NAME _____

ID # _____

ORGANIC CHEMISTRY II (2302)

9:05 – 9:55 am, May 4, 2016

Exam 4

If you want to pick this exam up Friday in class (in public), please check the box on the right: ☐

If you do not check the box, I will not bring your exam to class on Friday, and you will need to pick up your exam in private from Chemistry department staff in 115 Smith beginning Monday, May 9th. Exams that are not picked up within two weeks will be disposed of.

A periodic table, a chart of reaction conditions, and charts of nucleic and amino acid structures 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).

Right now, write your name and student ID number at the top of this page. 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 _____

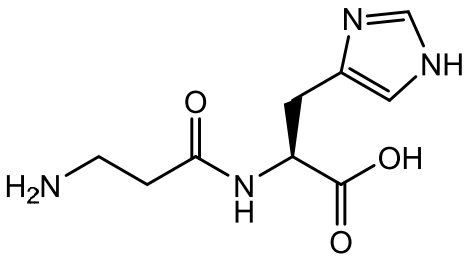
Scoring: 1. _____ / 25 4. _____ / 20

2. _____ / 14 5. _____ / 12

3. _____ / 13 6. _____ / 16

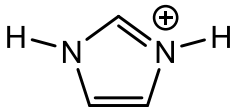
Total Score: _____ / 100

1. (25 pts) Carnosine (shown at right) is an antioxidant dipeptide found in muscle. Carnosine is unusual in that it contains β-glycine—a variant of glycine that contains two carbons in between the amine and the carboxylic acid, rather than just one.



carnosine

Helpful information for this problem:



imidazolium (pK_a = 6.9)

a. In the box at right, draw the structure of carnosine that you would expect to find most commonly at its isoelectric point (pI).

carnosine structure at pH = pI:

b. What would you predict for the isoelectric point (pI) of carnosine?

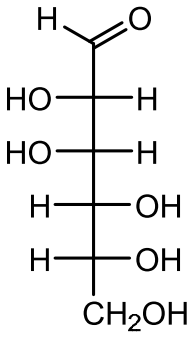
pI = ☐

c. Carnosine could be synthesized via solid-phase peptide synthesis, using *t*Boc-protected β-glycine ("*t*Boc-β-Gly") as a reagent. Draw the complete chemical structure of *t*Boc-β-Gly in the box at right.

structure of tBoc-β-Gly:

d. In the box below, propose a multistep solid-phase synthesis of carnosine, using chloromethylated polystyrene ("PS—Cl") and the *t*Boc-protected amino acids *t*Boc-β-Gly and *t*Boc-His. In addition to these starting materials, you can use any reagents and reactions we've learned about in class. You do not need to draw any chemical structures to answer this problem; you can refer to molecules by name or chemical abbreviation.

2. (14 pts) D-Mannose, like D-glucose, is an aldohexose. The acyclic structure of mannose is shown at right, as a Fischer projection.



D-mannose

a. Acyclic D-mannose equilibrates with a cyclic, 6-membered-ring, α-anomer mannopyranose form. Draw the most stable chair conformer of that cyclic α-anomer in the box on the next page on the left.

b. The α-anomer is influenced by the "anomeric effect", a specific molecular orbital interaction. Illustrate that molecular orbital interaction on your drawing on the next page, drawing lobes for orbitals.

c. Does the anomeric effect stabilize

the α-anomer more? **the β-anomer more?** *or* **both anomers equally?**

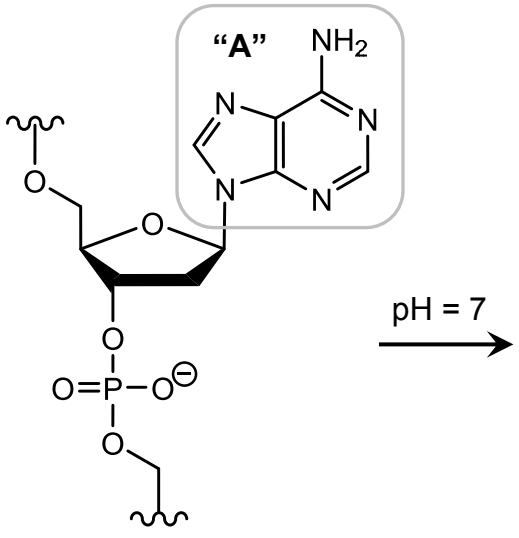
(Circle one answer.)

d. The 6-membered α-D-mannopyranose you drew below, on the left, equilibrates with a 5-membered-ring, α-furanose form. Draw that 5-membered ring as a Haworth projection in the box on the right.

