Name: Key

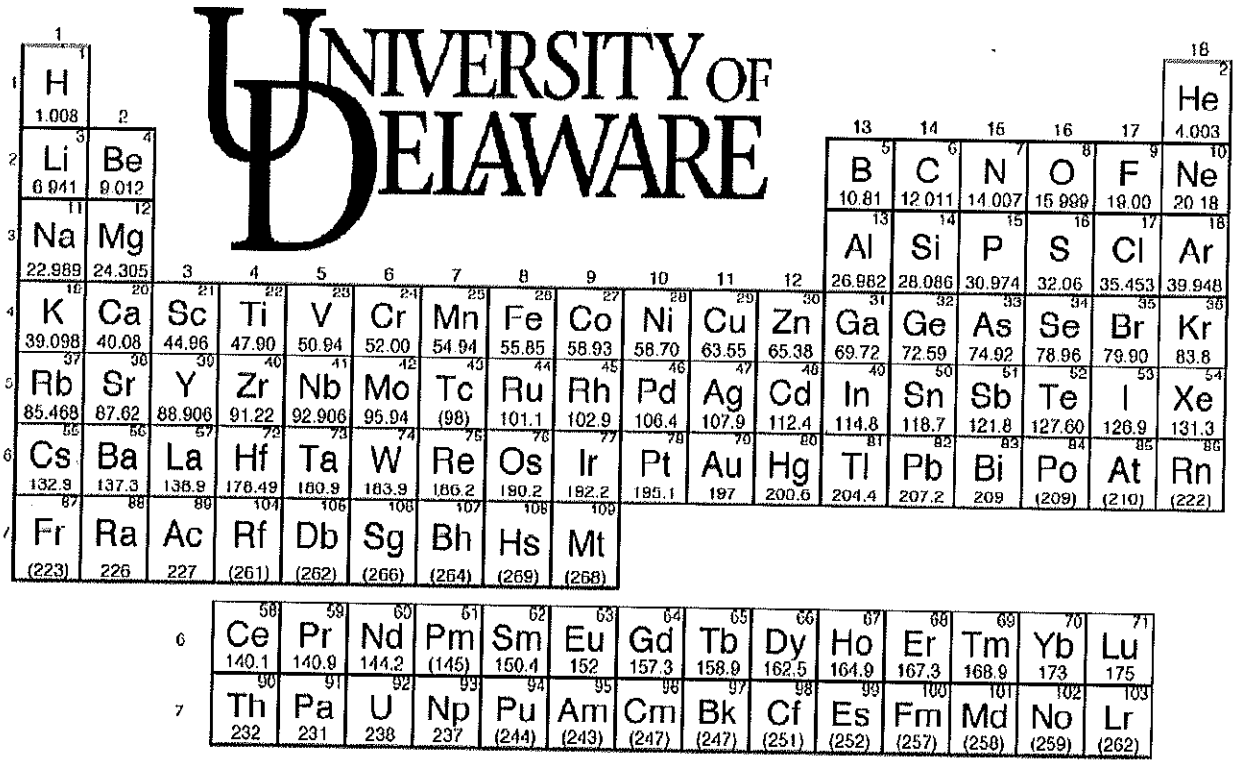
(Print your name clearly!)

Th

Sametz: CHEM 322 Spring 2013

Organic Chemistry Exam 1

All answers should be written CLEARLY in the space provided. (If it's not clear, it's wrong).



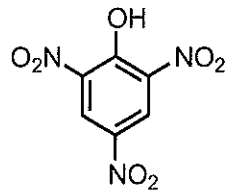
1	1 H 1.008																18 2 He 4.003
2	3 Li 6.941	4 Be 9.012											13 5 B 10.81	14 6 C 12.011	15 7 N 14.007	16 8 O 15.999	17 9 F 19.00	10 Ne 20.18
3	11 Na 22.989	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.8
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.60	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.49	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226	89 Ac 227	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)									

6	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175
7	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

You may raise your hand to ask a question if you are unsure what a question is asking of you.

