

Please read the following before proceeding

1. Materials: Turn off cell phones and wireless PDA devices. Place all other materials on the floor. You will only need a pencil. Molecular models are optional.
2. Show your Buzz Card when you turn in your completed exam.
3. You must work alone.
4. This is a closed book exam. Give or take no assistance from other students. Recall the Georgia Tech Honor Code.

"I have always worked better alone."-- Claude Monet

"I pledge my honor that I have not violated the Honor Code during this examination."

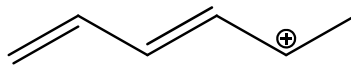
Signed _____

Note: pKa and periodic tables are provided on the last page.

1. (40 points, 4 points each) Circle the correct answer. There is only one correct answer.

- a. Which statement about curved arrows is **not** correct?
- A) Arrows are drawn away from negative charges and/or toward positive charges.
 - B) Several curved arrows might have to be used to describe one reaction.
 - C) Curved arrows always start at the nucleus of an atom.**
 - D) The arrow is drawn in the direction of the electron flow.
 - E) Curved arrows are drawn to indicate the movements of electrons.
- b. What product is formed from the reaction of methanol and propene, $\text{CH}_3\text{-CH=CH}_2$, in the presence of a trace amount of sulfuric acid?
- A) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$
 - B) $(\text{CH}_3)_2\text{CH}(\text{OCH}_3)$**
 - C) $\text{HO-C}(\text{CH}_3)_3$
 - D) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_3$
 - E) $\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$
- c. How could you synthesize 1-butene from ethyne (acetylene)?
- A) deprotonate ethyne with appropriate base, react with ethyl bromide, react with hydrogen + Pt or Pd catalyst
 - B) add propene to methyl bromide
 - C) add ethane to ethyne
 - D) deprotonate ethyne with appropriate base, react with ethyl bromide
 - E) deprotonate ethyne with appropriate base, react with ethyl bromide, react with hydrogen and Lindlar's catalyst**
- d. Which sequence of reagents would you use to synthesize 2-butanol from propyne?
Lindlar's catalyst is Pd/CaCO_3 and quinoline
- A) 1. NaNH_2 2. CH_3Br 3. $\text{H}_2/\text{Lindlar's catalyst}$ 4. $\text{H}^+/\text{H}_2\text{O}$**
 - B) 1. NaOH 2. CH_3Br 3. $\text{H}_2/\text{Lindlar's catalyst}$ 4. $\text{H}^+/\text{H}_2\text{O}$
 - C) 1. NaNH_2 2. CH_3Br 3. H_2 4. $\text{H}^+/\text{H}_2\text{O}$
 - D) 1. NaNH_2 2. $\text{CH}_3\text{CH}_2\text{Br}$ 3. $\text{H}_2/\text{Lindlar's catalyst}$ 4. $\text{H}^+/\text{H}_2\text{O}$
 - E) 1. NaNH_2 2. CH_3Br 3. $\text{H}_2/\text{Lindlar's catalyst}$ 4. H_2O

- e. How many different products could be obtained in the reaction of the following carbocation intermediate with a bromide ion? *Ignore stereoisomers.*



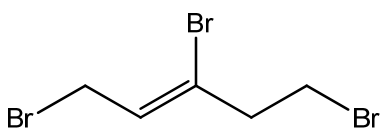
- A) 1
B) 2
C) 3
D) 4
E) 5
- f. What carbon is protonated in the first step of the reaction of 3-methyl-2,4-heptadiene with one equiv of HBr?
- A) C-1
B) C-2
C) C-3
D) C-4
E) C-5
- g. Which of the following compounds reacts most rapidly with $\text{Cl}_2/\text{FeCl}_3$?
- A) $\text{C}_6\text{H}_5\text{-COOH}$
B) $\text{C}_6\text{H}_5\text{-CN}$
C) $\text{C}_6\text{H}_5\text{-OCH}_3$
D) $\text{C}_6\text{H}_5\text{-NO}_2$
E) $\text{C}_6\text{H}_5\text{-CF}_3$
- h. Which of the following is **not** a true statement?
- A) A nitrile (cyano) substituent is a meta director.
B) A nitro substituent is a meta director.
C) A chloro substituent is an ortho-para director.
D) A protonated amino substituent is an ortho-para director.
E) A methyl substituent is an ortho-para director.
- i. Which of the following compounds does **not** have at least one chirality center?
- A) 3,4-dibromoheptane
B) 2,3-dibromoheptane
C) 2-bromoheptane
D) 4-bromoheptane
E) 3-bromoheptane

