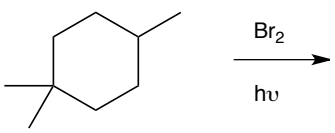
CHEM 235 ✈ Exam 2 ✈ Fall 2017 Name: _____

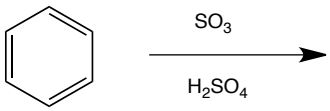
1. (16 points) Predict the organic product(s) for the following reactions. A reaction takes place in each.
Answer 4 of the 5 parts (A-E). Cross out the one you do not want graded, or the first 4 answered will be graded.

- Show all organic product(s). Indicate relative amounts.
- Pay attention to stereochemistry, unless indicated otherwise. Indicate relative amounts of stereoisomers.
- If a workup step is not indicated where one is typically expected, it is intentional. In such a case, indicate the product(s) before workup.

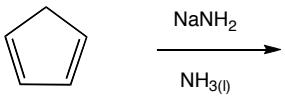
A)



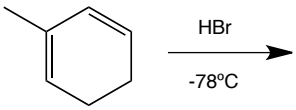
B)



C)

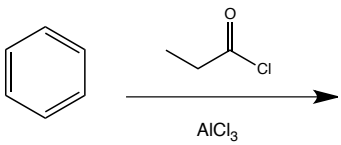


D)

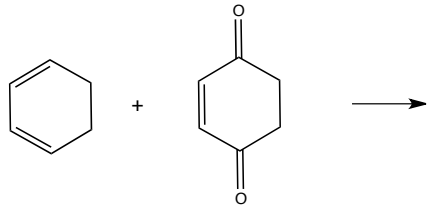


Two significant products -
Indicate major & minor

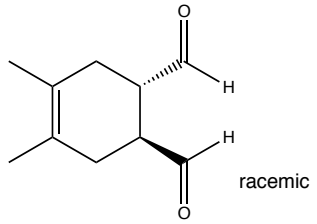
E)



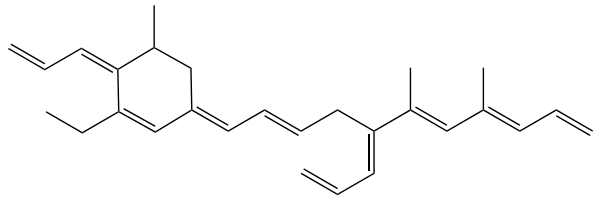
2. (7 points) Predict the single, major product of the following Diels-Alder reaction under kinetic control and provide a complete arrow-pushing mechanism. Pay close attention to the orientation of bonds in space in the product.



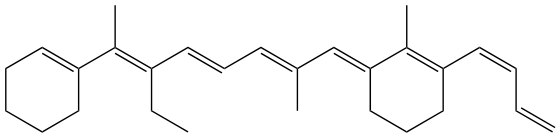
3. (5 points) Provide the structures for the diene and dienophile required to prepare the following compound by a Diels-Alder reaction.



4. (3 points) Which of the following compounds (A or B) will have the ***shorter*** λ_{max}?

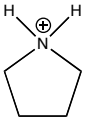


A

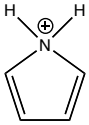


B

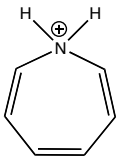
5. (4 points) Put the following in order from MOST acidic to LEAST acidic. Clearly indicate the order. No explanation is needed.



