NAME _____

ID # _____

ORGANIC CHEMISTRY II (2302)

10:30 am – 12:30 pm, December 18, 2015

Final Exam

You will be able to pick up your graded exam from Chemistry department staff in 115 Smith beginning Tuesday, December 22nd at 9 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.

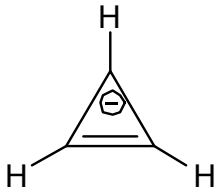
NAME _____

Scoring:

1. _____ / 16	6. _____ / 6
2. _____ / 6	7. _____ / 29
3. _____ / 52	8. _____ / 28
4. _____ / 26	9. _____ / 10
5. _____ / 27	

Total Score: _____ / 200

1. (16 pts) For cyclopropenyl anion,



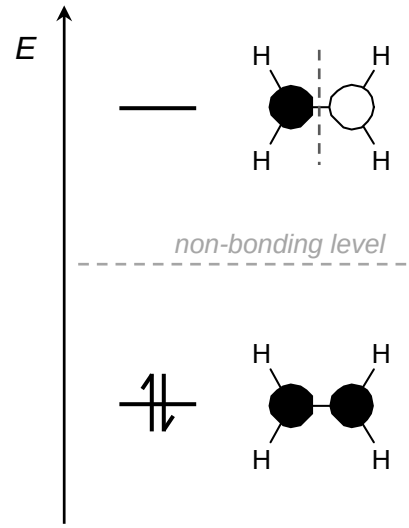
cyclopropenyl anion

- How many molecular orbitals describe the conjugated π-system?

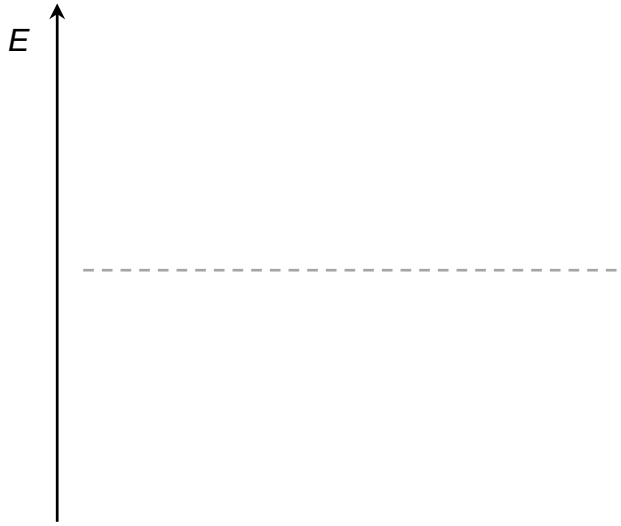
# of π MO's

- Draw all of these molecular orbitals on the energy diagram below. Draw both the shapes of the orbitals (as viewed from the top) and their energies, and fill the orbitals with the appropriate number of electrons.

example of answer format (for C_2H_4):



your answer:



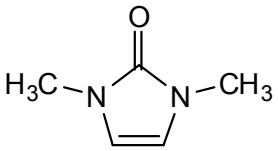
- Is the ion **AROMATIC** *or* **ANTIAROMATIC** ? *(Circle one.)*

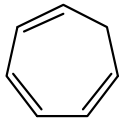
2. (6 pts) For each of the following molecules, circle whether the molecule is aromatic, anti-aromatic, or neither.

AROMATIC

ANTI-AROMATIC

NEITHER



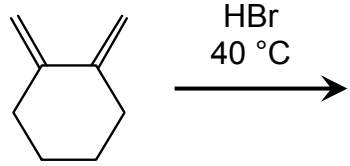


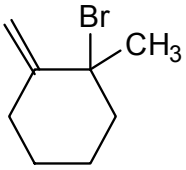
AROMATIC

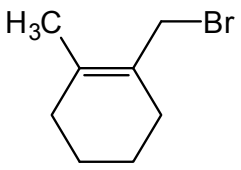
ANTI-AROMATIC

NEITHER

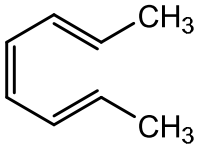
3. (52 pts) Each of the reactions below is drawn with two possible products. If one of the two products predominates, circle that preferred product. If the two products are produced equally, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

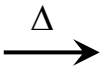




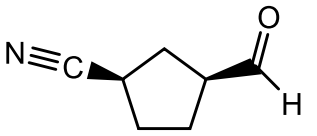


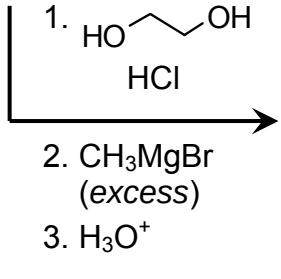
BOTH (equally)	NEITHER

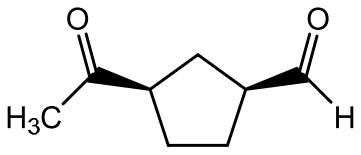


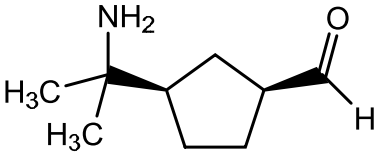


a product with **shorter λ_{max}** than the starting material	a product with **longer λ_{max}** than the starting material
BOTH (equally)	NEITHER

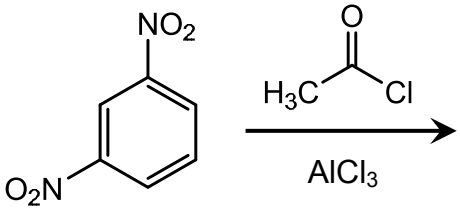


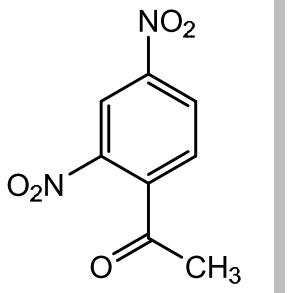
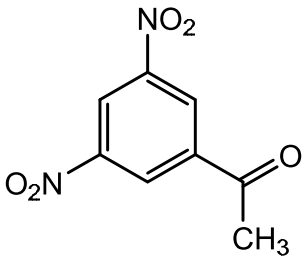