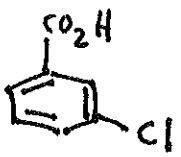
1. Nomenclature (6 points)

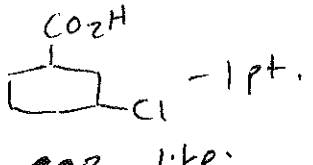
a) Picric acid, shown below is highly explosive (as one of my former lab mates in grad school proved). Give a proper IUPAC name for it.



2,4,6- tri.nitro phenol
1 1 1

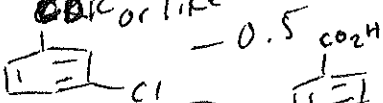
b) mCPBA (*meta*-chloroperoxybenzoic acid) is a common peracid oxidizing agent that is also dangerously reactive. It's commonly sold impure, with ~15% of the precursor *meta*-chlorobenzoic acid present, because the impure mixture is more stable. Draw the structure of this precursor.





-1 pt.

OR or like.

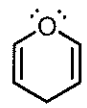


-0.5

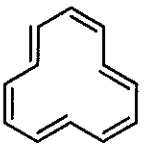
no oxygen -1 pt.

para Cl (-0.5)

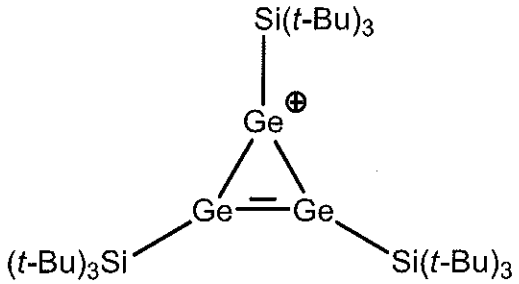
2. (6 points) Indicate whether the following structures are aromatic, antiaromatic, or neither.



neither

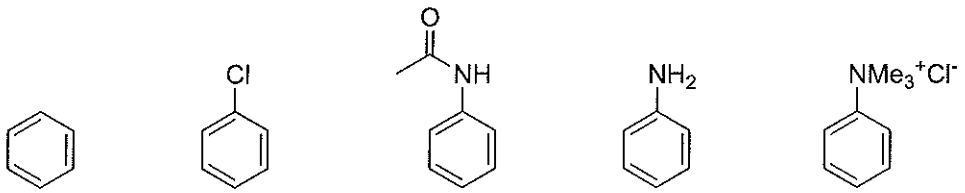


aa



9

3. (8 points) Rank the following compounds in order of reactivity to electrophilic aromatic substitution (1 = most reactive, 5 = least reactive):



3 4 2 1 5

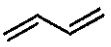
1 ~~most~~ most reactive
1 least
1 2nd most
1 2nd least

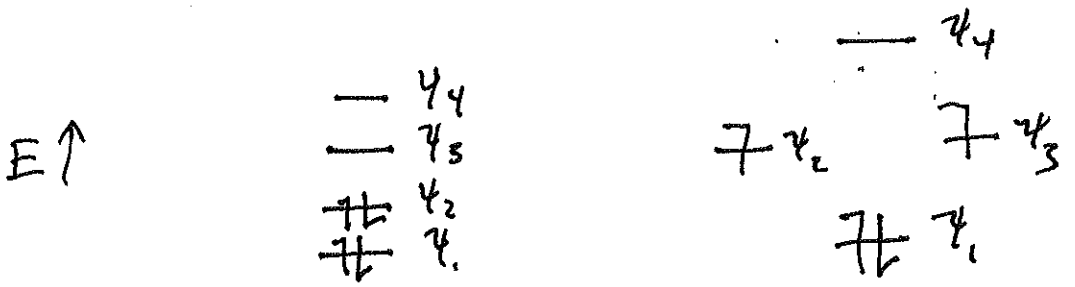
All wrong: -8

4 wrong: -4 pt.
3 wrong: -3 pt.
etc.

TOTAL: 20

4. (10 points) The relative stabilities of 1,3-butadiene and cyclobutadiene are very different. Give Molecular Orbital (MO) energy diagrams for both molecules (hint: you can use a Frost circle for cyclobutadiene if you wish). You do not have to draw what the orbitals look like physically—I am looking for a set of lines indicating molecular orbitals of various energy levels (E being the vertical axis). For each molecule, place the correct number of π electrons into its MO diagram. Use these diagrams to predict which molecule is more stable, and which molecule is less stable (you are being graded for your explanation, not just guessing!).





