CH 334 Form A

First Midterm Exam Monday, October 16, 2017

Name____KEY_____

You may use model kits but no other material with chemical information without instructor approval.

Please do not use any electronic devices (calculators, phones, ipods, smart watches).

IUPAC Periodic Table of the Elements

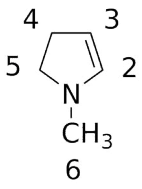
1																	18
1 H hydrogen 1.008 [1.0078, 1.0082]	2		Key: atomic number **Symbol** name conventional atomic weight standard atomic weight									13	14	15	16	17	2 He helium 4.0026
3 Li lithium 6.94 [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron 10.81 [10.806, 10.821]	6 C carbon 12.011 [12.009, 12.012]	7 N nitrogen 14.007 [14.006, 14.008]	8 O oxygen 15.999 [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium 24.305 [24.304, 24.307]	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 26.982	14 Si silicon 28.085 [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur 32.06 [32.059, 32.076]	17 Cl chlorine 35.45 [35.446, 35.457]	18 Ar argon 39.948
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine 79.904 [79.901, 79.907]	36 Kr krypton 83.798(2)
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.07(2)	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(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	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 [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

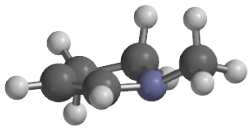
57 La lanthanum 138.91	58 Ce cerium 140.12	59 Pr praseodymium 140.91	60 Nd neodymium 144.24	61 Pm promethium	62 Sm samarium 150.36(2)	63 Eu europium 151.96	64 Gd gadolinium 157.25(3)	65 Tb terbium 158.93	66 Dy dysprosium 162.50	67 Ho holmium 164.93	68 Er erbium 167.26	69 Tm thulium 168.93	70 Yb ytterbium 173.05	71 Lu lutetium 174.97
89 Ac actinium	90 Th thorium 232.04	91 Pa protactinium 231.04	92 U uranium 238.03	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.

1. (24 points) 2-D and calculated 3-D structures for a molecule C_5H_9N is shown at the right. Carbon atoms are labeled numerically; the 3-D orientation is looking down the H-C2 bond vector.

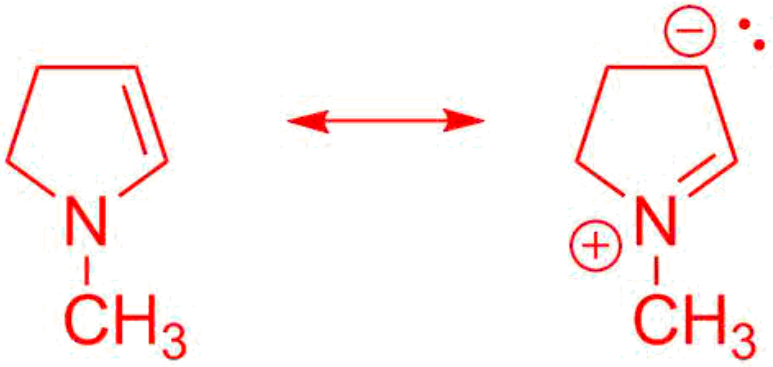




a. Based on the structure, list the approximate atomic orbital hybridization of each of the following:

The methyl carbon:___sp^3____ Carbon 3:___sp^2___ The nitrogen:_sp2, but we'll accept sp^3

b. Draw two proper, complete resonance structures for this molecule.



c. Based on your answers above, describe the components of the C2-N bond in terms of bond type (sigma, pi). You may use any descriptions or drawings you wish.

All covalently bonded atoms have a σ bond arising from the overlap of appropriate hybridized atomic orbitals. Based on the resonance forms in (b), there is also a partial π bond between C2 and nitrogen. That justifies claiming sp^2 hybridization for nitrogen (despite a bit of pyramidalization evident in the picture in (a)); C2 is clearly sp^2 regardless.

1. d. Based on the bond lengths shown below (and your prior answers) describe whether you think the C-N bonds in C_5H_9N are single, double or triple bonds and why.

Compound	C-N Bond Length
C2-N in C_5H_9N (shown above)	1.399 Å
C5-N in C_5H_9N (shown above)	1.473 Å
CH_3CH_2-NH_2	1.467 Å
$CH_3CH{=}NH$	1.266 Å
$CH_3C{\equiv}N$	1.149 Å

The C2-N bond is in between a single and a double bond, as expected from the resonance description.