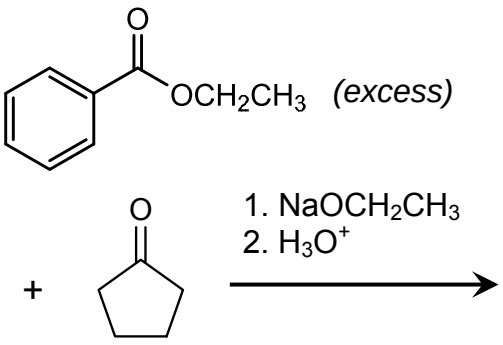


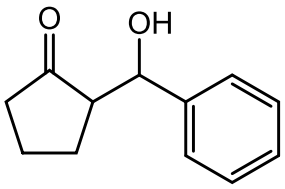
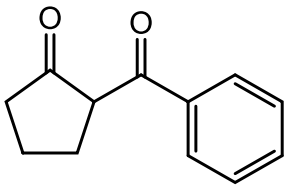


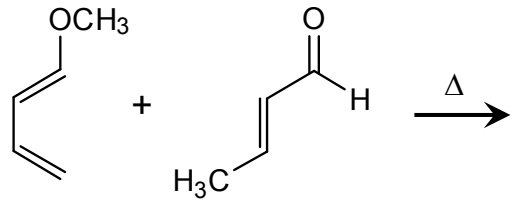
BOTH (equally)	NEITHER

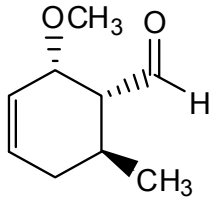
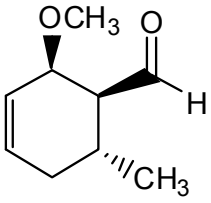


	
BOTH (equally)	NEITHER

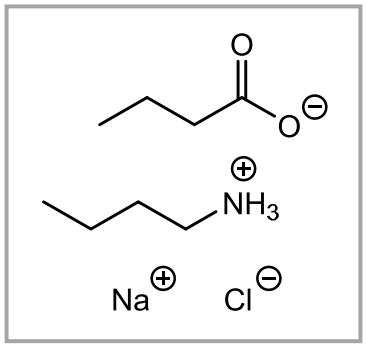


	
BOTH (equally)	NEITHER

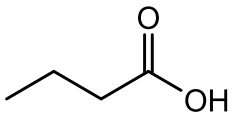
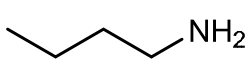


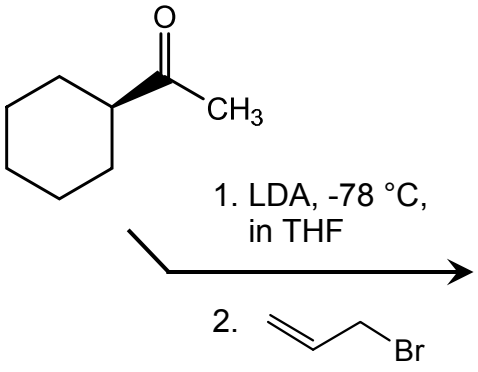
	
BOTH (equally)	NEITHER

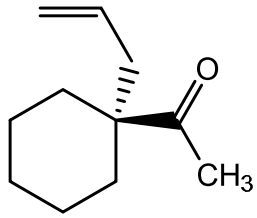
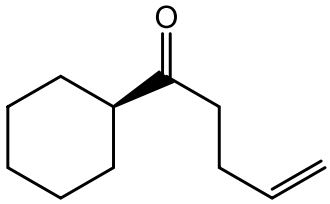
a mixture containing:

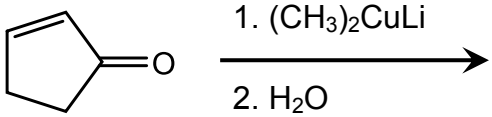


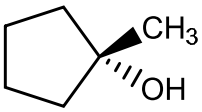
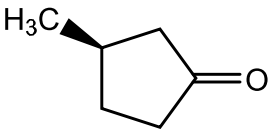
1. Dissolve in a mixture of aqueous base ($NaOH/H_2O$) and $CHCl_3$.
2. Discard $CHCl_3$ layer.
3. Add fresh $CHCl_3$, and enough HCl to make the H_2O solution acidic.
4. Discard H_2O layer.

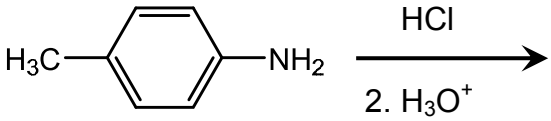
	
BOTH (equally)	NEITHER

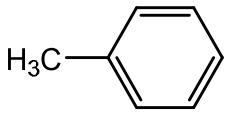
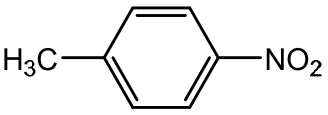


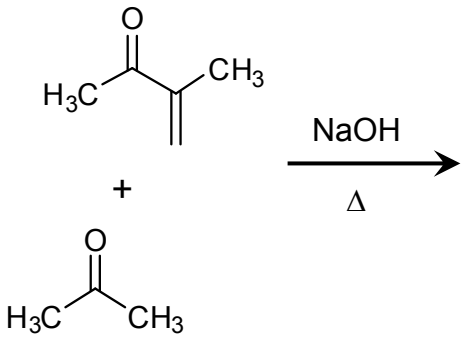
	
BOTH (equally)	NEITHER

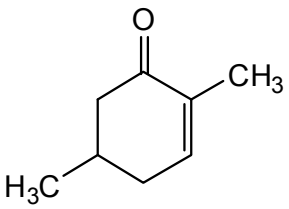
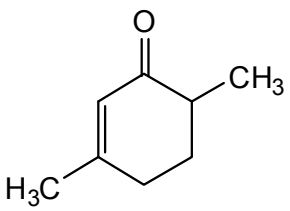