*cyclic α-D-manno**pyranose** (chair conformer), with anomeric effect shown w/ orbitals*	*cyclic D-manno**furanose** (Haworth projection)*

3. (13 pts)
   a. A generic structure of an adenine nucleotide in DNA is shown below. **Draw one change to that structure** so that it shows RNA instead. Draw directly onto my structure—there is no need to draw a whole new molecule.

   b. This change helps RNA undergo intramolecular cleavage. In the box below, draw the cyclic phosphate that is formed from RNA strand cleavage at pH = 7. Feel free to abbreviate the adenine base as "**A**".



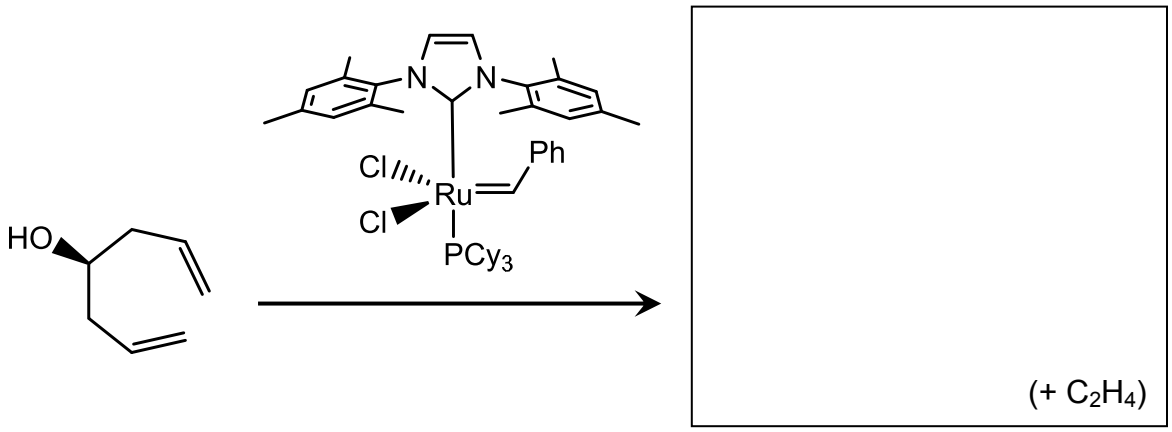
RNA cleavage product

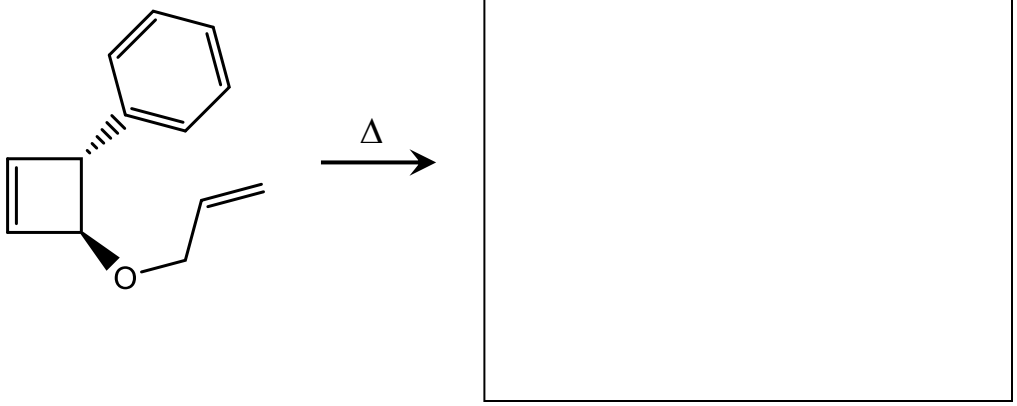
   c. On your drawing above, add curved arrows to illustrate the first step in the mechanism of this cleavage reaction.

