NAME _____

ID # _____

ORGANIC CHEMISTRY II (CHEM 2302)

8:00 – 8:50 am, June 27, 2016

Exam 1

If you want to pick this exam up tomorrow 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 tomorrow, and you will need to pick up your exam in private from Chemistry department staff in 115 Smith beginning Wednesday, June 29th. Exams that are not picked up within two weeks will be disposed of.

A periodic table and a chart of reaction conditions 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).

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. _____ / 12 5. _____ / 9

2. _____ / 20 6. _____ / 28

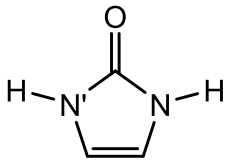
3. _____ / 10 7. _____ / 16

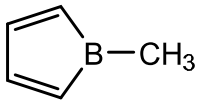
4. _____ / 5

Total Score: _____ / 100

1. (12 pts) For each of the molecules on the next page, circle whether the molecule is aromatic, anti-aromatic, or neither.

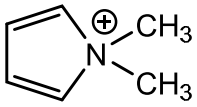
AROMATIC **ANTI-AROMATIC** **NEITHER**

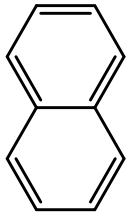




AROMATIC **ANTI-AROMATIC** **NEITHER**

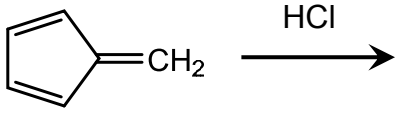
AROMATIC **ANTI-AROMATIC** **NEITHER**

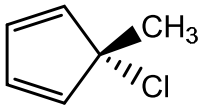


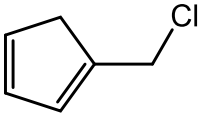


AROMATIC **ANTI-AROMATIC** **NEITHER**

2. (20 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 <u>equally</u>, circle "BOTH". If neither product would result from the reaction, circle "NEITHER". **Circle one answer only.**

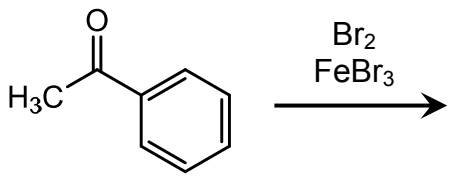


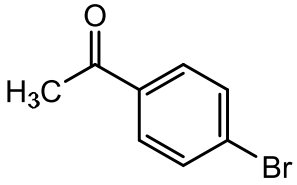
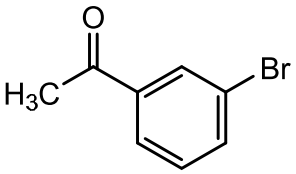


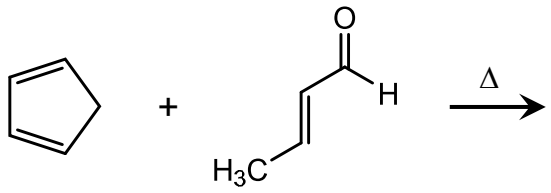


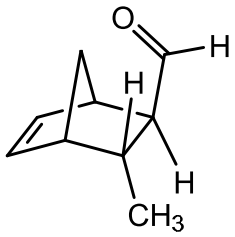
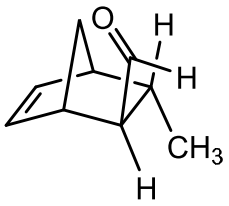
BOTH (equally)

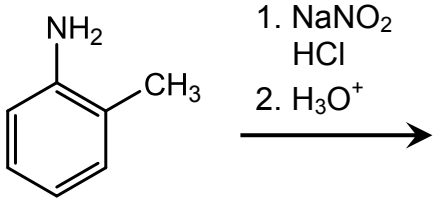
NEITHER

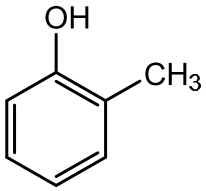
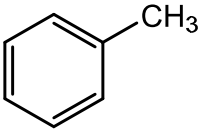


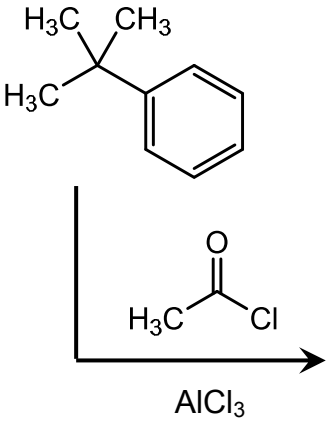
	
BOTH (equally)	NEITHER

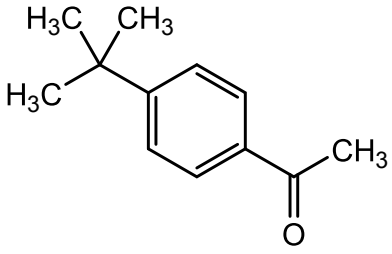
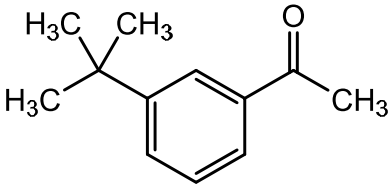