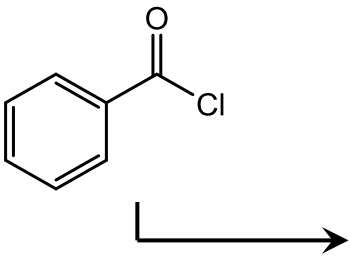
	
BOTH (equally)	NEITHER



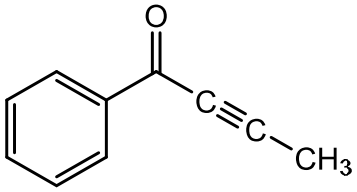
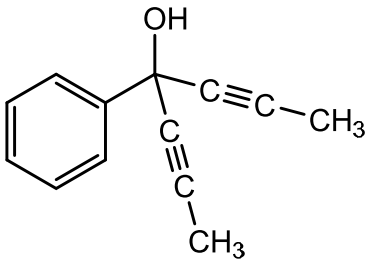
	
BOTH (equally)	NEITHER

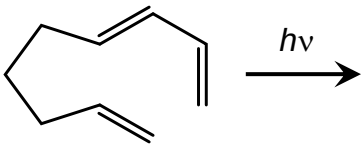


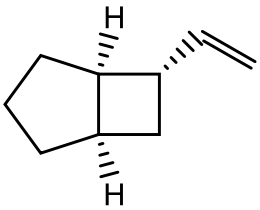
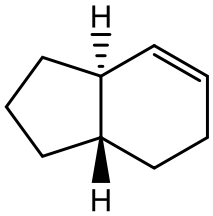
	
BOTH (equally)	NEITHER



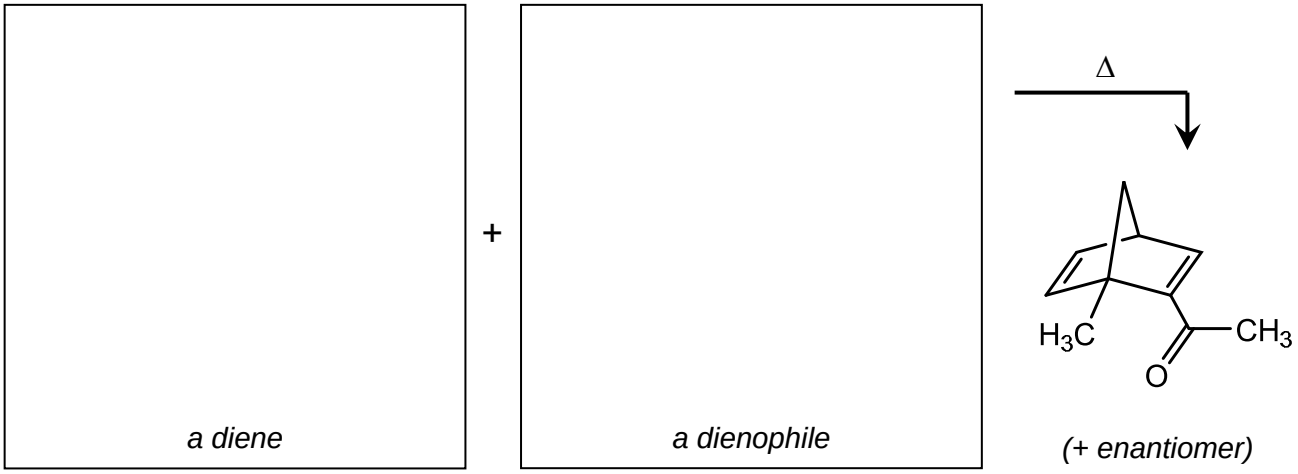
1. $H_3C-C\equiv C-Na$ *(excess)*
2. H_3O^+

