Chemistry 2030
"Introduction to Organic Chemistry"
Fall Semester 2012
Dr. Rainer Glaser

Examination #2
"Arenes, Stereochemistry, and Organic Halogen Compounds, with Nucleophilic Substitution and Elimination."

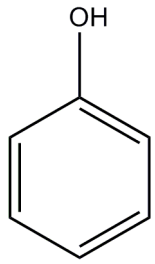
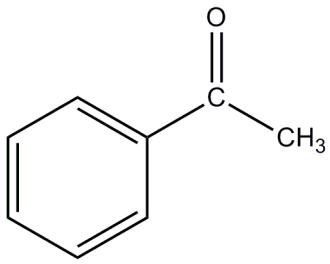
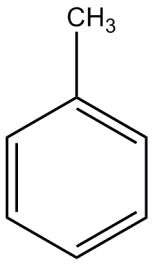
Handout 10/04/12 @ 9:15 am; Return 10/05/12 @ 1pm (DoCh Office)

Name: Answer Key

Question 1. Aromatic Compounds – Names, Bonding and Properties	20	
Question 2. Electrophilic Aromatic Substitution	20	
Question 3. Stereoisomers – Chirality & Geometrical Isomers	20	
Question 4. Mechanisms of Nucl. Subst. and Elim. Reactions	20	
Question 5. Reactions of Organic Halides with Nucleophiles	20	
Total	100	

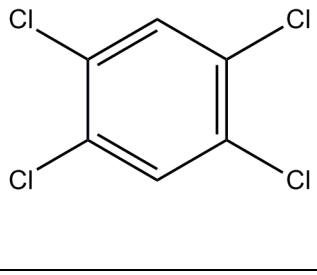
Question 1. Aromatic Compounds – Names, Bonding and Properties. (20 points)

(a) Provide abbreviated structural formulas of phenol, acetophenone, and toluene. (6 points)

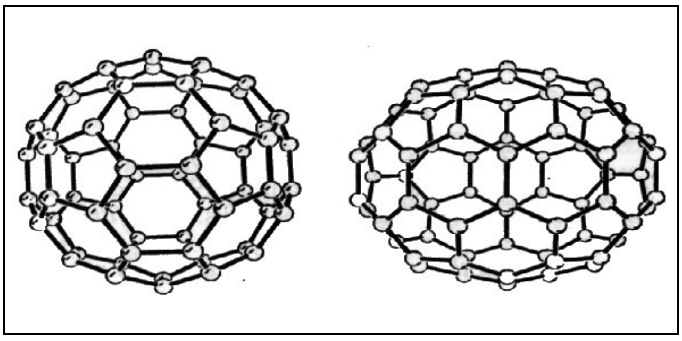
Phenol	**acetophenone**	**Toluene**
		

(b) Measurements show that the hydrogenation of benzene to cyclohexane releases about 50 kcal/mol. One might have expected that the hydrogenation of a "hypothetical 1,3,5-cyclohexatriene" would release about _____ (56, 66, 76, **86**) kcal/mol. Thus we must conclude that the real benzene molecule must be _____ (**more**, less) stable than the "hypothetical 1,3,5-cyclohexatriene" molecule by about __**36**__ kcal/mol; this stabilization energy is called the _____**resonance**____ energy of benzene. (4 points)

(c) Draw the structure of **1,2,4,5-tetrachloro-benzene**.
The chlorine atoms in positions 1 & 2 are _____ (**ortho**, meta, para) relative to each other.
The chlorine atoms in positions 2 & 4 are _____ (ortho, **meta**, para) relative to each other.
The chlorine groups in positions 1 & 5 are _____ (ortho, **meta**, para) relative to each other.
(5 points)