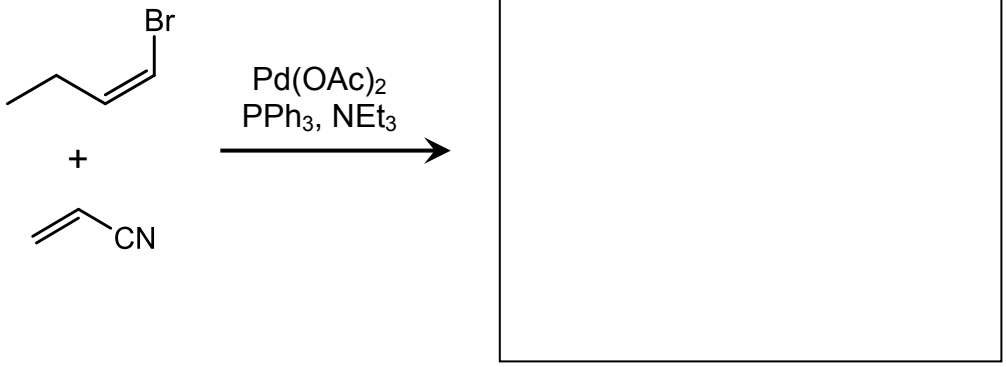
d. At pH = 7, which of the following statements about DNA and RNA is true?

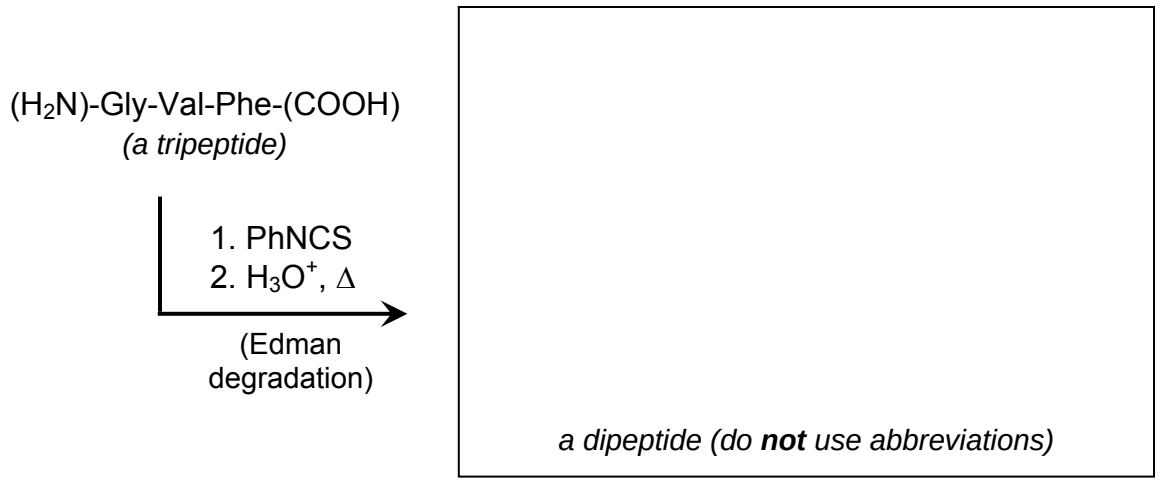
RNA is more stable than DNA.	**RNA is less stable than DNA.**	*or*	**RNA and DNA are equally stable.**	*(Circle one.)*

4. (20 pts) For each of the reactions below, fill in the empty box corresponding to products. 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".