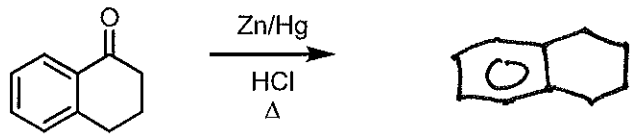
"normal" stability of a conjugated ~~polyene~~ diene

anti-aromatic – 2 unpaired e⁻s in the HOMOs.

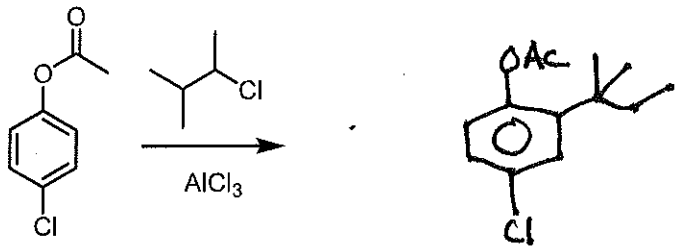
2×2 for orbital energy levels
2×2 for e⁻ correct – avoid double jeopardy
2 for explanation.

5. (30 points) Give the major organic product(s) for the following reactions.

a)



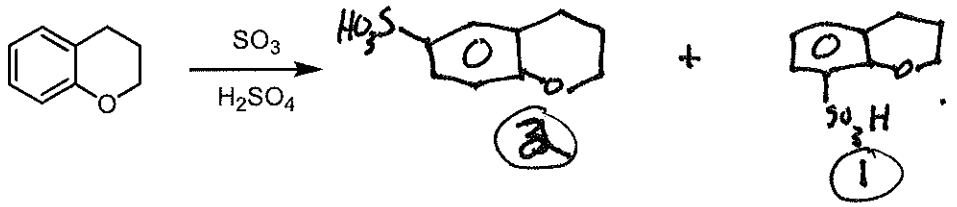
b)



(2) alkylation
(1) regioselectivity

(-1) if Ar

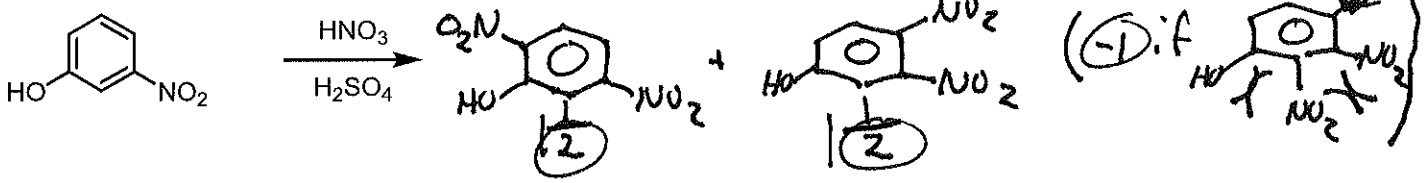
c)



3

1

d)

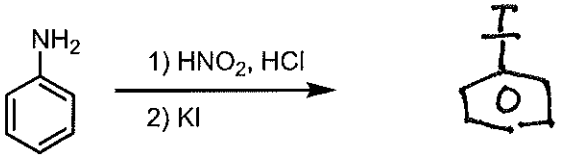


2

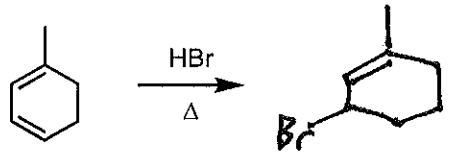
2

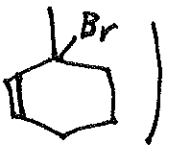
(-1) if

e)



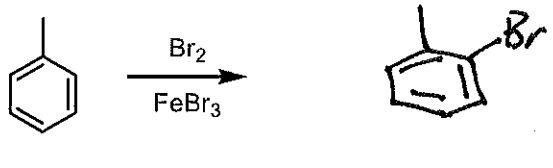
f)