C

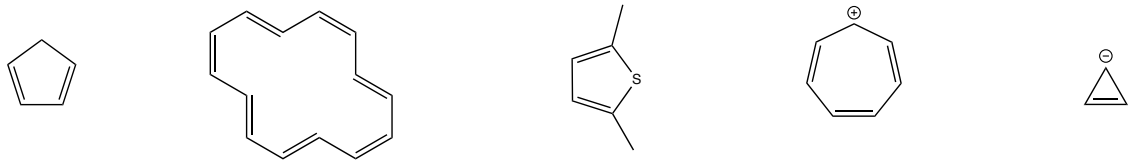


D

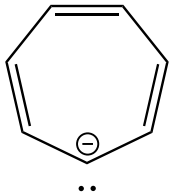


E

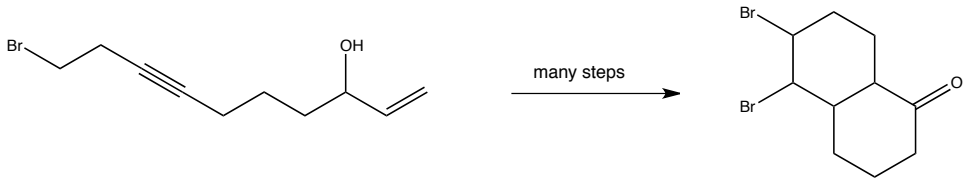
6. (5 points) Which of the following species are **aromatic** or **anti-aromatic**? Assume all π-systems are in a planar arrangement.
CIRCLE those that are aromatic. Put an X through those that are anti-aromatic. Leave others unmarked.
No explanations are needed.



7. (4 points) Draw an Aufbau (energy level) diagram for the π-bonding system in following compound.
Properly label each of the pi (π) orbitals as π, π^{nb}, or π* orbitals. Identify the compound as **aromatic** or **anti-aromatic** based on the diagram. No additional explanation needed.

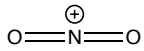


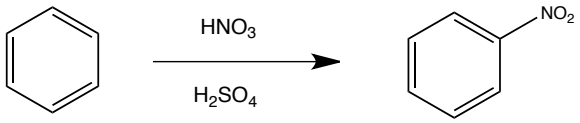
BONUS (8 points): Suggest a reasonable reaction scheme to produce the following product in good yield. (Do this problem only after you have completed the exam).



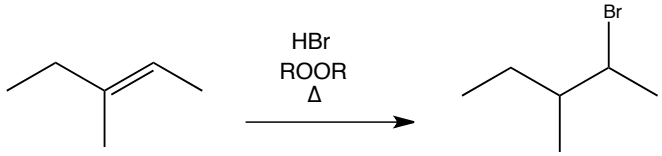
8. (11 points) Provide a complete arrow-pushing mechanism for the reaction below, including the formation of the electrophile all important resonance structures for the EAS intermediate, and the arrows needed to move to each subsequent resonance structure.

electrophile:



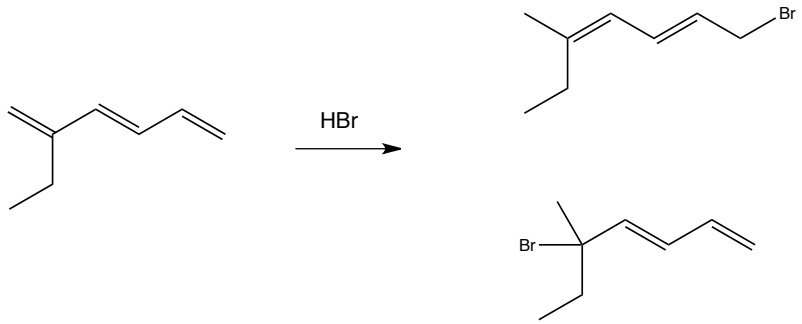


9. (11 points) Provide a complete arrow-pushing mechanism for the following reaction. Provide initiation and propagation steps and one termination step. You may ignore stereochemistry.