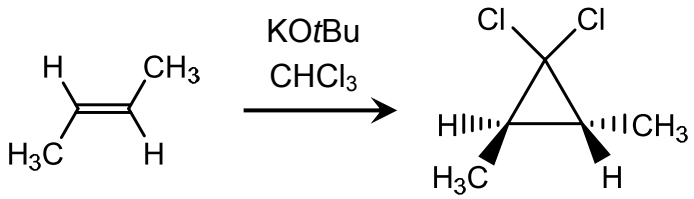








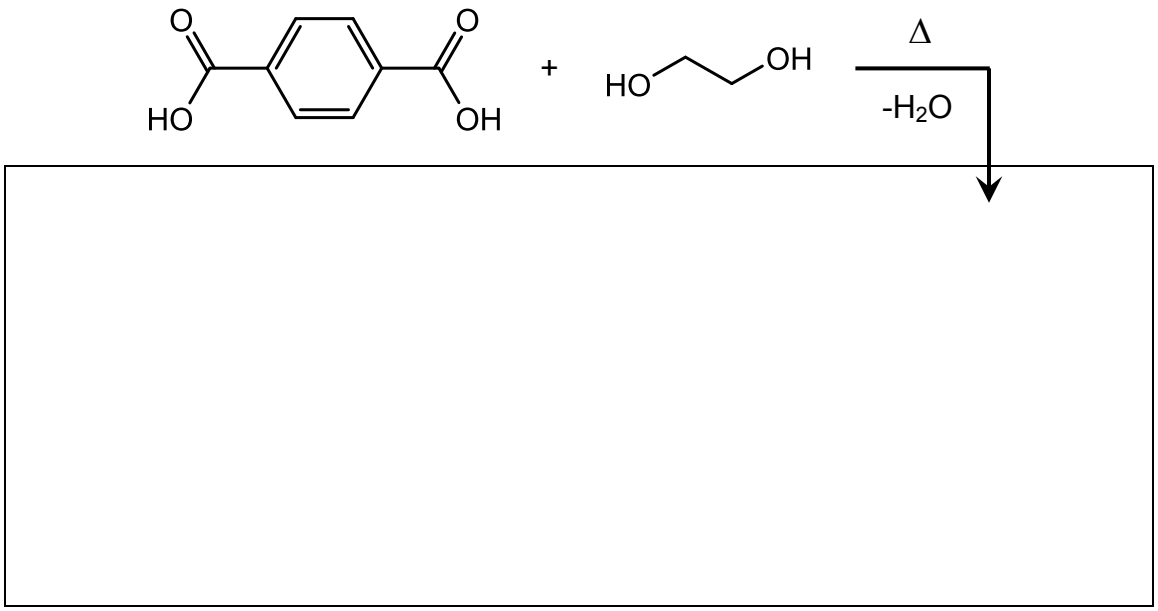
5. (12 pts) **Draw a mechanism** (using "electron pushing") for the reaction shown below. Draw each mechanistic step explicitly; don't cheat by combining multiple processes in a single step, or by taking shortcuts. Use only the molecules shown in the problem.

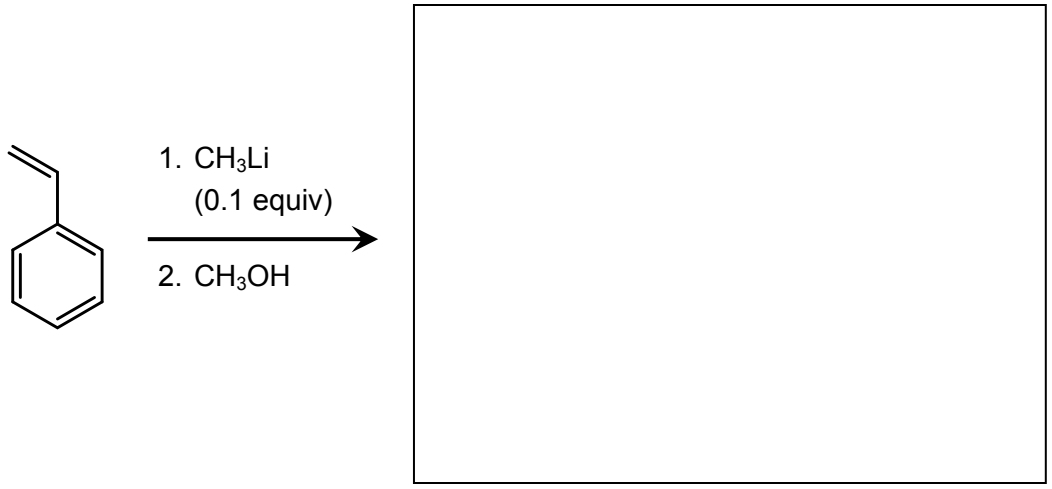


Mechanism:

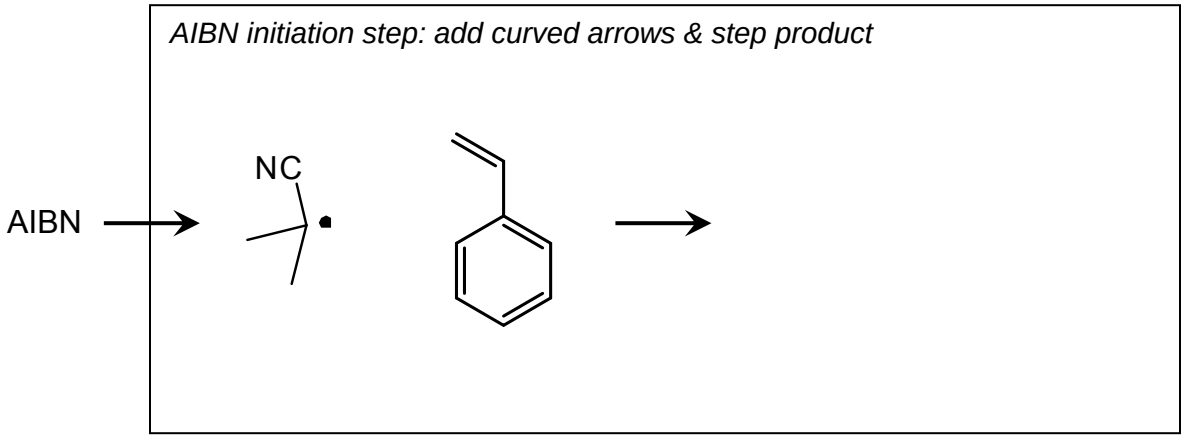
What unique type of reactive intermediate is generated in this reaction? (Answer in one word, in the box on the right.)