j. Select the substituent with the highest priority in the *R/S* system.

- A) $-\text{CH}_2\text{CH}_2\text{OH}$
- B) $-\text{CH}_2\text{OCH}_3$
- C) $-\text{CH}_2\text{CH}=\text{O}$
- D) $-\text{CH}=\text{O}$
- E) $-\text{CH}=\text{CH}_2$

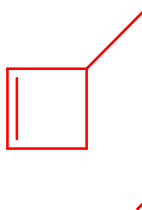
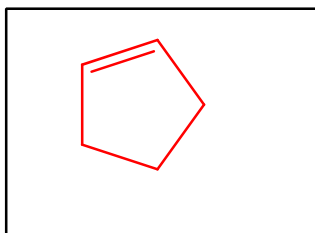
2. (40 points, 4 points each) **SHORT ANSWER.** Draw the structure, or write the word or phrase that best completes each statement or answers the question.

a. Name the following compound

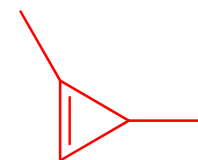
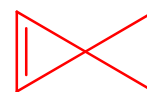
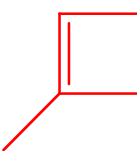


(Z)-1,3,5-tribromopent-2-ene or
(Z)-1,3,5-tribromo-2-pentene
2 pts. If correct, except (Z)

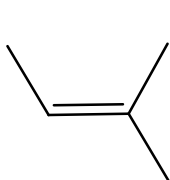
b. Draw any mono-alkene with the molecular formula C_5H_8



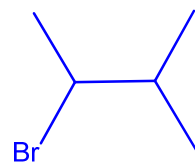
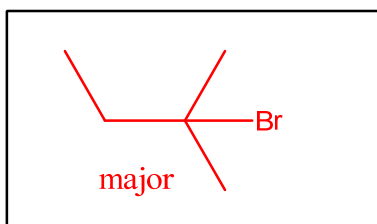
others possible



c. Draw the major product from the following reaction

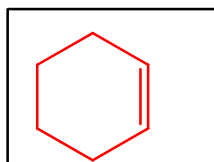


HBr

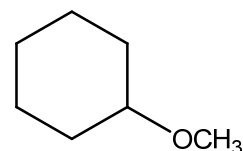
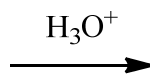
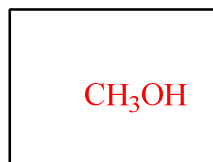


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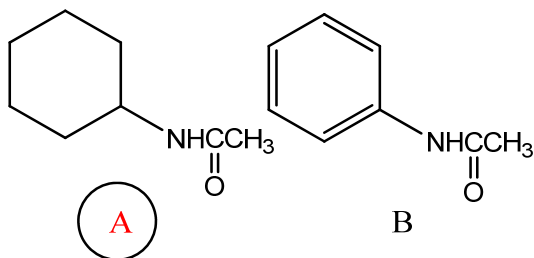
d. What two substances need to react to complete the following reaction?