(1½ if 

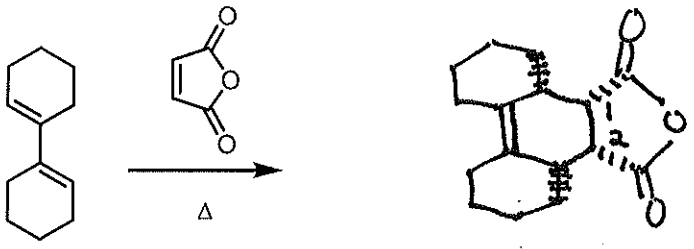
)

g)



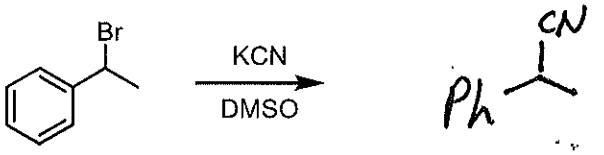
1½ each

h)

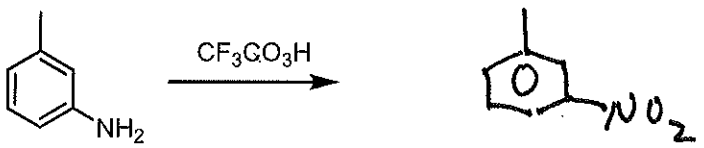


(2) structure
(1) C-1/C-2 cis-
(+1) extra credit if correct endo-stereochem. shown

i)

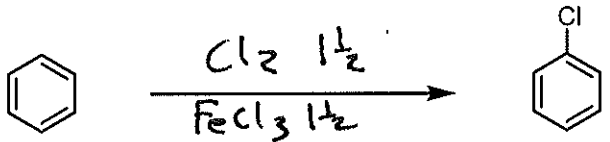


j)

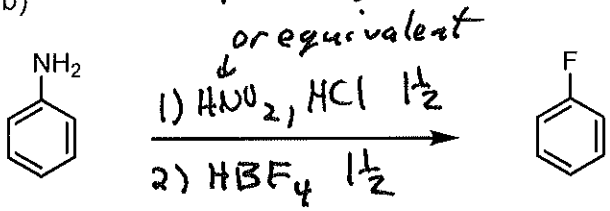


6. (18 points) Give reagents that will effect the following transformations.

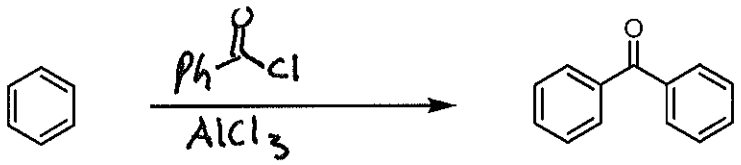
a)



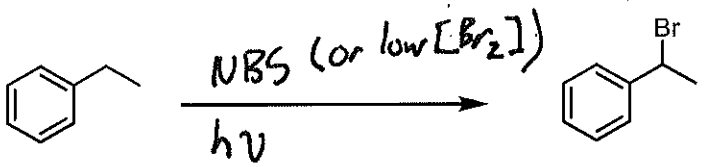
b)



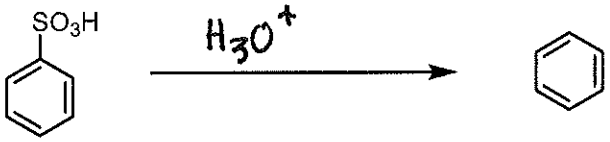
c)



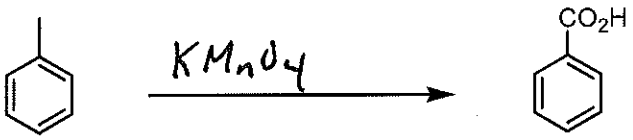
d)



e)

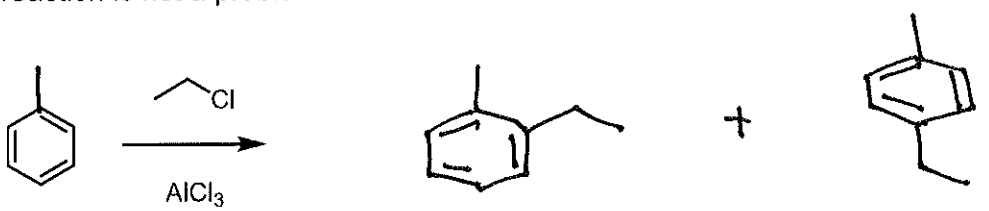


f)