6. (16 pts)
   a. For each of the polymer syntheses proposed on the next page, draw the polymer product using bracket notation ("$[\text{-M-}]_n$"). 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.





b. If the second polymerization above were initiated with AIBN instead of with an anion, the mechanism of polymerization would be different. In the box below, **add curved arrows** (using "electron pushing") that show how the 2-cyanopropyl radical from AIBN would initiate polymerization. Then draw the product of this step.



Exam 4 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

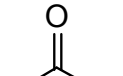
1. $NaNO_2$
   HCl
2. CuCN *or*
   H_3PO_2 *or*
   CuX *or*
   H_3O^+

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

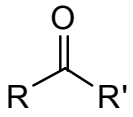
RLi

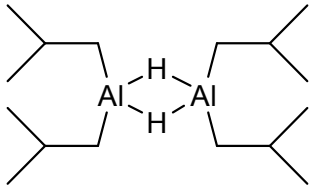
R_2CuLi

$Na_2Cr_2O_7$
H_2SO_4

$LiAlH(OtBu)_3$

1. Ag_2O
   NH_3
2. H_3O^+

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



(DIBAL-H)

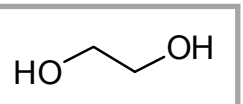
$Bu_4N^+F^-$

$PhCH_2Br$
Ag_2O

1. $LiAlH_4$
2. H_2O

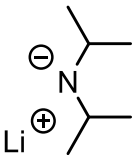
$(COCl)_2$

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



HCl

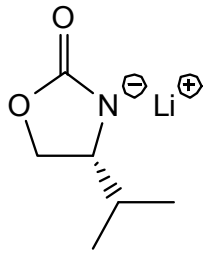
$NaNH_2$



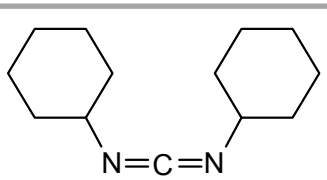
(LDA)

$SOCl_2$
(& pyridine,
usually)

1. $NaBH_4$
2. H_2O

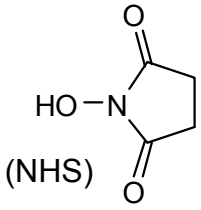
1. 

2. base
3. R-X
4. LiOH



(DCC)

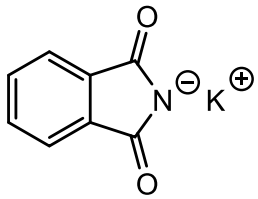
$CHCl_3$
$KOtBu$



(NHS)

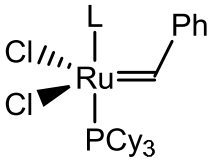
1. CH_3I
   (excess)
2. Ag_2O
   H_2O
3. Δ

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

1. 

2. N_2H_4 (or ^-OH)

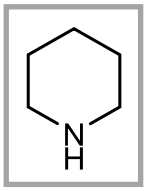
1. PhNCS
2. H^+
   (Edman degradation)

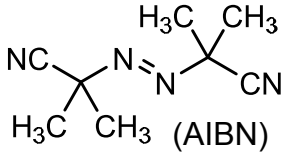


(Grubbs catalyst)

1. NaN_3
2. PPh_3
   H_2O

HF





(AIBN)