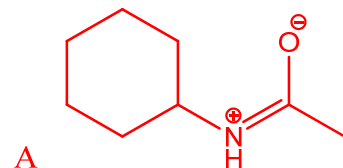
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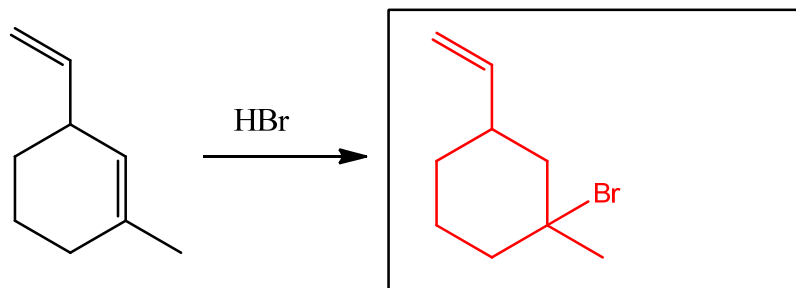
- e. Which compound has the greater electron density on its oxygen atom? Circle A or B and provide a brief explanation or drawing.



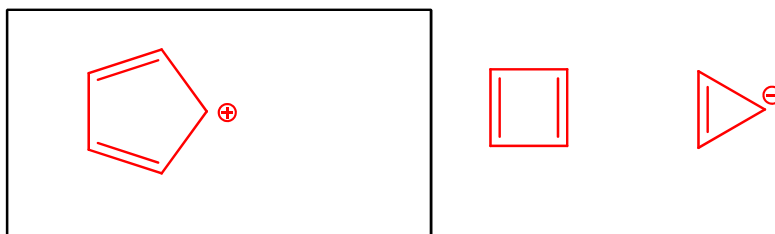
A has the greater electron density on its oxygen because the lone pair on the nitrogen can be delocalized onto the oxygen. With B, the ring draws electron density towards the ring which takes some e-density from oxygen.



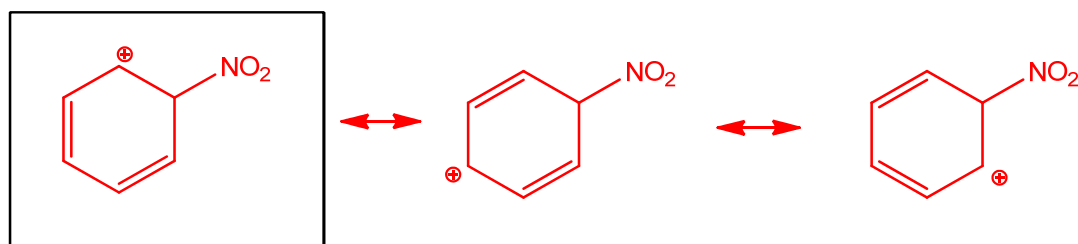
- f. Give the major product of the following reaction (one equivalent of reagent is used).



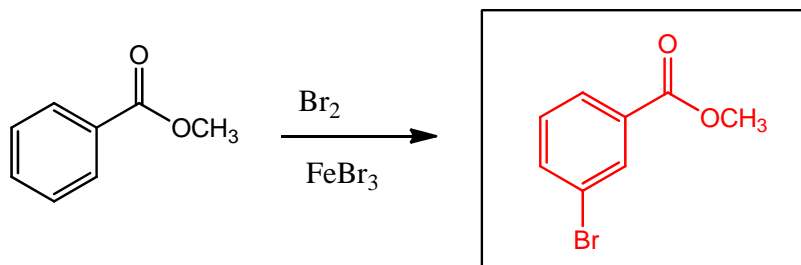
- g. Draw any carbon based anti-aromatic species with less than six carbon atoms.



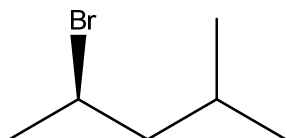
- h. Draw any one of the key intermediates when benzene reacts with $\text{HNO}_3 / \text{H}_2\text{SO}_4$.



- i. Give the major product of the following electrophilic aromatic bromination reaction.