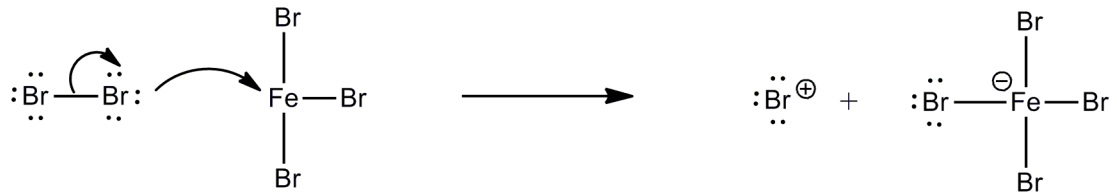


(d) The **models** show **buckyballs** C_{60} and C_{70}.
Bucky-balls are somewhat related to _____ (diamond, **graphite**). Buckyballs contain _**5**-membered rings and _**6**-membered rings, while graphene sheets contain only _**6**-membered rings.
The carbon atoms in both buckyballs are approximately _____ (sp, **sp^2**, sp^3) hybridized.
(5 points)

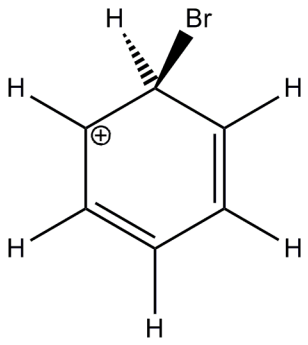


Question 2. Electrophilic Aromatic Substitution. (20 points)

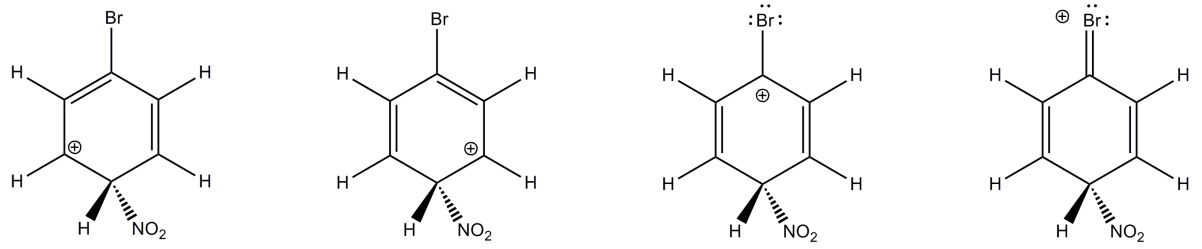
(a) Provide complete structural formulas for the **formation reaction of the electrophile** which is the reactive species in the **bromination** of benzene by way of aromatic electrophilic substitution. (6 points)



(b) Draw (one resonance form of) the complete, unabbreviated structural formula of **sigma-complex** which occurs as an intermediate in the **bromination of benzene**. (4 points)



(c) Consider the **nitration of bromobenzene**. The Br substituent of bromobenzene is _____ (activating, **deactivating**) and _____ (**o/p**, meta) directing. In the space below, draw the four most relevant resonance forms of the sigma-complex which would occur as an intermediate in the formation of para-bromonitrobenzene. [Do only consider this one sigma-complex here; do not consider the sigma-complexes for the respective formations of ortho- or meta-bromonitrobenzene.] Explain whether any of the resonance forms have any special advantage or disadvantage. State whether para-bromonitrobenzene will be formed. (10 points)

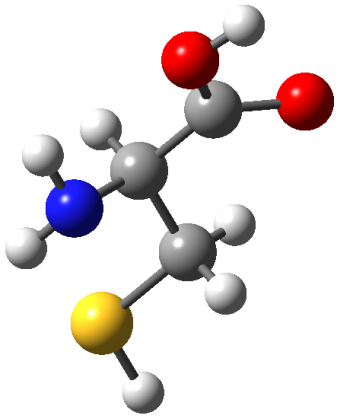
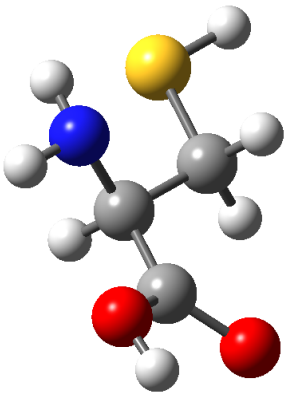


Bromine has lone pairs which can be used, at least to a small extent, to stabilize charge on the adjacent C-atom.