	
BOTH (equally)	NEITHER

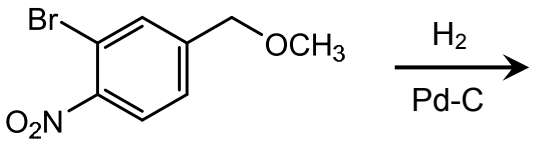


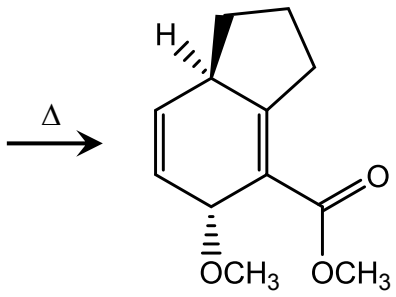
	
BOTH (equally)	NEITHER



	
BOTH (equally)	NEITHER

3. (10 pts) For each of the reactions below, fill in the empty box corresponding to reactants or products. Give only one answer in each box. For reactions that you expect to yield multiple products, give the major product. For reactions that yield multiple enantiomers, draw only one enantiomer in the box, and include the note "+ enantiomer".



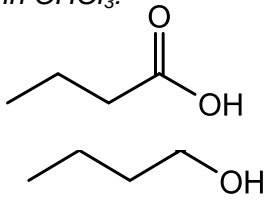


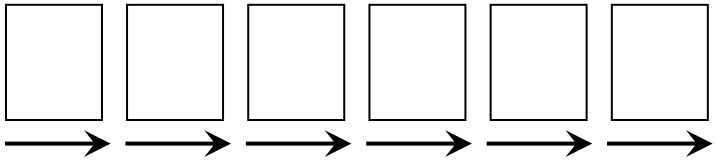
an acyclic molecule

4. (5 pts) How would you use acid-base extraction to separate a carboxylic acid from an alcohol? Below are listed five possible steps you might take to selectively remove an alcohol from a chloroform ($CHCl_3$) solution of an acid. **Write the letters of these steps in the empty boxes, in the correct order.** Keep in mind that you may not need to use all the letters, or all the boxes. (I may have given you extra boxes.)

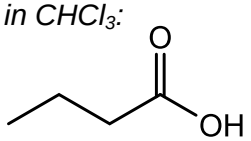
A	Add H_2O and HCl (such that the water layer is acidic). Shake.
B	Add H_2O and NaOH (such that the water layer is basic). Shake.
C	Add fresh $CHCl_3$. Shake.
D	Discard the H_2O layer.
E	Discard the $CHCl_3$ layer.

in $CHCl_3$:

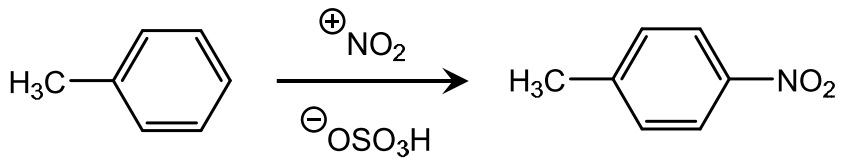




in $CHCl_3$:



5. (9 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. Use only the molecules shown in the problem; don't invoke generic species. (E.g., don't use "B:" as a generic base.)

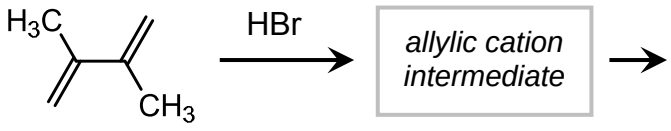


NO_2^+ and $^-OSO_3H$ are generated from HNO_3/ H_2SO_4. You do not need to draw a mechanism for the formation of NO_2^+ and $^-OSO_3H$—just use them.

Mechanism:

6. (28 pts) 2,3-Dimethylbutadiene (the reactant below) reacts with HBr to form two different products, both of which come from one allylic cation intermediate. The preferred product depends on whether the reaction is performed at low or high temperature.

   a. In the boxes below and on the next page, draw the structures of the two products of the reaction between 2,3-dimethylbutadiene and HBr. Draw each product in the box corresponding to its preferential conditions.



2,3-dimethyl-butadiene

allylic cation intermediate

*preferred at **low** temperature:*

b. In the box below, **draw a mechanism** (using "electron pushing") that shows how the **high-temperature product** is formed from 2,3-dimethylbutadiene. Make sure your mechanism shows the structure of the allylic cation intermediate.