The C5-N bond is actually a bit longer than that in the reference compound, but is clearly a single bond as it is the longest C-N bond under discussion.

2. (9 points) Given the pK_as of protonated species shown below, predict the magnitude of K_{eq} for each of the following reactions ($K_{eq} >> 1$, $K_{eq} << 1$, or $K_{eq} \approx 1$)

a. $HC{\equiv}C^{\ominus}$ + NH_3 ⇌ $HC{\equiv}CH$ + $NH_2^{\ominus}$

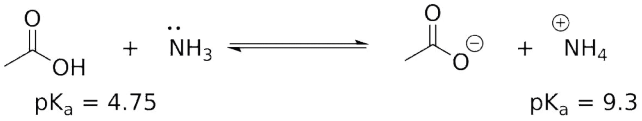
$pK_a = 36$ $pK_a = 25$

K <<1 (actually, 10^{-11})

b. Br^- + CH_3OH ⇌ HBr + CH_3O^-

$pK_a = 15.5$ $pK_a = -9.0$

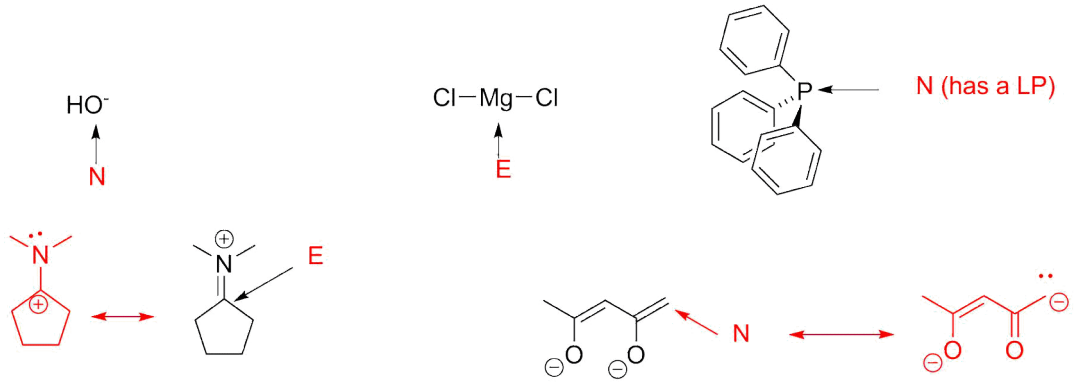
K <<1 (actually, $10^{-24.5}$)

c. 

$pK_a = 4.75$ $pK_a = 9.3$

K >1 (actually $10^{4.55}$)

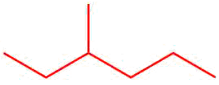
3. (15 points) Identify each atom highlighted with an arrow in the structures below as either nucleophilic (N) or electrophilic (E). (Label each as N or E.)



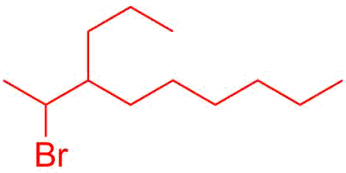
4. (12 points) Draw structures for each of the following compounds.

a. n-Hexane

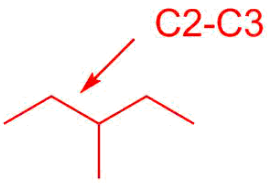
b. 3-methylheptane



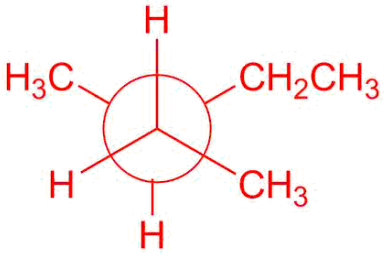
c. 2-bromo-3-(1-propyl)nonane



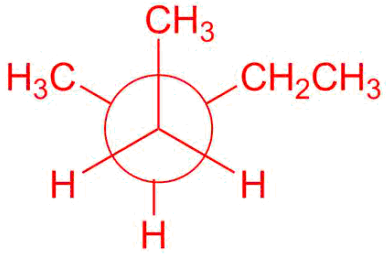
5. (16 points) Using Newman projections, show the possible staggered rotamers of 3-methylpentane, looking down the C2-C3 bond. Rank them in order of stability. (Hint: draw 3-methylpentane and identify the bond down which you need to look.)



