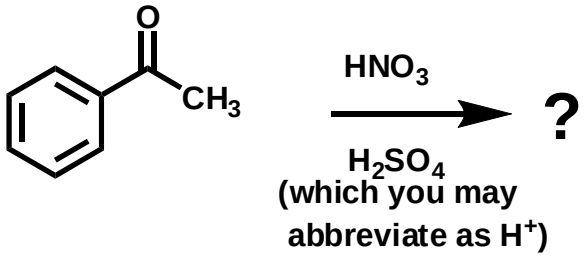
University of Windsor
Chemistry and Biochemistry

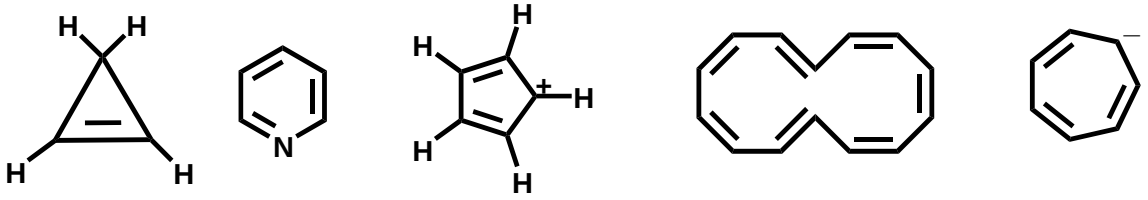
Chemistry 59-235 **Feb. 10, 2016**
First Test **Time: 60 minutes**

*Note: There are questions **on both sides** of this page.*
Note: Please write in exam booklets. Tests written in pencil will be marked, but cannot be returned for remarking.
Note: I also wish to see an appropriate valence bond structure for complex substituents such as sulfonic acids, nitro groups, diazonium ions, etc…. at least one time somewhere.

1. Give the **complete** mechanism for the following nitration of acetophenone (shown). The complete answer will include showing the generation of the reactive electrophilic species, all reasonable resonance forms of the cyclohexdienyl cationic intermediate, and the step showing the creation of the final product. (**15 marks**)



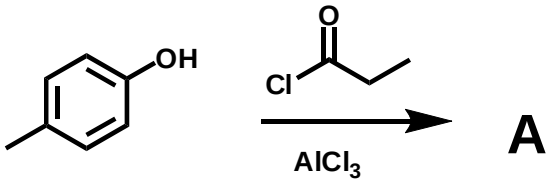
2. Indicate whether the following systems are aromatic, antiaromatic, or non-aromatic by Hückel's Rule, ***and*** give the number of π- electrons in the *conjugated* cyclic system (**5 marks**)



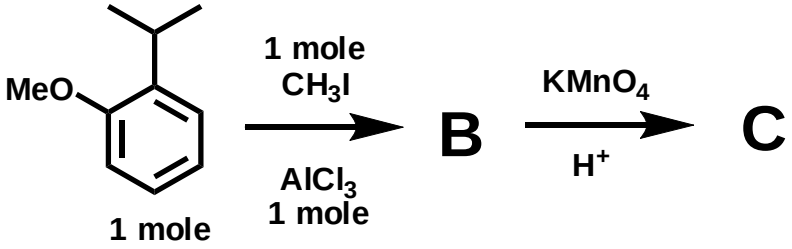
3. Draw the lowest energy of all π- molecular orbital of cyclobutadiene and **one** of the highest *occupied* molecular orbitals (HOMO's) of benzene. (**5 marks**)

4. Predict the most reasonable structure of the major product(s) from each of the following reactions. Mechanisms are not necessary, but showing your work is likely to be a help. *Note: If there is >1 significant product, show them all and take the **major** one on to any further step. Note 2. In complex substituents such as sulfonic acids, nitro groups and diazonium salts, the correct valence bond structure must be drawn (at least) one time.* (**5 marks for each letter, 30 marks total**).