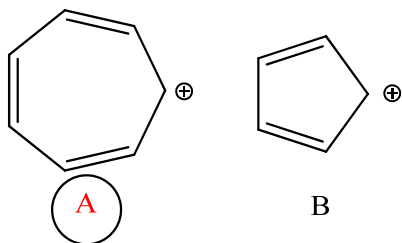


- j. Name the following compound



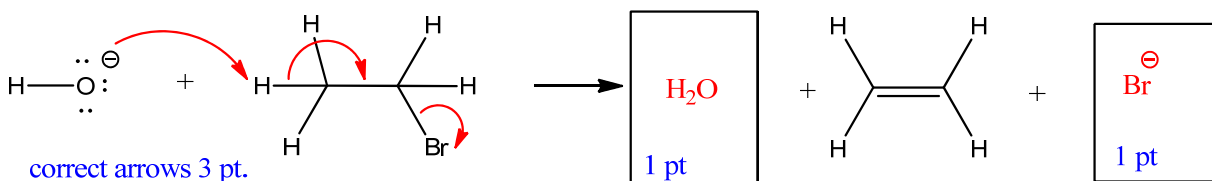
(R)-2-bromo-4-methylpentane
2 pts. if correct, except (R)

3. (5 points) Which of the following pairs is more stable? Circle A or B and explain your choice briefly.

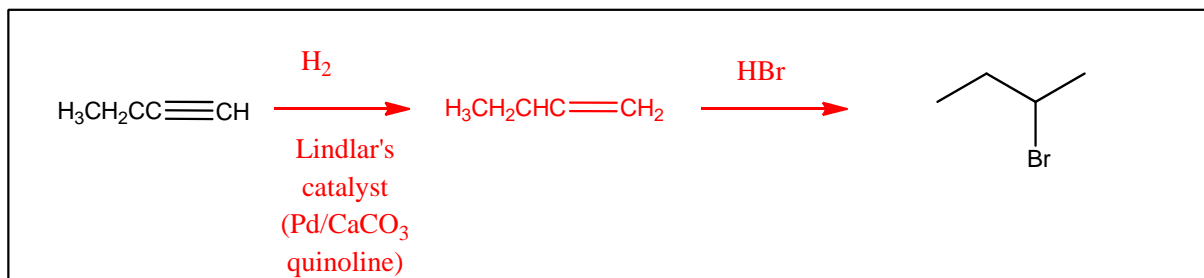
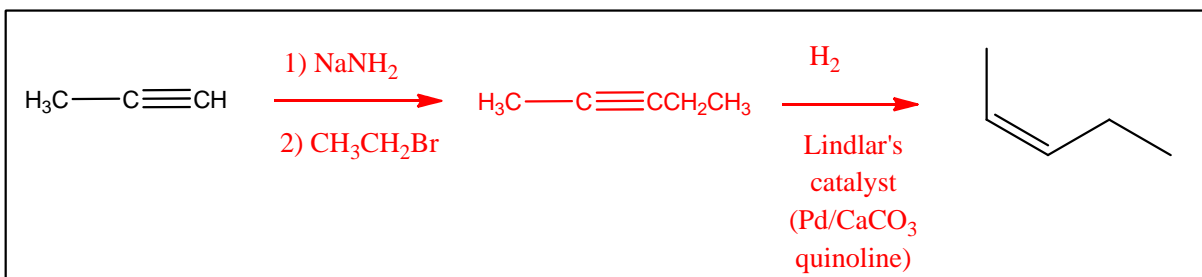
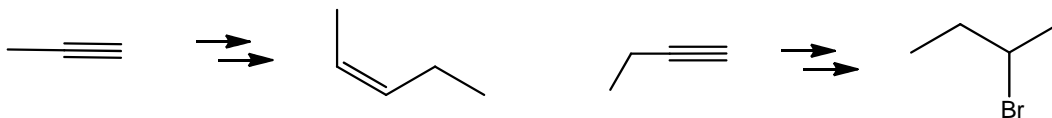


A is more stable because it is aromatic with 6 electrons ($4n+2$) in 7 p orbitals

4. (5 points)) **Mechanistic understanding:** Draw curved arrows to show the flow of electrons responsible for the conversion of ethyl bromide to ethylene and two other products



5. (10 points)) **Multistep synthesis:** *Select one of the following two transformations.* Provide a sequence of reactions to perform the transformation, showing the reagents and structures of all intermediates products. The synthesis must use the given starting material. You may use any other substrate materials and/or reagents.