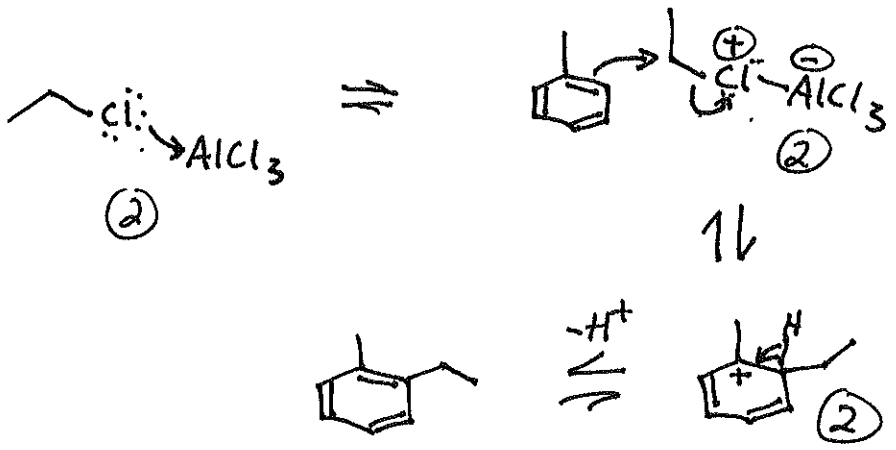


7. (10 points) Give the major product(s) for the reaction below, and show a complete reaction mechanism that accounts for formation of a major product (i.e. if there is only one major product, give the mechanism for its formation; if there is more than one, choose one to work with). Your mechanism must show formation of the electrophile as well as addition of the electrophile to the ring. Use the mechanism to explain the observed regioselectivity for the reaction.

Note: assume that you can get a single addition of electrophile to the ring, and that over-reaction is not a problem.



take off points for wrong arrows, missing charges etc.

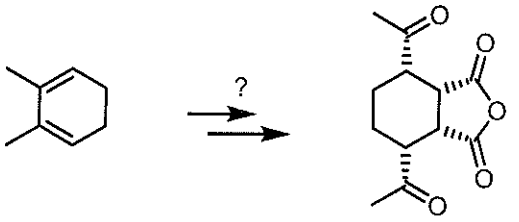


(2) show a resonance structure with ⊕ adjacent to Me

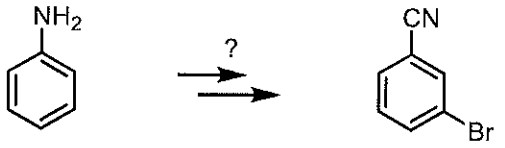
(2) explanation: o/p substitution results in ⊕ δ⊕ adjacent to the EDG Me

8. (4 points) Multistep synthesis: choose **ONE** of the following two syntheses, and show how the compound on the right can be synthesized from the compound on the left. Retrosynthetic analysis can be worth partial credit, but for full credit write the sequence of reactions in the forward direction. If you work on more than one, **CLEARLY** indicate which you want graded for credit, or the grader chooses for you.

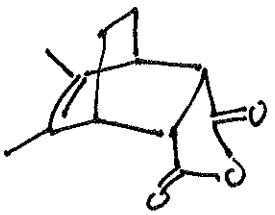
a)



b)



a)



1) O_3

2) suitable workup

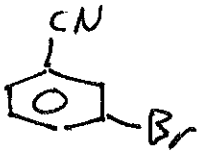
prod.

b)

1) $NaNO_2$, HCl or equivalent

2) $CuCN$

Br_2, $FeBr_3$ ($AlBr_3$)



(2) per step

9. (8 points) Multistep synthesis: choose **ONE** of the following two compounds, and show how it can be synthesized from benzene. Retrosynthetic analysis can be worth partial credit, but for full credit write the sequence of reactions in the forward direction. Again, if you work on more than one, **CLEARLY** indicate which you want graded for credit, or the grader chooses for you.