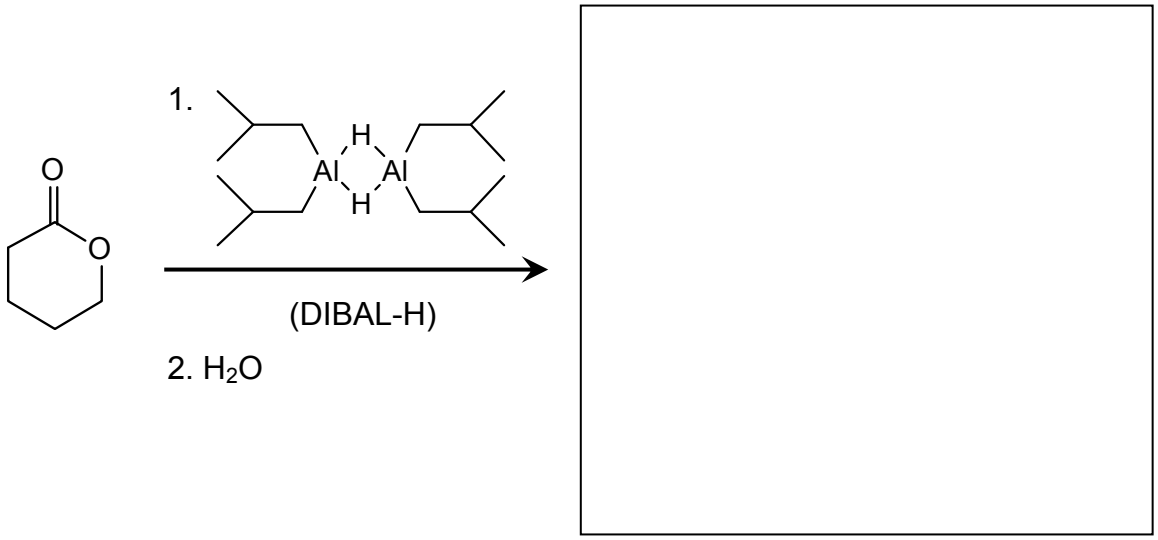
	
BOTH (equally)	NEITHER

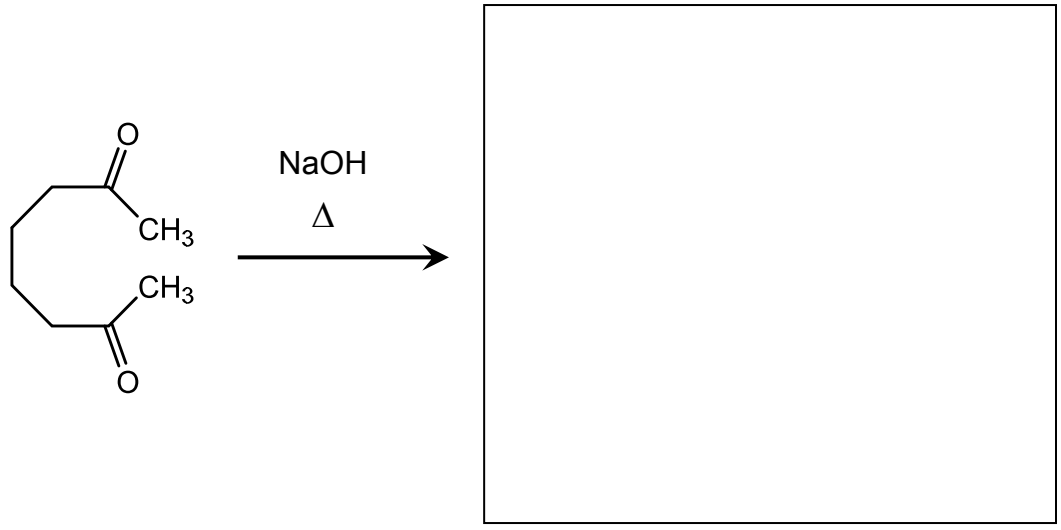


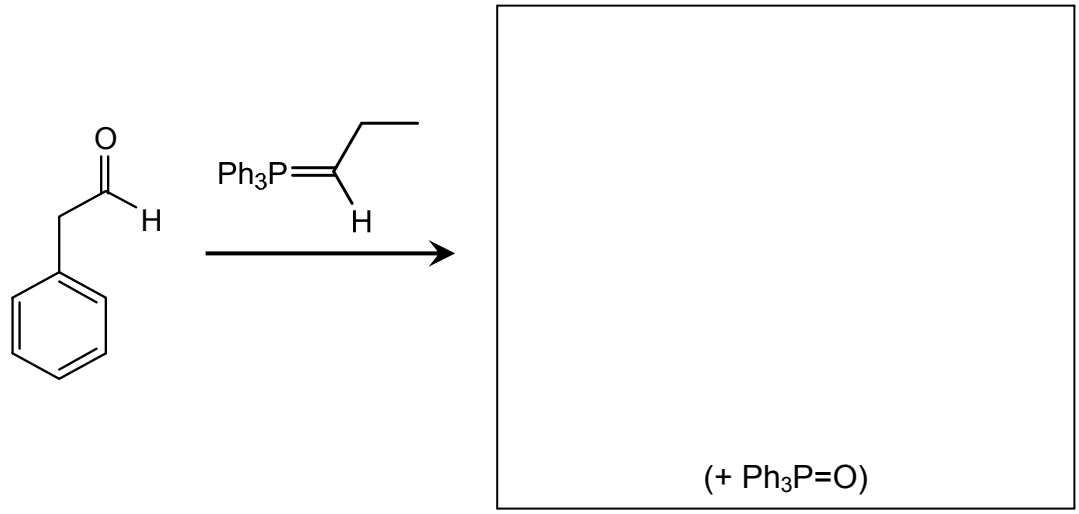
	
BOTH (equally)	NEITHER

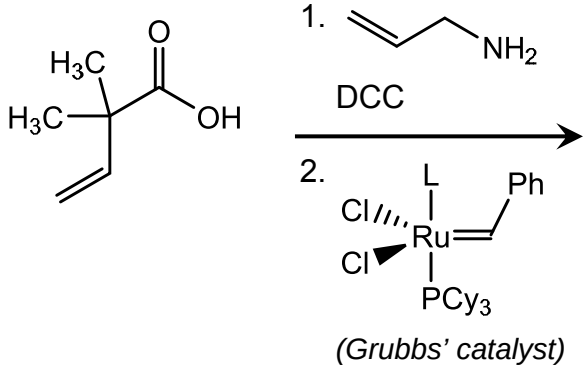
4. (26 pts) For each of the reactions below, fill in the empty box corresponding to reactants or product. Give only one answer in each box. For reactions that you expect to yield multiple products, draw one major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".




1.
H
Al
Al
H
O
O
(DIBAL-H)
2. H_2O

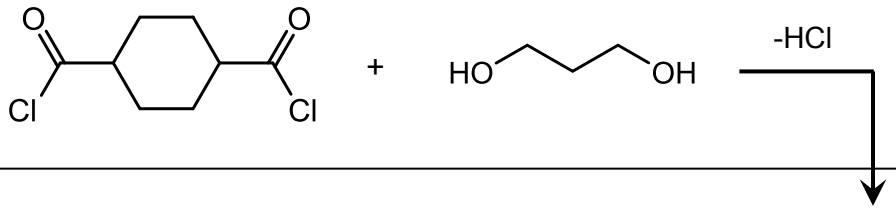

O
CH_3
CH_3
O
NaOH
Δ

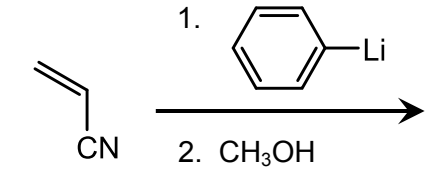

O
H
Ph_3P
H
(+ Ph_3P=O)



(Grubbs' catalyst)

5. (27 pts)
   a. For each of the polymer syntheses proposed below, draw the polymer product using bracket notation ("[-M-]$_n$"). 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.