1A 1 H Hydrogen 1.008																	7A 17 H Hydrogen 1.008	8A 18 He Helium 4.003																															
3 Li Lithium 6.941	4 Be Beryllium 9.012																	5A 15 N Nitrogen 14.01	6A 16 O Oxygen 16.00	7A 17 F Fluorine 19.00	8A 18 Ne Neon 20.18																												
11 Na Sodium 22.99	12 Mg Magnesium 24.31	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	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 65.41	31 Ga Gallium 69.72	32 Ge Germanium 72.64	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80																								
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 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.8	53 I Iodine 126.9	54 Xe Xenon 131.3	55 Cs Cesium 132.9	56 Ba Barium 137.3	57 La Lanthanum 138.9	58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.8	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium 226.0	89 Ac Actinium 227.0	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)																																							

58 Ce Cerium 140.1	59 Pr Praseodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.0	71 Lu Lutetium 175.0
90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	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)

Acid	Approximate pK_a	Conjugate Base
HSbF_6	< -12	SbF_6^-
HI	-10	I^-
H_2SO_4	-9	HSO_4^-
HBr	-9	Br^-
HCl	-7	Cl^-
$\text{C}_6\text{H}_5\text{SO}_3\text{H}$	-6.5	$\text{C}_6\text{H}_5\text{SO}_3^-$
$(\text{CH}_3)_2\text{OH}^+$	-3.8	$(\text{CH}_3)_2\text{O}$
$(\text{CH}_3)_2\text{C}=\text{OH}^+$	-2.9	$(\text{CH}_3)_2\text{C}=\text{O}$
CH_3OH_2^+	-2.5	CH_3OH
H_3O^+	-1.74	H_2O
HNO_3	-1.4	NO_3^-
$\text{CF}_3\text{CO}_2\text{H}$	0.18	CF_3CO_2^-
HF	3.2	F^-
$\text{CH}_3\text{CO}_2\text{H}$	4.75	CH_3CO_2^-
H_2CO_3	6.35	HCO_3^-
$\text{CH}_3\text{COCH}_2\text{COCH}_3$	9.0	$\text{CH}_3\text{COCH}^-\text{COCH}_3$
NH_4^+	9.2	NH_3
$\text{C}_6\text{H}_5\text{OH}$	9.9	$\text{C}_6\text{H}_5\text{O}^-$
HCO_3^-	10.2	CO_3^{2-}
CH_3NH_3^+	10.6	CH_3NH_2
H_2O	15.7	OH^-
$\text{CH}_3\text{CH}_2\text{OH}$	16	$\text{CH}_3\text{CH}_2\text{O}^-$
$(\text{CH}_3)_3\text{COH}$	18	$(\text{CH}_3)_3\text{CO}^-$
CH_3COCH_3	19.2	$^-\text{CH}_2\text{COCH}_3$
$\text{HC}\equiv\text{CH}$	25	$\text{HC}\equiv\text{C}^-$
H_2	35	H^-
NH_3	38	NH_2^-
$\text{CH}_2=\text{CH}_2$	44	$\text{CH}_2=\text{CH}^-$
CH_3CH_3	50	CH_3CH_2^-

Write your class roll number on (1) the top of the first page and (2) below.

***** If you need to verify your class roll number, you can do this at the front of the room when you turn in your exam paper. *****

Roll Number _____

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Page 3 (20) _____

Page 4 (20) _____

Page 5 (16) _____

Page 6 (18) _____

Page 7 (10) _____

Total 100 _____