polymer product using bracket notation ("[-M-]$_n$"). If n is known, define it. If there is a part of the polymer structure that isn't known (*e.g.*, the initiating or terminating group), draw this as a squiggle in your structure.





"polymer **A**"

b. In the box below, draw a mechanism for the initiation step and the first propagation step in the formation of polymer **A** above, using "electron pushing".

Mechanism:

c. If half as much styrene monomer were used in the synthesis above, the average product "polymer **B**" molecule would be half as long. How would the mobility of polymer **B** in gel permeation chromatography (GPC) relate to polymer **A**? Would polymer **B** elute

earlier than , **later than** *or* **at the same time as**

polymer **A**? *(Circle one.)*

Final Exam Chart of Reaction Conditions

Br_2, $FeBr_3$

Cl_2, $AlCl_3$

H_2SO_4, HNO_3

Sn *or* Fe, HCl/H_2O

H_2SO_4, SO_3

$KMnO_4$, ^{-}OH, 100 °C

Mg, Et_2O

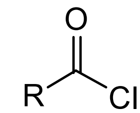
1. $NaNO_2$, HCl
2. CuCN *or* H_3PO_2 *or* CuX *or* H_3O^+

R-X (R = alkyl), $AlCl_3$ *or* $FeBr_3$

Zn(Hg), HCl/H_2O

Li, hexane

H_2, Pd-C



$AlCl_3$

1. N_2H_4
2. KOH, Δ

1. O_3
2. H_2O

RMgX

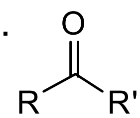
RLi

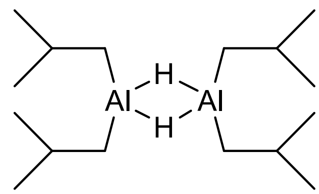
R_2CuLi

$Na_2Cr_2O_7$, H_2SO_4

$LiAlH(OtBu)_3$

1. Ag_2O, NH_3
2. H_3O^+

1. PPh_3
2. *n*-BuLi
3. 



(DIBAL-H)

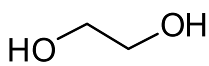
$Bu_4N^+F^-$

$PhCH_2Br$, Ag_2O

1. $LiAlH_4$
2. H_2O

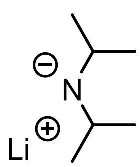
$(COCl)_2$

$(CH_3)_3SiCl$ {TMSCl}, *or* TBDMSCl; Et_3N *or* imidazole



HCl

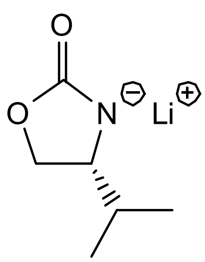
$NaNH_2$



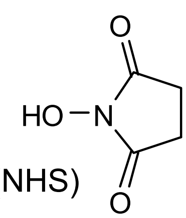
(LDA)

$SOCl_2$ (& pyridine, usually)

1. $NaBH_4$
2. H_2O

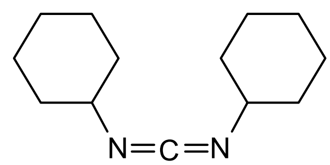
1. 

2. base
3. R-X
4. LiOH



(NHS)

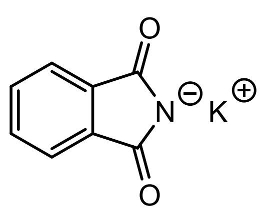
1. CH_3I (excess)
2. Ag_2O, H_2O
3. Δ



(DCC)

$CHCl_3$, KO*t*Bu

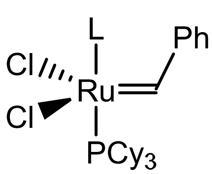
RCHO, $Na(OAc)_3BH$ *or* $NaBH_3CN$

1. 

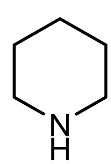
2. N_2H_4 (or ^{-}OH)

1. PhNCS
2. H^+

(Edman degradation)



(Grubbs catalyst)



1. NaN_3
2. PPh_3, H_2O

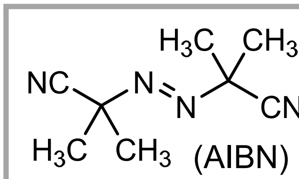
HF

$Pd(PPh_3)_4$, NaOH

CH_2I_2, Zn(Cu)

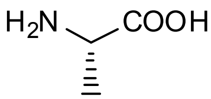
$Pd(OAc)_2$, PPh_3, NEt_3

CF_3COOH

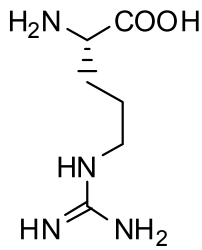


(AIBN)