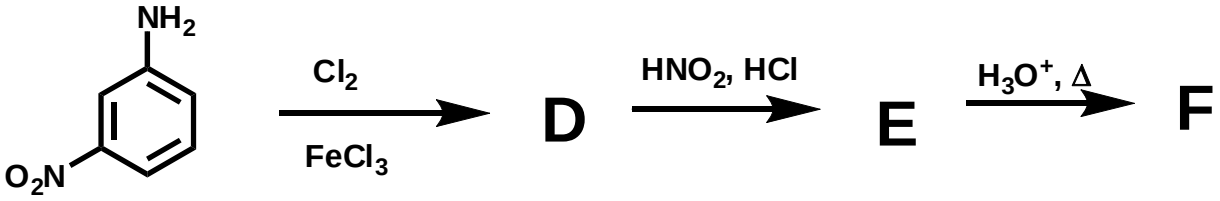
a)



b)

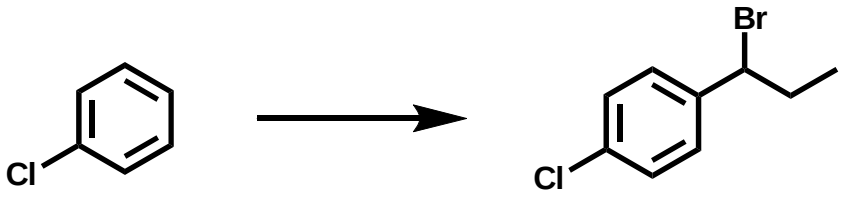


c) Don't forget the valence bond structures (at least once) of complex functional groups.

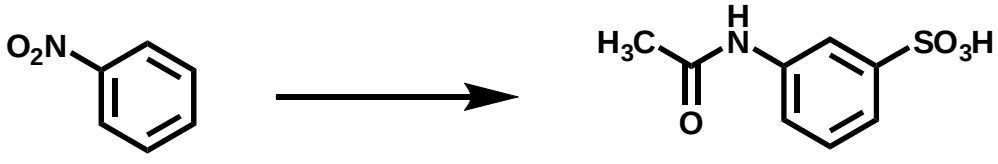


5. Show by equation (in one or several steps) how you could prepare the illustrated products from the given starting material. You may use any other reagents which you deem fit. Show all reagents, conditions, and intermediates which could be isolated. I also wish to see an appropriate valence bond structure for complex substituents such as sulfonic acids, nitro groups, diazonium ions, etc…. at least one time somewhere. Mechanisms are not necessary, but may be a help (**10 marks each, 20 marks total**).

a.



b.



WebElements: the periodic table on the world-wide web

http://www.webelements.com/

Key: element name / **atomic number** / **symbol** / 2001 atomic weight (mean relative mass)