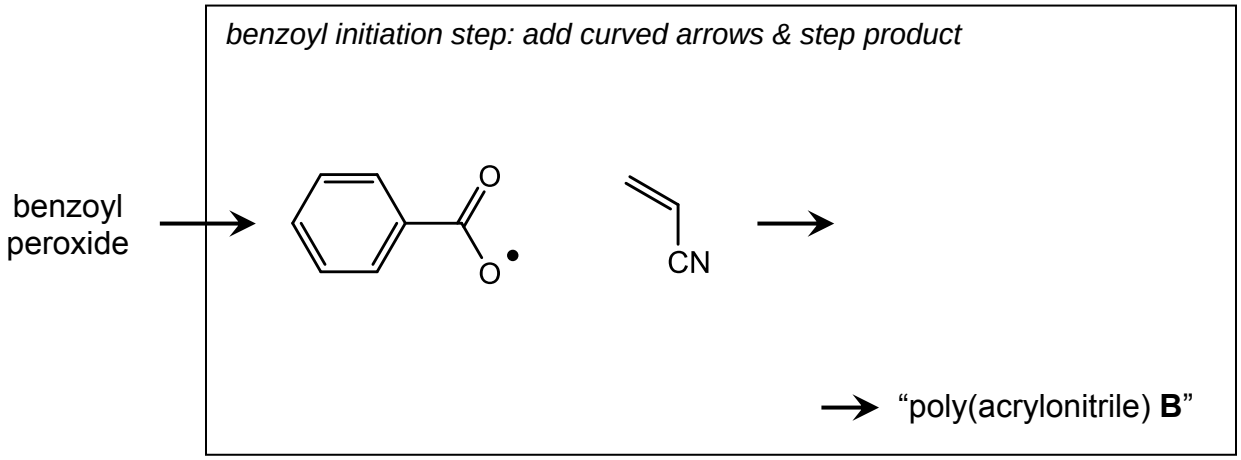




acrylonitrile

"poly(acrylonitrile) **A**"

b. If the second polymerization above were initiated with benzoyl peroxide 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 benzoyl radical would initiate polymerization. Then draw the product of this step.

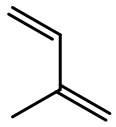


c. How would you expect the molecular weight distribution (or "polydispersity", measured by *PDI*) of the poly(acrylonitrile) polymers **A** and **B** described on this and the previous page to compare? Would you expect

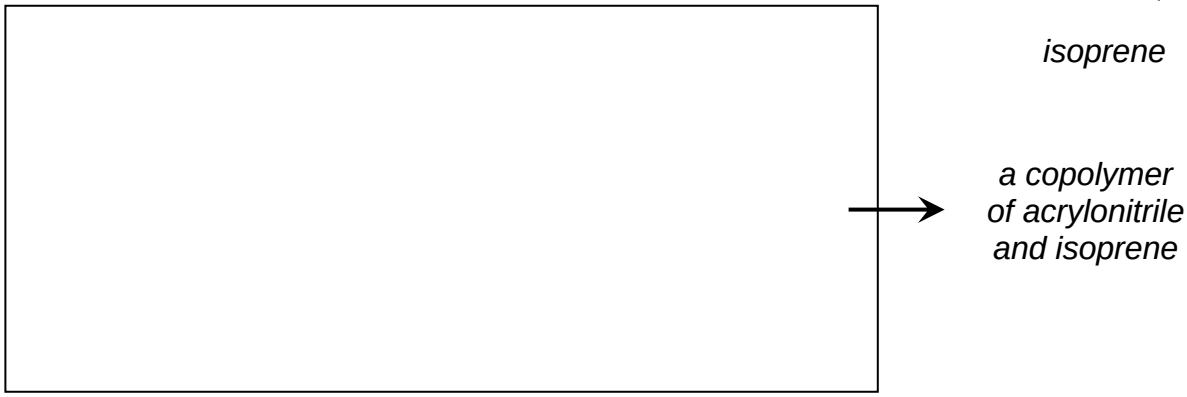
PDI(polymer **A**) **>** , **<** , or **=** *PDI*(polymer **B**)?

(Circle one answer.)

d. How would you synthesize a **co-polymer** of acrylonitrile and isoprene (the monomer shown at right)? Draw a synthetic recipe for the copolymer in the box below.



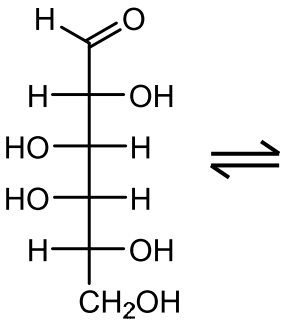
isoprene



e. In two words or less, how would you convert your copolymer from a plastic into an elastomer?

6. (6 pts) D-Galactose, a common aldohexose found in nature, is the C-4 epimer of D-glucose. A Fischer projection of acyclic D-galactose is shown below.

   a. Acyclic D-galactose equilibrates with a cyclic, 6-membered-ring (pyranose) form. Draw the structure of the β-anomer of this cyclic galactose as a Haworth projection in the box at right.

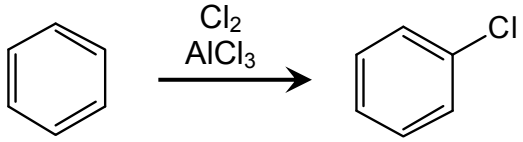


D-galactose

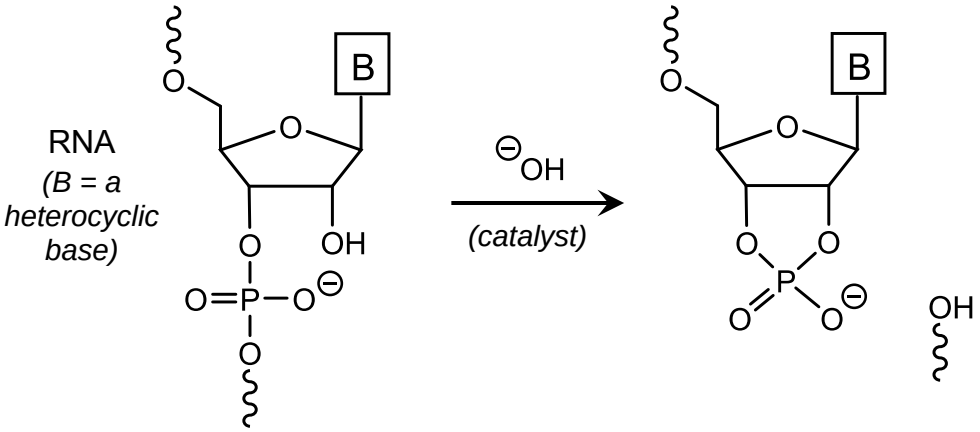
β-*D-galactopyranose*
(drawn as a Haworth projection)

   b. D-Galactose is combined in nature with D-glucose to form lactose, a disaccharide. Lactose is a glycoside of galactose. Which -OH group in your structure above would be replaced to form a glycoside? **Circle one -OH group.**

7. (29 pts) **Draw a mechanism** (using "electron pushing") for each of the reactions shown on the next two pages. 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.

