Chemistry 261: Organic Chemistry

Examination #2

October 14, 2013

Name:

Student ID Number:

Exams will be returned via the Chem 261 wall-mount racks outside Lab Sci 300.

☐ Please check the box if you would prefer to pick up your graded examination directly from Prof. Ponder during office hours.

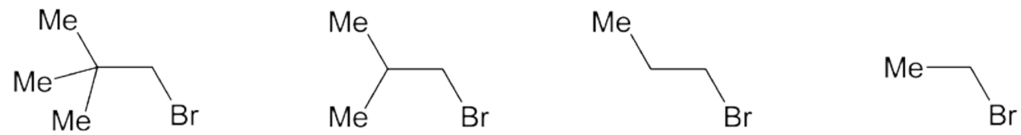
20101

Problem 1 (12 points; A = 7 points, B = 5 points) Bromine chloride (BrCl) is a caustic yellow gas with a bond length of 2.14 Å and bond energy of 52 kcal/mol, values almost exactly intermediate between those for chlorine (Cl_2) and bromine (Br_2).

(A) Write a complete mechanism, including initiation, propagation and termination steps, for the reaction of bromine chloride with butane. Estimate the heat of reaction for the individual propagation steps and the overall mechanism.

(B) We have discussed the relative selectivity of reactions of alkanes with chlorine and bromine. What do you expect for the selectivity of the BrCl reaction? Explain.

Problem 2 (10 points; A & C = 4 points each, B = 2 points) All of the alkyl bromides shown below react with lithium iodide (LiI) in acetone at 25°C. The relative reaction rates (assuming EtBr = 1) are given. Note Boltzmann's constant (k) is 1.38×10^{-23} JK^{-1}, and the gas constant (R) is 1.987 cal/mol/K.



	neo-Pentyl Bromide	*iso*-Butyl Bromide	*n*-Propyl Bromide	Ethyl Bromide
Relative Rate =	0.00002	0.036	0.8	1

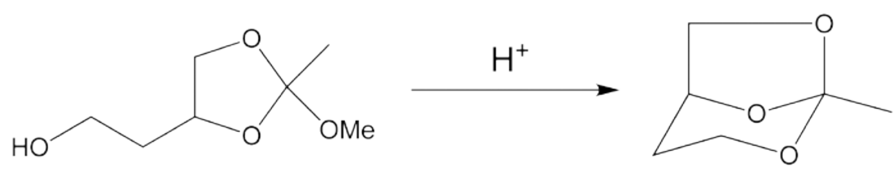
(A) Calculate the difference in activation energy for the reaction of ethyl bromide *vs.* *neo*-pentyl bromide.

(B) How will the relative rates change if the concentration of LiI is doubled?

(C) Why does *iso*-butyl bromide react 1800× faster than *neo*-pentyl bromide, but only 22× slower than *n*-propyl bromide. Use pseudo-3D drawings and/or Newman projections to illustrate your answer. *[Note: The bromides on the left are obviously more "crowded" than those on the right. We are looking for a more detailed, specific explanation of the large difference between 22× and 1800×.]*

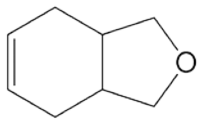
Problem 3 (10 points)

Write a detailed reaction mechanism for the acid-catalyzed transformation shown below. Be sure to show all steps, including proton transfers. Use curved arrows to indicate the flow of electrons, and include all reasonable resonance structures.

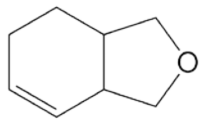


Problem 4 (10 points; A = 4 points, B & C = 3 points each)

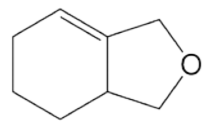
(A) How many stereoisomers are there for each of the four fused-ring cyclic ethers shown below, molecules *(1)–(4)*?