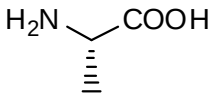
$Pd(PPh_3)_4$
NaOH

CH_2I_2
$Zn(Cu)$

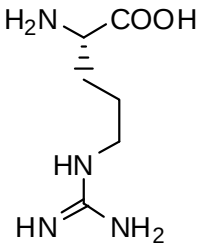
$Pd(OAc)_2$
PPh_3, NEt_3

CF_3COOH

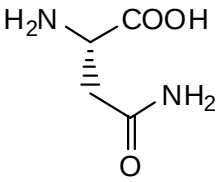
Exam 4 Chart of Amino Acids
(in Alphabetical Order)



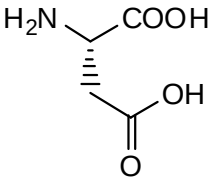
alanine
(Ala, A)



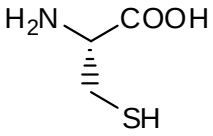
arginine
(Arg, R)



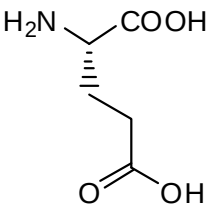
asparagine
(Asn, N)



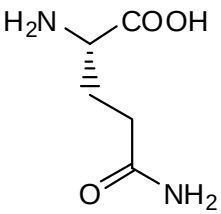
aspartic acid
(Asp, D)



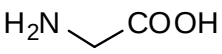
cysteine
(Cys, C)



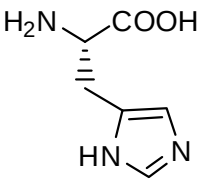
glutamic acid
(Glu, E)



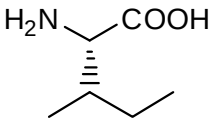
glutamine
(Gln, Q)



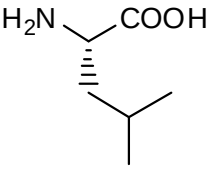
glycine
(Gly, G)



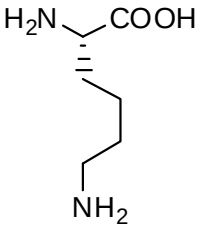
histidine
(His, H)



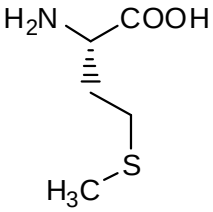
isoleucine
(Ile, I)



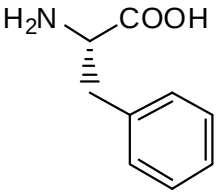
leucine
(Leu, L)



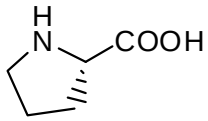
lysine
(Lys, K)



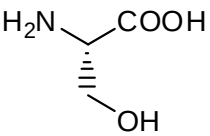
methionine
(Met, M)



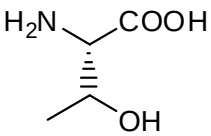
phenylalanine
(Phe, F)



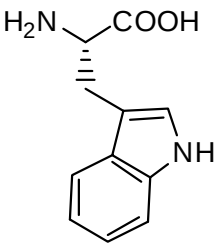
proline
(Pro, P)



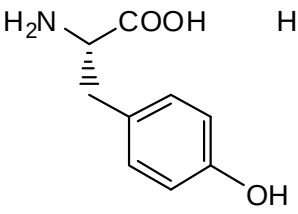
serine
(Ser, S)



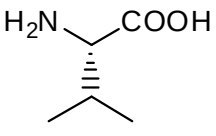
threonine
(Thr, T)



tryptophan
(Trp, W)

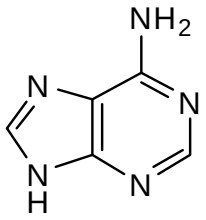


tyrosine
(Tyr, Y)



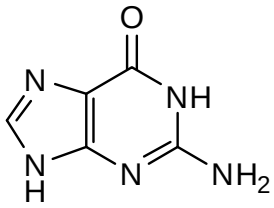
valine
(Val, V)

Exam 4 Chart of Nucleic Acid Bases
(in Alphabetical Order)

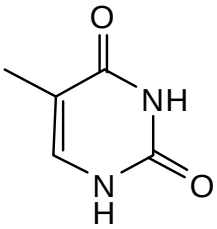


adenine
(A)

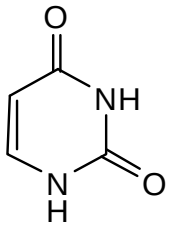
cytosine
(C)



guanine
(G)



thymine
(T)



uracil
(U)

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	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.