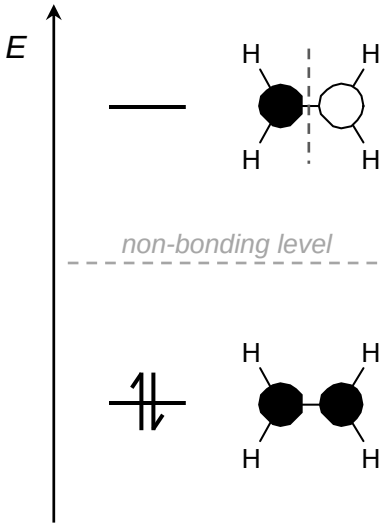
*preferred at **high** temperature:*

Mechanism:

c. In the box below, draw a molecular orbital diagram for the conjugated π system in the **allylic cation intermediate**. In your diagram, make sure to:

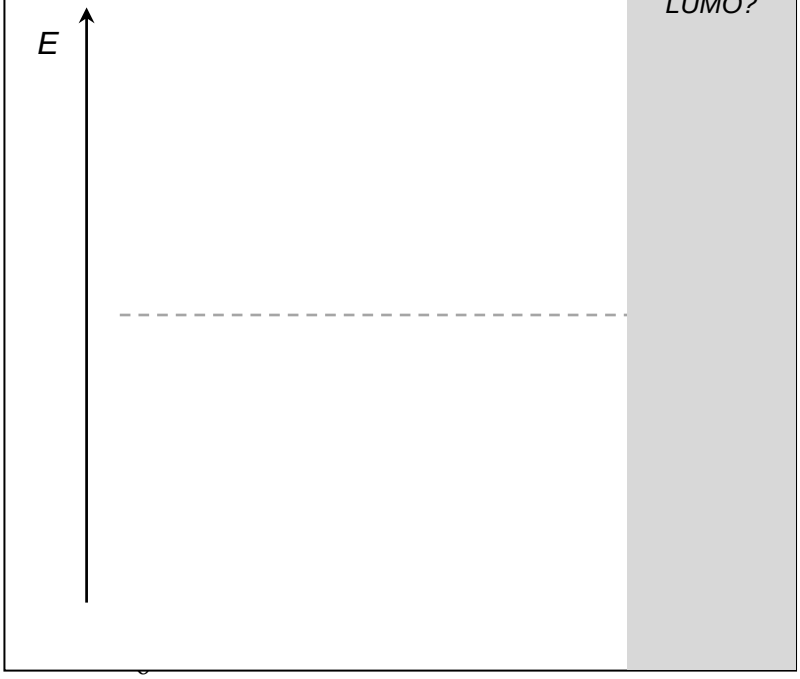
- Draw orbital energy levels;
- Draw a molecular orbital for each energy level. Use dark and light shading to indicate the phase in each orbital lobe.
- Fill your orbitals with the appropriate number of electrons.

example of answer format (for C_2H_4):



your answer:

Which is LUMO?

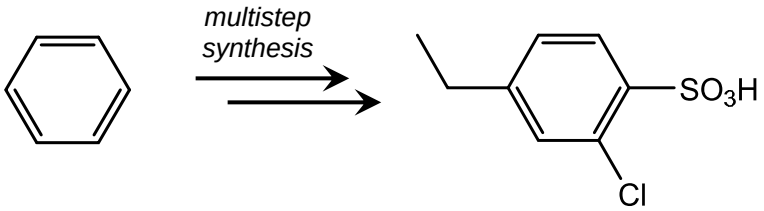


d. Which of the orbitals you drew is the LUMO? On your diagram on the previous page, write "**LUMO**" next to this orbital.

e. Would you expect
λ_{max}(products) to be **>** , **<** , *or* **=** λ_{max}(2,3-dimethylbutadiene)?

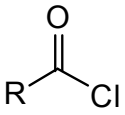
(circle one)

7. (16 pts) **Propose a multistep synthesis** of the product shown below, starting from benzene. You may use any reagents and reactions we've learned about in class and/or in the text. You might discover multiple answers to this problem; draw only your best (one) synthetic route. Feel free to draw an incomplete route—we will give you partial credit where we can.



Exam 1 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

1. $NaNO_2$ HCl 2. CuCN *or* H_3PO_2 *or* CuX *or* H_3O^+	 $AlCl_3$	R-X (R = alkyl) $AlCl_3$ *or* $FeBr_3$	Zn(Hg), HCl/H_2O	1. N_2H_4 2. KOH, Δ	
		H_2 Pd-C	1. Ag_2O NH_3 2. H_3O^+	1. O_3 2. H_2O	$Na_2Cr_2O_7$ H_2SO_4

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.