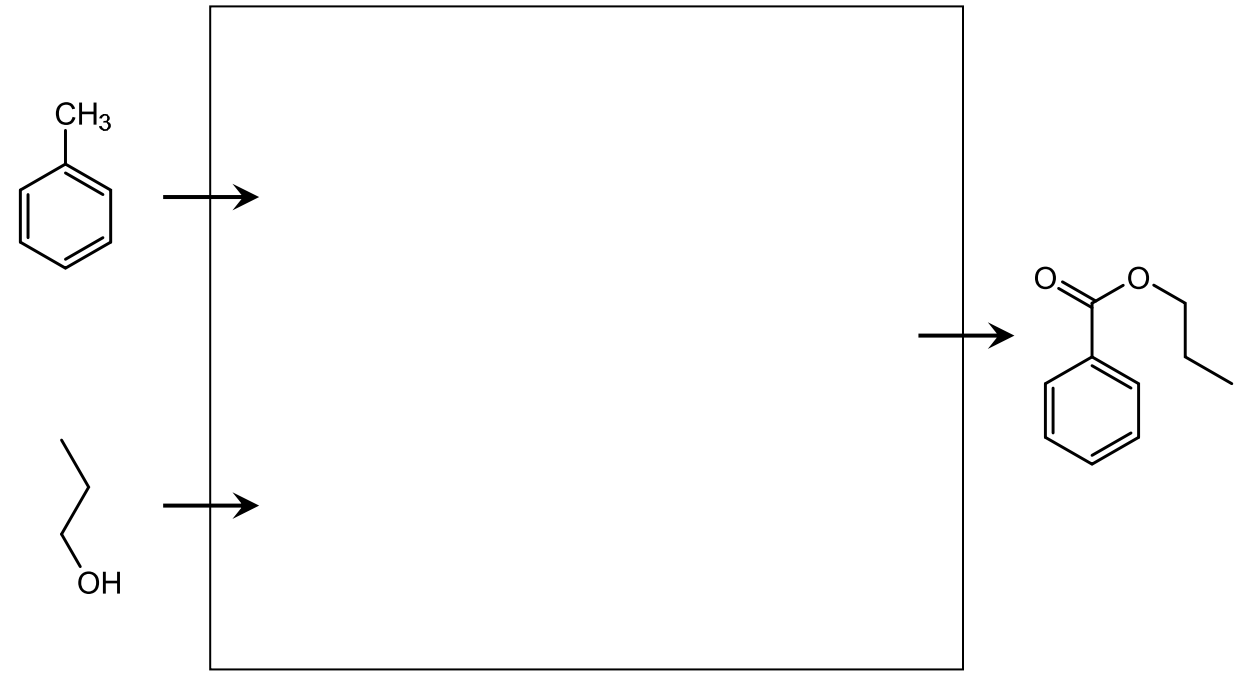


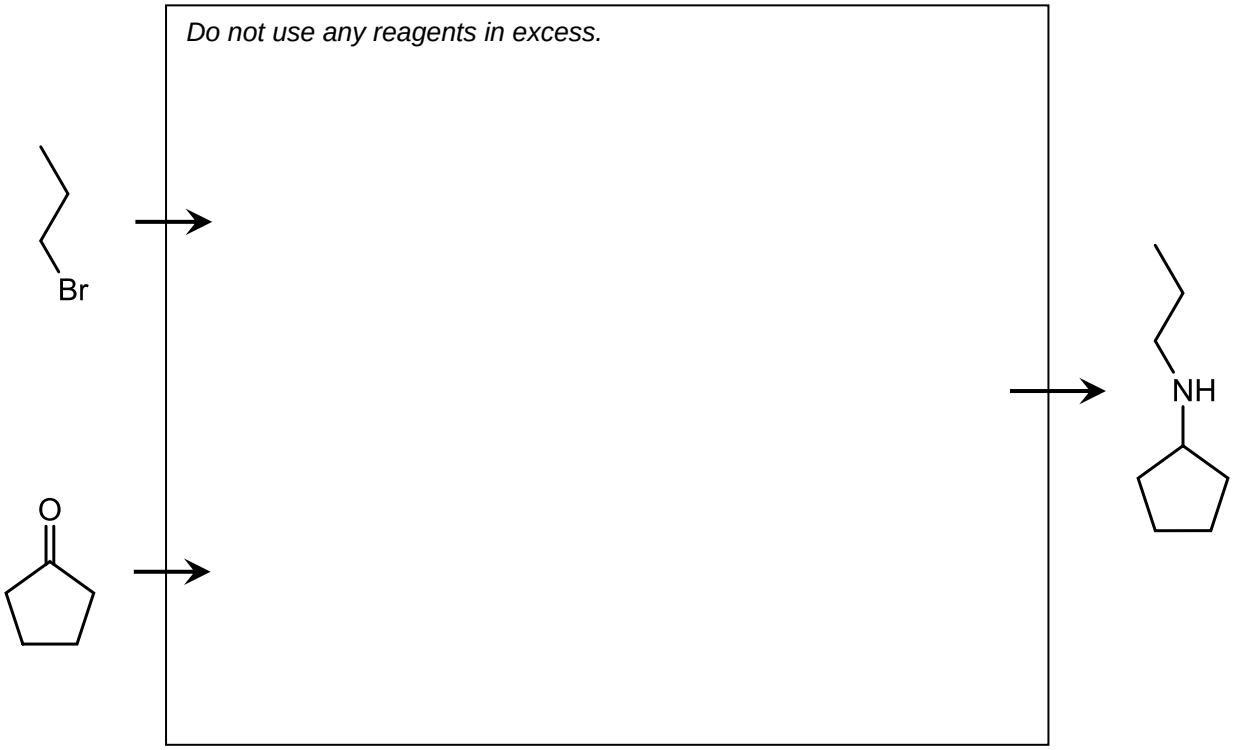
Mechanism:

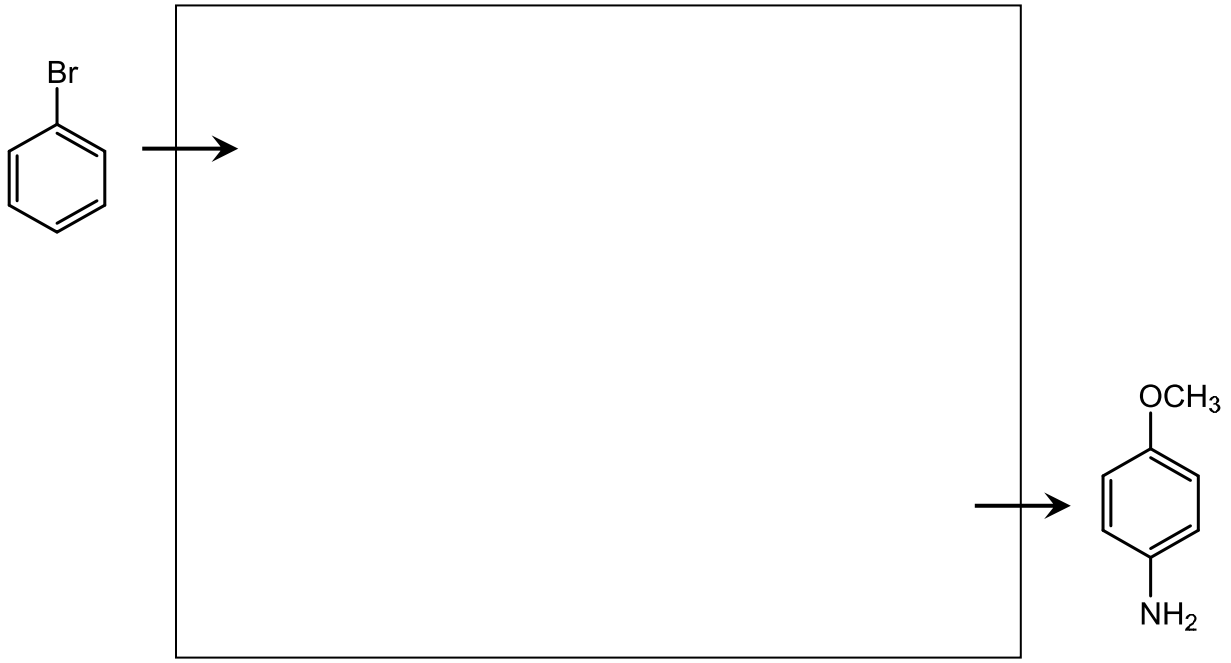


Mechanism:

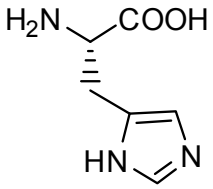
8. (28 pts) Each of the syntheses shown below can be accomplished in just a few steps. For each starting material or set of starting materials, **propose a multistep synthesis** of the product shown. You may use any reagents and reactions we've learned about in class and/or in the text.



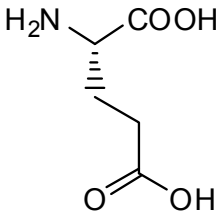




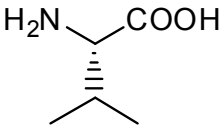
9. (10 pts)
   a. Sort the three amino acids histidine (His), glutamic acid (Glu), and valine (Val) in order of increasing isoelectric point (pI). Write their three-letter abbreviations in the appropriate boxes below.



histidine (His)



glutamic acid (Glu)



valine (Val)

lowest pI → **highest pI**

   b. When valine is used in solid-phase peptide synthesis, it typically bears a *tert*-butyloxycarbonyl (*t*Boc) protecting group. In the box at right, draw the structure of *t*Boc-protected valine.

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

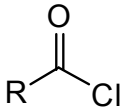
1. $NaNO_2$
   HCl
2. CuCN *or*
   H_3PO_2 *or*
   CuX *or*
   H_3O^+

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

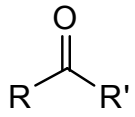
RLi

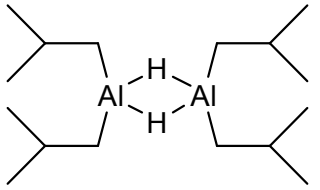
R_2CuLi

$Na_2Cr_2O_7$
H_2SO_4

$LiAlH(OtBu)_3$

1. Ag_2O
   NH_3
2. H_3O^+

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



(DIBAL-H)

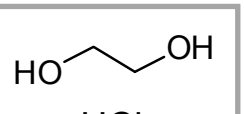
$Bu_4N^+F^-$

$PhCH_2Br$
Ag_2O

1. $LiAlH_4$
2. H_2O

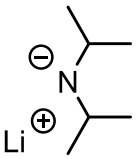
$(COCl)_2$

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



HCl

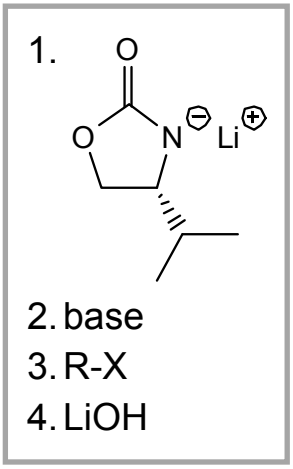
$NaNH_2$

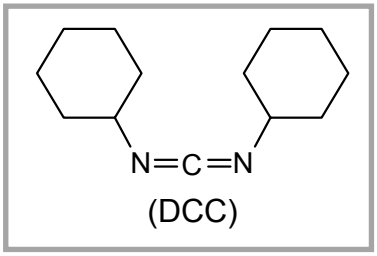


(LDA)

$SOCl_2$
(& pyridine,
usually)

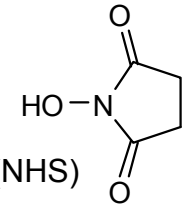
1. $NaBH_4$
2. H_2O





(DCC)