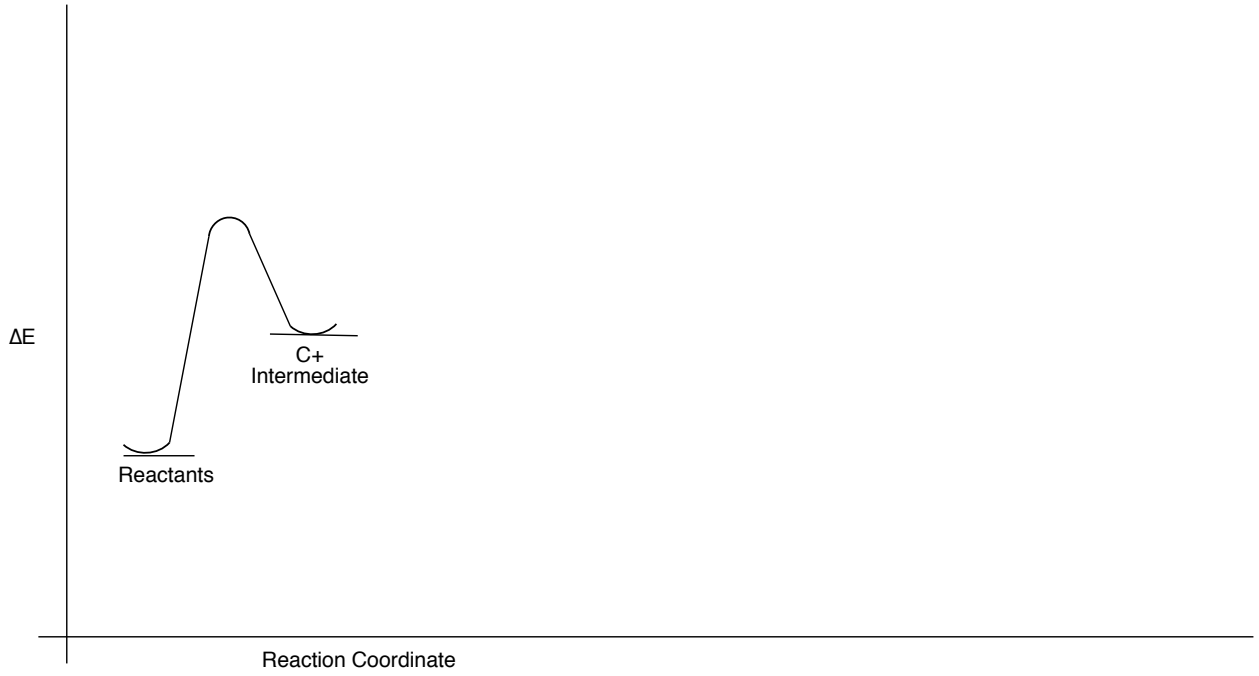
10. (14 points) Consider the addition reaction of HBr to the conjugated triene below at high and low temperature. The same 2 products are formed in significant quantity (>5%) at each temperature, but in different quantities.

A) Label the isomer that is the major product that forms at high temperature (60ºC) with the word HIGH and label the isomer that is the MAJOR product at low temperature (-78ºC) with the word LOW.

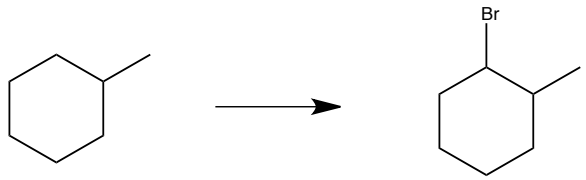


B) Provide a complete, arrow-pushing mechanism for the formation of the product at HIGH temperature. Be sure to show ALL of the resonance structures of the resonance-stabilized intermediate. Show arrows needed to move to each new resonance structure.

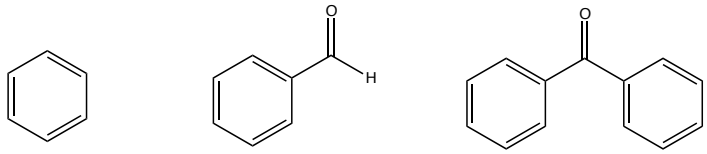
C) Complete the sketch of a reaction energy diagram for the reaction. Indicate the relative energies of the two products and transition states to each other and the reactants and intermediate (as already shown on the diagram).



11. (10 points) Devise a synthetic scheme for the following transformation (you may ignore stereochemistry):



12. (10 points) Using benzene and benzaldehyde as your only sources of carbon in the final structure, outline a scheme for the formation of benzophenone. You may use other reagents and solvents as needed. Show the major product at each intermediate step. You may use the abbreviation –Ph for a benzene ring in a structure.



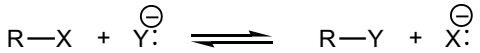
benzene benzaldehyde benzophenone

General Reactions:

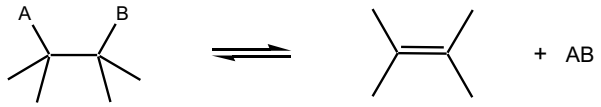
- Reaction conditions are not given for all reactions.
- Reaction conditions and/or substrates may be general and can vary.
- Some processes are reversible with varying conditions.
- Stereochemistry of reactions is NOT given except where indicated.