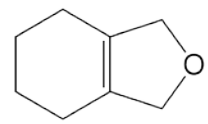
(1)



(2)



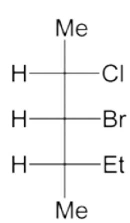
(3)



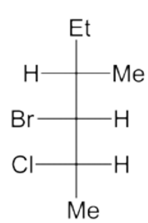
(4)

(B) Chosing from the possible stereoisomers in part (A), draw a *meso* compound. Similarly, draw a pair of diastereomers from among the stereoisomers in part (A).

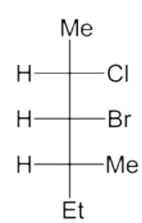
(C) Given the four Fischer projections below, describe the stereochemical relationship of structure *(1)* to each of the structures *(2)–(4)*. In other words, what is the relationship of *(1)* to *(2)*, of *(1)* to *(3)*, and of *(1)* to *(4)*?



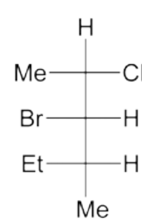
(1)



(2)



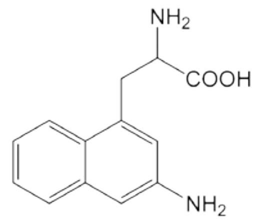
(3)



(4)

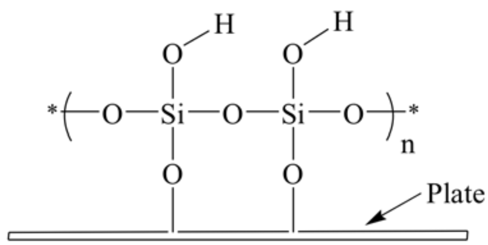
Problem 5 (10 points; A & B = 5 points each)

(A) A WashU graduate student has developed a new procedure for preparing racemic 3-aminonaphthylalanine, an unnatural amino acid. The melting point of the synthesized compound is 303-304 °C, in exact agreement with the literature value.

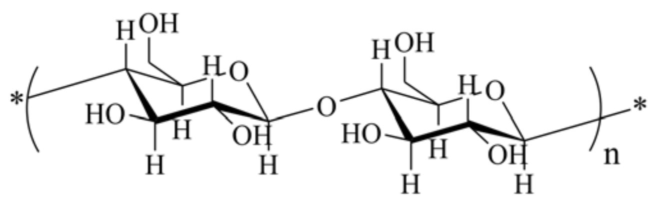


3-Aminonaphthylalanine

The student then carried out two different chromatographic procedures on the compound. Using thin layer chromatography (TLC) on silica gel, one spot was observed. In contrast, paper chromatography on cellulose gave two spots. Explain the different number of spots observed via TLC and paper chromatography.



Silica Gel

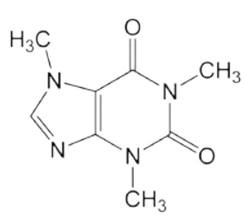


Cellulose

Procedure One:
Solid support – Silica Gel
Eluent – 3:12:5 $MeCO_2H$:*n*-BuOH:H_2O
Visualization – Ninhydrin
Found – One spot, R_f = 0.45

Procedure Two:
Solid support – Cellulose
Eluent – 3:12:5 $MeCO_2H$:*n*-BuOH:H_2O
Visualization – Ninhydrin
Found – Two spots, R_f = 0.36, 0.55

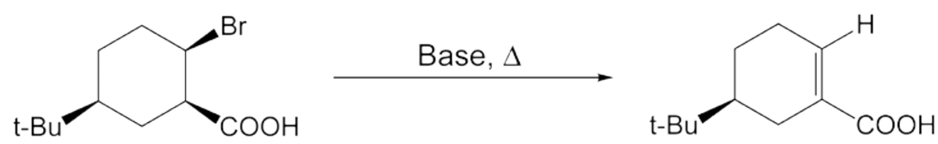
(B) When 1.0 gram (g) of caffeine is placed in a mixture of 25 mL of dichloromethane and 50 mL of water, the caffeine partitions, resulting in 0.20 g of caffeine in the water and 0.80 g of caffeine in the dichloromethane. What is the value of the distribution coefficient for caffeine between dichloromethane and water?