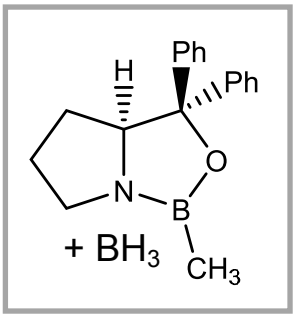
$CHCl_3$
$KOtBu$



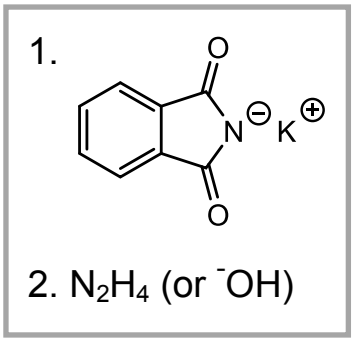
(NHS)

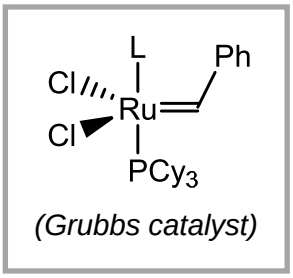
1. CH_3I
   (excess)
2. Ag_2O
   H_2O

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



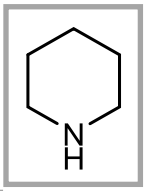
+ BH_3





(Grubbs catalyst)

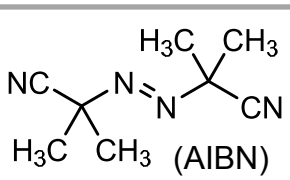
1. $PhNCS$
2. H^+
   (Edman degradation)



1. NaN_3
2. PPh_3
   H_2O

$Pd(PPh_3)_4$
NaOH

CH_2I_2
Zn(Cu)



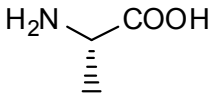
(AIBN)

CF_3COOH

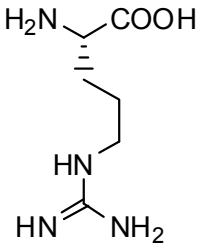
$Pd(OAc)_2$
PPh_3, NEt_3

HF

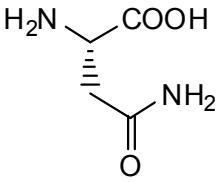
Final Exam Chart of Amino Acids
(in Alphabetical Order)



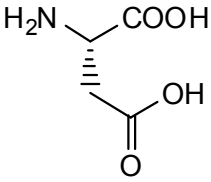
alanine
(Ala, A)



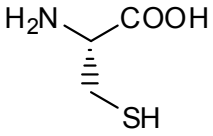
arginine
(Arg, R)



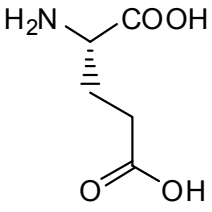
asparagine
(Asn, N)



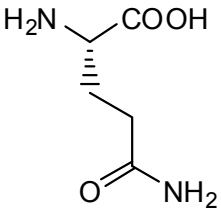
aspartic acid
(Asp, D)



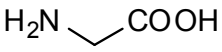
cysteine
(Cys, C)



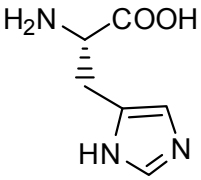
glutamic acid
(Glu, E)



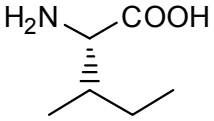
glutamine
(Gln, Q)



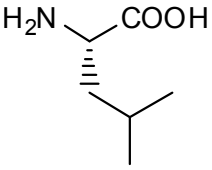
glycine
(Gly, G)



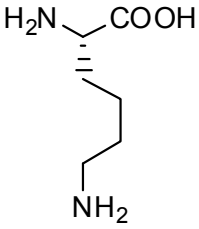
histidine
(His, H)



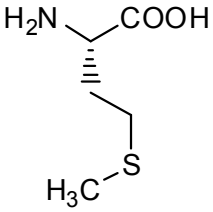
isoleucine
(Ile, I)



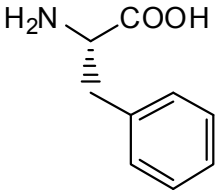
leucine
(Leu, L)



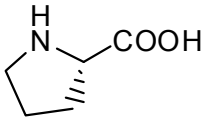
lysine
(Lys, K)



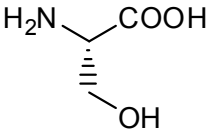
methionine
(Met, M)



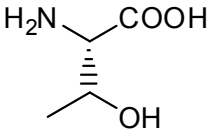
phenylalanine
(Phe, F)



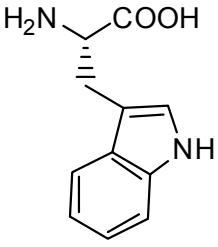
proline
(Pro, P)



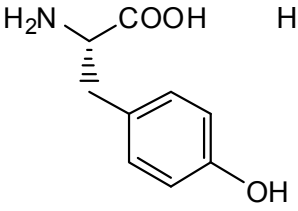
serine
(Ser, S)



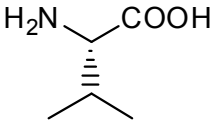
threonine
(Thr, T)



tryptophan
(Trp, W)

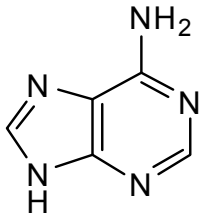


tyrosine
(Tyr, Y)



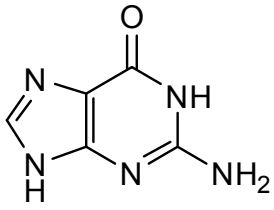
valine
(Val, V)

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

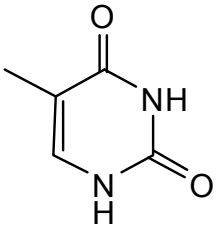


adenine
(A)

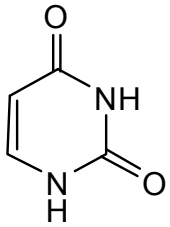
cytosine
(C)



guanine
(G)



thymine
(T)



uracil
(U)

Periodic Table of the Elements

Chemistry Reference Sheet

California Standards Test

	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.