1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
hydrogen 1 **H** 1.00794(7)																		helium 2 **He** 4.002602(2)
lithium 3 **Li** 6.941(2)	beryllium 4 **Be** 9.012182(3)												boron 5 **B** 10.811(7)	carbon 6 **C** 12.0107(8)	nitrogen 7 **N** 14.00674(7)	oxygen 8 **O** 15.9994(3)	fluorine 9 **F** 18.9984032(5)	neon 10 **Ne** 20.1797(6)
sodium 11 **Na** 22.989770(2)	magnesium 12 **Mg** 24.3050(6)												aluminium 13 **Al** 26.981538(2)	silicon 14 **Si** 28.0855(3)	phosphorus 15 **P** 30.973761(2)	sulfur 16 **S** 32.065(5)	chlorine 17 **Cl** 35.453(2)	argon 18 **Ar** 39.948(1)
potassium 19 **K** 39.0983(1)	calcium 20 **Ca** 40.078(4)		scandium 21 **Sc** 44.955910(8)	titanium 22 **Ti** 47.867(1)	vanadium 23 **V** 50.9415(1)	chromium 24 **Cr** 51.9961(6)	manganese 25 **Mn** 54.938049(9)	iron 26 **Fe** 55.845(2)	cobalt 27 **Co** 58.933200(9)	nickel 28 **Ni** 58.6934(2)	copper 29 **Cu** 63.546(3)	zinc 30 **Zn** 65.409(4)	gallium 31 **Ga** 69.723(1)	germanium 32 **Ge** 72.64(1)	arsenic 33 **As** 74.92160(2)	selenium 34 **Se** 78.96(3)	bromine 35 **Br** 79.904(1)	krypton 36 **Kr** 83.798(2)
rubidium 37 **Rb** 85.4678(3)	strontium 38 **Sr** 87.62(1)		yttrium 39 **Y** 88.90585(2)	zirconium 40 **Zr** 91.224(2)	niobium 41 **Nb** 92.90638(2)	molybdenum 42 **Mo** 95.94(1)	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07(2)	rhodium 45 **Rh** 102.90550(2)	palladium 46 **Pd** 106.42(1)	silver 47 **Ag** 107.8682(2)	cadmium 48 **Cd** 112.411(8)	indium 49 **In** 114.818(3)	tin 50 **Sn** 118.710(7)	antimony 51 **Sb** 121.760(1)	tellurium 52 **Te** 127.60(3)	iodine 53 **I** 126.90447(3)	xenon 54 **Xe** 131.293(6)
caesium 55 **Cs** 132.90545(2)	barium 56 **Ba** 137.327(7)	57-70 *	lutetium 71 **Lu** 174.967(1)	hafnium 72 **Hf** 178.49(2)	tantalum 73 **Ta** 180.9479(1)	tungsten 74 **W** 183.84(1)	rhenium 75 **Re** 186.207(1)	osmium 76 **Os** 190.23(3)	iridium 77 **Ir** 192.217(3)	platinum 78 **Pt** 195.078(2)	gold 79 **Au** 196.96655(2)	mercury 80 **Hg** 200.59(2)	thallium 81 **Tl** 204.3833(2)	lead 82 **Pb** 207.2(1)	bismuth 83 **Bi** 208.98038(2)	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 **	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [285]		ununquadium 114 **Uuq** [289]				

*lanthanoids	lanthanum 57 **La** 138.9055(2)	cerium 58 **Ce** 140.116(1)	praseodymium 59 **Pr** 140.90765(2)	neodymium 60 **Nd** 144.24(3)	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36(3)	europium 63 **Eu** 151.964(1)	gadolinium 64 **Gd** 157.25(3)	terbium 65 **Tb** 158.92534(2)	dysprosium 66 **Dy** 162.500(1)	holmium 67 **Ho** 164.93032(2)	erbium 68 **Er** 167.259(3)	thulium 69 **Tm** 168.93421(2)	ytterbium 70 **Yb** 173.04(3)
**actinoids	actinium 89 **Ac** [227]	thorium 90 **Th** 232.0381(1)	protactinium 91 **Pa** 231.03588(2)	uranium 92 **U** 238.02891(3)	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]

Element symbols and names: symbols, names, and spellings are those recommended by IUPAC (http://www.iupac.org/). After controversy, the names of elements 101-109 are now confirmed (Pure & Appl. Chem., 1997, **69**, 2471–2473). Names have yet to be proposed for the elements 110–112, and 114 - those used here are IUPAC's temporary systematic names (Pure & Appl. Chem., 1979, **51**, 381–384). In the USA and some other countries, the spellings **aluminum** and **cesium** are normal while in the UK and elsewhere the usual spelling is **sulphur**.

Atomic weights (mean relative masses): Apart from the heaviest elements, these are IUPAC 2001 values (Pure & Appl. Chem., 2001, **73**, 667–683). Elements with values given in brackets have no stable nuclides and are represented by 5-figure values for the longest-lived isotope. The elements thorium, protactinium, and uranium have characteristic terrestrial abundances and these are the values quoted. The last significant figure of each value is considered reliable to ±1 except where a larger uncertainty is given in parentheses.

Periodic table organisation: for a justification of the positions of the elements La, Ac, Lu, and Lr in the WebElements periodic table see W. B. Jensen, "The positions of lanthanum (actinium) and lutetium (lawrencium) in the periodic table", J. Chem. Ed., 1982, **59**, 634–636.

Group labels: the numeric system (1–18) used here is the current IUPAC convention. For a discussion of this and other common systems see: W. C. Fernelius and W. H. Powell, "Confusion in the periodic table of the elements", J. Chem. Ed., 1982, **59**, 504–508.