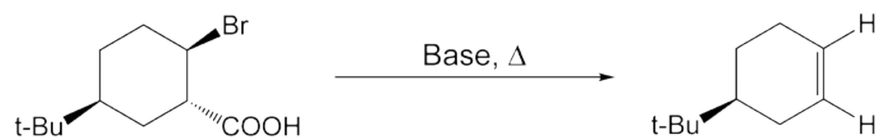


Caffeine

Problem 6 (8 points)

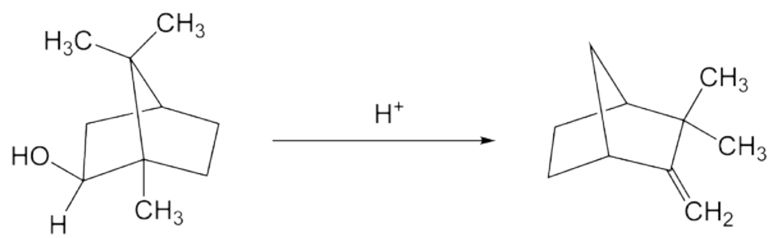
Upon heating under basic conditions, the two reactions below produce the major products shown. Use 3D drawings to assist in writing the mechanisms leading to formation of each product, and to explain the different products.





Problem 7 (8 points)

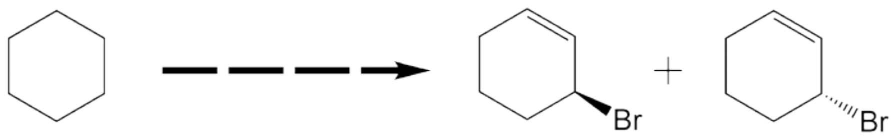
Isoborneol is a component of several essential oils, and is a natural insect repellant. It undergoes acid-catalyzed elimination to yield camphene. What type of reaction is occurring? Write the complete mechanism. Use an orbital drawing to explain the interconversion of the two key intermediates.



Isoborneol   Camphene

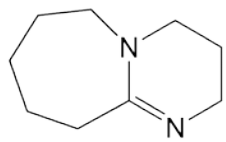
Problem 8 (10 points)

Provide a multi-step sequence of reactions to synthesize racemic 3-bromocyclohexene. You may start from cyclohexane and use any reactions and reagents. Mechanisms are not required – you only have to provide the starting materials, reaction conditions, and products for each step. Your synthesis will be evaluated based on the likely yield and selectivity of the proposed steps.



Problem 9 (10 points; A & B = 3 points each, C = 4 points)

(A) The molecule commonly known as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) is a non-nucleophilic base sometimes used to facilitate E2 eliminations. Explain why DBU is a good base, and also explain why it is a poor nucleophile.



DBU

(B) Concisely state the Hammond Postulate.

(C) Draw a "reaction coordinate" diagram for the conversion of A into two alternative products, B and C, where B is the kinetic product and C is the thermodynamic product. Does the production of a kinetic product as the major product of a reaction violate the Hammond Postulate? Explain.

Problem 10 (12 points; A & B = 6 points each)

Chloroform ($CHCl_3$) reacts with methylamine ($CH_3–NH_2$) in the presence of potassium *t*-butoxide in *t*-butanol to form methyl isocyanide. The overall transformation is shown below. The product is a colorless liquid, which is used as a reagent in organic synthesis and as a ligand in organometallic chemistry.

$$CHCl_3 + H_3C\text{—}NH_2 \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} H_3C\text{—}\overset{+}{N}{\equiv}C^{-}$$

(A) The first part of the overall transformation is reaction of chloroform with *t*-butoxide to make dichlorocarbene. Write a complete "curved arrow" mechanism.