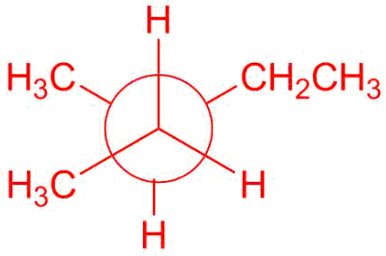
3-methylpentane



Second-most stable



Least stable

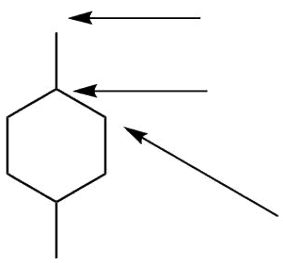


Most stable

All of these have gauche interactions with the C1-methyl group. The most stable has 1 only, with the C-3 methyl. The least stable has 2, one each with the C3-methyl and with the C4/C5 ethyl group. The second-most stable is just a tad less stable because most of the time the ethyl group is pointed away, but to the extent it can rotate around it will affect the overall energy.

6. (24 points) Consider the free-radical halogenation of 1,4-dimethylcyclohexane (shown below in part a).

a. Label each of the different carbons as primary, secondary or tertiary.

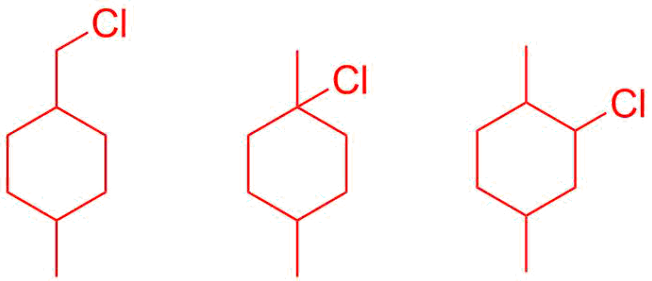


Primary

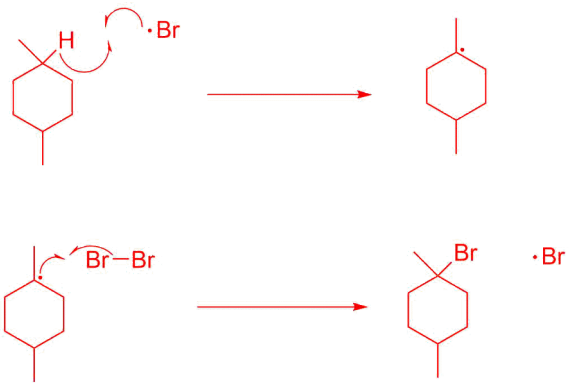
Tertiary

Secondary

b. Chlorination, as we know, is relatively nonselective. Draw all possible isomers for monochlorination of 1,4-dimethylcyclohexane (ignore cis/trans isomerism and other aspects of stereochemistry).



c. Bromination, on the other hand, tends to be more selective. Show the mechanistic propagation steps (including electron-pushing arrows) that illustrate selective formation of a single product from 1,4-dimethylcyclohexane.



Note: Br• is generated in the initiation step (I haven't asked for that). A common error is to have the organic radical react with Br• instead of Br_2. This is statistically very, very unlikely (the radical species never build up to any large concentration), and such a reaction is actually one of several chain termination steps. Reaction with Br_2 regenerates Br•, which goes back to react with another molecule of reactant and carry the chain.

Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH_3-H	105
CH_3CH_2-H	101
$(CH_3)_2CH$-H	98.5
$(CH_3)_3C$-H	96.5
CH_3-F	110
CH_3-Cl	85
CH_3-Br	70
CH_3-I	57
CH_3CH_2-F	111
CH_3CH_2-Cl	84
CH_3CH_2-Br	70
CH_3CH_2-I	56
$(CH_3)_2CH$-F	111
$(CH_3)_2CH$-Cl	84
$(CH_3)_2CH$-Br	71
$(CH_3)_2CH$-I	56
$(CH_3)_3C$-F	110
$(CH_3)_3C$-Cl	85
$(CH_3)_3C$-Br	71
$(CH_3)_3C$-I	55