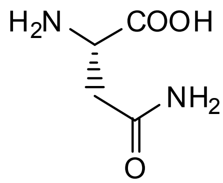
Final Exam Chart of Amino Acids
(in Alphabetical Order)



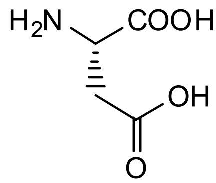
alanine
(Ala, A)



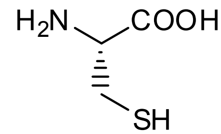
arginine
(Arg, R)



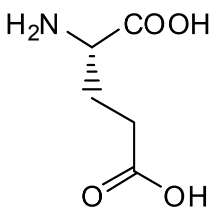
asparagine
(Asn, N)



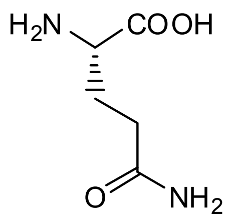
aspartic acid
(Asp, D)



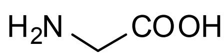
cysteine
(Cys, C)



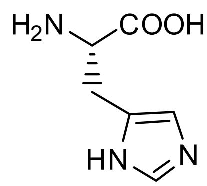
glutamic acid
(Glu, E)



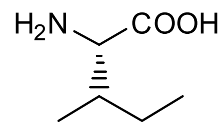
glutamine
(Gln, Q)



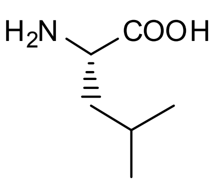
glycine
(Gly, G)



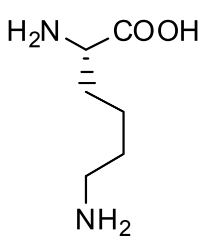
histidine
(His, H)



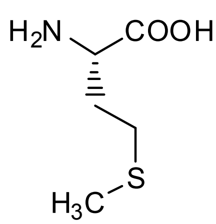
isoleucine
(Ile, I)



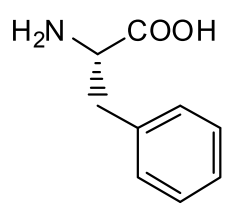
leucine
(Leu, L)



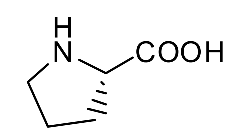
lysine
(Lys, K)



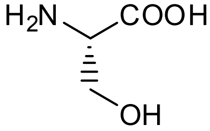
methionine
(Met, M)



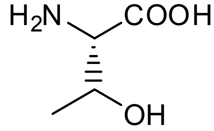
phenylalanine
(Phe, F)



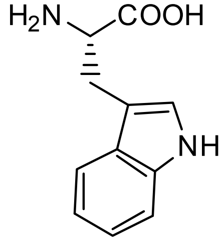
proline
(Pro, P)



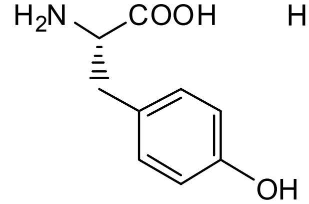
serine
(Ser, S)



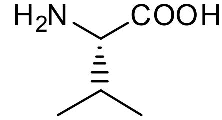
threonine
(Thr, T)



tryptophan
(Trp, W)

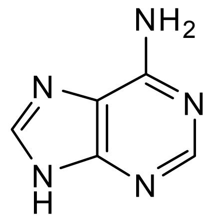


tyrosine
(Tyr, Y)

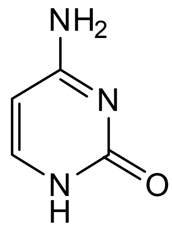


valine
(Val, V)

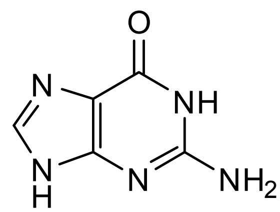
Final Exam Chart of Nucleic Acid Bases
(in Alphabetical Order)



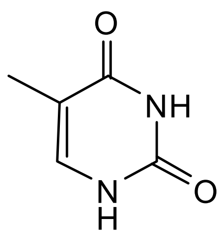
adenine
(A)



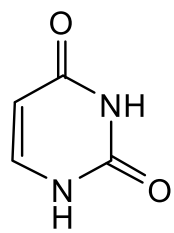
cytosine
(C)



guanine
(G)



thymine
(T)



uracil
(U)

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

Key

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

Period	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** Hydrogen 1.01																	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											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)

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