(B) The second part of the overall transformation is dichlorocarbene reacting with methylamine to form the isocyanide. Write the full mechanism for this process. Some portions of the mechanism are analogous to the E2 elimination we studied.

Score Sheet – Do Not Write on This Page!

Score	Question
/12	**Question 1**
/10	**Question 2**
/10	**Question 3**
/10	**Question 4**
/10	**Question 5**
/8	**Question 6**
/8	**Question 7**
/10	**Question 8**
/10	**Question 9**
/12	**Question 10**
/100	**TOTAL**

TABLE 4-2 Bond-Dissociation Enthalpies for Homolytic Cleavages

$$A{:}B \longrightarrow A\cdot + \cdot B$$

Bond	Bond-Dissociation Enthalpy kJ/mol	Bond-Dissociation Enthalpy kcal/mol
H—X bonds and X—X bonds		
H—H	435	104
D—D	444	106
F—F	159	38
Cl—Cl	242	58
Br—Br	192	46
I—I	151	36
H—F	569	136
H—Cl	431	103
H—Br	368	88
H—I	297	71
HO—H	498	119
HO—OH	213	51
Methyl bonds		
CH_3—H	435	104
CH_3—F	456	109
CH_3—Cl	351	84
CH_3—Br	293	70
CH_3—I	234	56
CH_3—OH	381	91
Bonds to primary carbons		
CH_3CH_2—H	410	98
CH_3CH_2—F	448	107
CH_3CH_2—Cl	339	81
CH_3CH_2—Br	285	68
CH_3CH_2—I	222	53
CH_3CH_2—OH	381	91
$CH_3CH_2CH_2$—H	410	98
$CH_3CH_2CH_2$—F	448	107
$CH_3CH_2CH_2$—Cl	339	81
$CH_3CH_2CH_2$—Br	285	68
$CH_3CH_2CH_2$—I	222	53
$CH_3CH_2CH_2$—OH	381	91

Bond	Bond-Dissociation Enthalpy kJ/mol	Bond-Dissociation Enthalpy kcal/mol
Bonds to secondary carbons		
$(CH_3)_2CH$—H	397	95
$(CH_3)_2CH$—F	444	106
$(CH_3)_2CH$—Cl	335	80
$(CH_3)_2CH$—Br	285	68
$(CH_3)_2CH$—I	222	53
$(CH_3)_2CH$—OH	381	91
Bonds to tertiary carbons		
$(CH_3)_3C$—H	381	91
$(CH_3)_3C$—F	444	106
$(CH_3)_3C$—Cl	331	79
$(CH_3)_3C$—Br	272	65
$(CH_3)_3C$—I	209	50
$(CH_3)_3C$—OH	381	91
Other C—H bonds		
$PhCH_2$—H (benzylic)	356	85
CH_2=$CHCH_2$—H (allylic)	364	87
CH_2=CH—H (vinyl)	464	111
Ph—H (aromatic)	473	113
HC≡C—H (acetylenic)	523	125
C—C bonds		
CH_3—CH_3	368	88
CH_3CH_2—CH_3	356	85
CH_3CH_2—CH_2CH_3	343	82
$(CH_3)_2CH$—CH_3	351	84
$(CH_3)_3C$—CH_3	339	81

The Periodic Table of Elements

6	C	CARBON	12
Atomic Number = Number of Protons = Number of Electrons	**Chemical Symbol**	**Chemical Name**	**Atomic Weight** = Number of Protons + Number of Neutrons*