Structural Elements
- –R = represents a generic alkyl group
- A, B, X, Y = represent various groups
- A line off of a carbon with no indicated substituent may be considered a H or an alkyl group.

Substitution:



Elimination / Addition:



Selected Hydration of Alkenes:

For reactions below – consider whether they are Markovnikov additions or anti-Markovnikov and if rearrangements are possible.

- Acid-catalyzed hydration:
  Water as solvent with strong acid (eg. sulfuric)

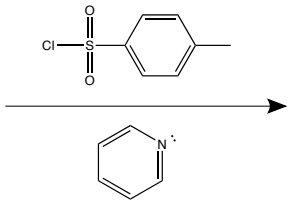
- Hydroboration-Oxidation:

  1) BH_3 in THF
  →
  2) H_2O_2 / NaOH / H_2O

Selected conversions of an alcohol to a halide:

- PBr_3 1º or 2º R-OH → R-Br
- $SOCl_2$ (with pyridine) 1º or 2º R-OH → R-Cl

Tosylate formation



Silyl Ether Protection / Deprotection

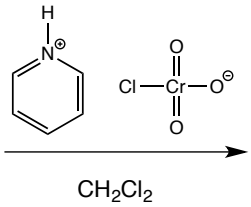
Reaction Conditions – Oxidation / Reduction:

- Chromic Acid

  CrO_3 / H_2SO_4
  →
  H_2O

  Note: Some variations possible. All are a source of CrO_3 and are in a solution where water is part of the solvent mixture.

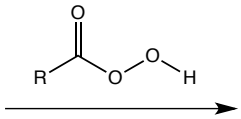
- Pyridinium Chlorochromate



- Alkene Cleavage

  1) O_3
  →
  2) CH_3SCH_3

- Epoxidation



- Hydride Reductions:
  - $LiAlH_4$
    (in Et_2O followed by aqueous acidic workup)
  - $NaBH_4$ (in H_2O)

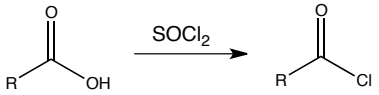
- Alkyne Hydrogenations

  H_2
  →
  Pt or Pd
  (2 equiv. H_2 add)

  H_2
  →
  Lindlar Catalyst
  (1 equiv. H_2 - syn addition)

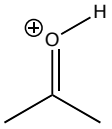
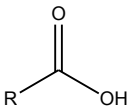
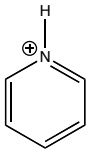
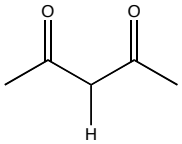
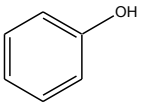
  Na
  →
  NH_3
  (1 equiv. H_2 - anti addition)

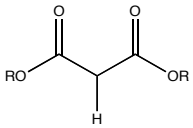
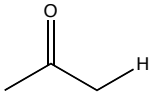
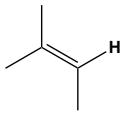
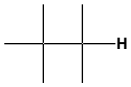
Conversion of a Carboxylic Acid to an Acid Chloride:



Organic Chemistry – pK_a chart

- Values are approximate.
- –R or a bond-line off of a carbon with no indicated substituent represents a generic alkyl group.

Species	pK_a
HI	–10
H_2SO_4	–9
HBr	–9
HCl	–7
ROH_2^+	–2 ~ –4
	~ –3
H_3O^+	–1.74
H_3PO_4	2
HF	3.2
	4 ~ 5
	5.2
H_2CO_3	6.4
H_2S	~ 7
	~ 9
HCN	9.2
NH_4^+	9.2
	9.9
R-SH	~ 10
HCO_3^-	10.2

Species	pK_a
$R\text{-}NH_3^+$	~ 10-11
	~ 13
H_2O	15.7
CH_3CH_2O-**H**	15.9
R-O-H	16
$(CH_3)_3CO$-**H**	18
	~ 19
R–C≡C–H	25
H_2	35
$R\text{-}NH_2$	38
NH_3	38
	~ 44
	> 50

Additional pK_a values (add other species studied)

Species	pK_a

The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	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)

1995 IUPAC masses and Approved Names from http://www.chem.qmw.ac.uk/iupac/AtWt/
masses for 107-111 from C&EN, March 13, 1995, p. 35
112 from http://www.gsi.de/z112e.html