METALS — NON-METALS

1 H HYDROGEN 1																	2 He HELIUM 4
3 Li LITHIUM 7	4 Be BERYLLIUM 9											5 B BORON 11	6 C CARBON 12	7 N NITROGEN 14	8 O OXYGEN 16	9 F FLUORINE 19	10 Ne NEON 20
11 Na SODIUM 23	12 Mg MAGNESIUM 24											13 Al ALUMINUM 27	14 Si SILICON 28	15 P PHOSPHORUS 31	16 S SULFUR 32	17 Cl CHLORINE 35	18 Ar ARGON 40
19 K POTASSIUM 39	20 Ca CALCIUM 40	21 Sc SCANDIUM 45	22 Ti TITANIUM 48	23 V VANADIUM 51	24 Cr CHROMIUM 52	25 Mn MANGANESE 55	26 Fe IRON 56	27 Co COBALT 59	28 Ni NICKEL 59	29 Cu COPPER 64	30 Zn ZINC 65	31 Ga GALLIUM 70	32 Ge GERMANIUM 73	33 As ARSENIC 75	34 Se SELENIUM 79	35 Br BROMINE 80	36 Kr KRYPTON 84
37 Rb RUBIDIUM 85	38 Sr STRONTIUM 88	39 Y YTTRIUM 89	40 Zr ZIRCONIUM 91	41 Nb NIOBIUM 93	42 Mo MOLYBDENUM 96	43 Tc TECHNETIUM 98	44 Ru RUTHENIUM 101	45 Rh RHODIUM 103	46 Pd PALLADIUM 106	47 Ag SILVER 108	48 Cd CADMIUM 112	49 In INDIUM 115	50 Sn TIN 119	51 Sb ANTIMONY 122	52 Te TELLURIUM 128	53 I IODINE 127	54 Xe XENON 131
55 Cs CESIUM 133	56 Ba BARIUM 137		72 Hf HAFNIUM 178	73 Ta TANTALUM 181	74 W TUNGSTEN 184	75 Re RHENIUM 186	76 Os OSMIUM 190	77 Ir IRIDIUM 192	78 Pt PLATINUM 195	79 Au GOLD 197	80 Hg MERCURY 201	81 Tl THALLIUM 204	82 Pb LEAD 207	83 Bi BISMUTH 209	84 Po POLONIUM 209	85 At ASTATINE 210	86 Rn RADON 222
87 Fr FRANCIUM 223	88 Ra RADIUM 226		104 Rf RUTHERFORDIUM 267	105 Db DUBNIUM 270	106 Sg SEABORGIUM 271	107 Bh BOHRIUM 274	108 Hs HASSIUM 277	109 Mt MEITNERIUM 278	110 Ds DARMSTADTIUM 281	111 Rg ROENTGENIUM 281	112 Cn COPERNICIUM 285	113 Uut UNUNTRIUM 286	114 Uuq UNUNQUADIUM 289	115 Uup UNUNPENTIUM 289	116 Uuh UNUNHEXIUM 291	117 Uus UNUNSEPTIUM 294	118 Uuo UNUNOCTIUM 294

57 La LANTHANUM 139	58 Ce CERIUM 140	59 Pr PRASEODYMIUM 141	60 Nd NEODYMIUM 144	61 Pm PROMETHIUM 145	62 Sm SAMARIUM 150	63 Eu EUROPIUM 152	64 Gd GADOLINIUM 157	65 Tb TERBIUM 159	66 Dy DYSPROSIUM 163	67 Ho HOLMIUM 165	68 Er ERBIUM 167	69 Tm THULIUM 169	70 Yb YTTERBIUM 173	71 Lu LUTETIUM 175
89 Ac ACTINIUM 227	90 Th THORIUM 232	91 Pa PROTACTINIUM 231	92 U URANIUM 238	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

- = **Solid** at room temperature
- = **Liquid** at room temperature
- = **Gas** at room temperature
- = **Radioactive**
- = **Artificially Made**

* The atomic weights listed on this Table of Elements have been rounded to the nearest whole number. As a result, this chart actually displays the **mass number** of a specific isotope for each element. An element's complete, unrounded atomic weight can be found on the It's Elemental web site: http://education.jlab.org/itselemental/index.html