Question 3. Stereoisomers – Chirality & Geometrical Isomers. (20 points)

(a) Two models are shown of the amino acid **cysteine**, $H_2N–CH(CH_2SH)–COOH$ (oxygen in red, nitrogen in blue, sulfur in yellow). Do both models show the same molecule or do they show different enantiomers? Provide the "R" or "S" label for each model. (6 points)

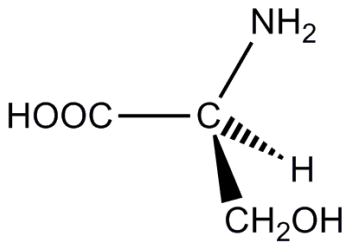
DIFFERENT!

Model #1	Model #2
	
S	**R**

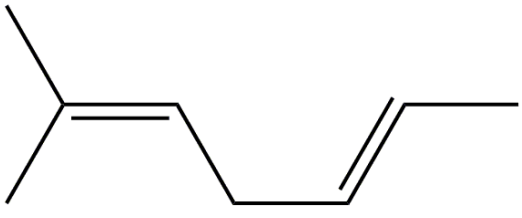
(b) The amino acid **serine** has the structure $H_2N–CH(CH_2OH)–COOH$ and contains one chiral C atom. Provide the CIP priorities of the four substituents. For the two C-substituents, apply the sequence rule and provide their "lists". (6 points)

Priority of H: 4
Priority of NH_2: 1
Priority of CH_2OH: 3 C(O H H)
Priority of COOH: 2 C(O O O)

(c) Perspective drawing of **(*S*)-enantiomer of serine**. The perspective drawing should have two bonds in the paper plane, one bond that goes behind the paper plane, and one bond that goes in front of the paper plane. In addition, the C–H bond should be the bond that goes behind the paper plane. (4 points)

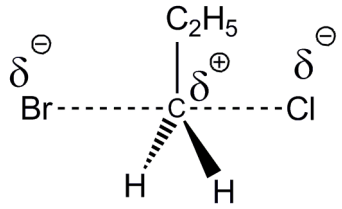


(d) The line segment drawing is provided of one isomer of **2-methylhepta-2,5-diene.** This molecule can form ____ (1, **2**, 3, 4) geometrical isomers. The isomer shown is the ____ (***E***; *Z*; *E*,*E*; *Z*,*Z*; *E*,*Z*) isomer. (4 points)

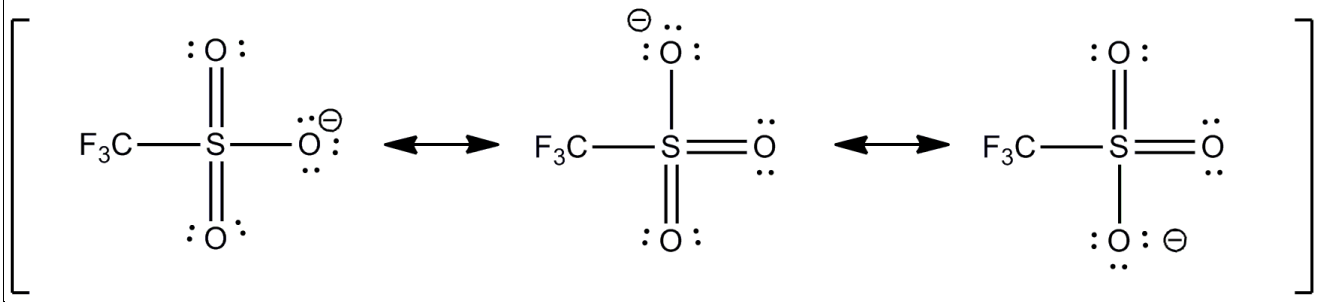


Question 4. Mechanisms of Nucleophilic Substitution Reactions. (20 points)

(a) The S_N2 mechanism is one of the most studied reaction mechanisms in organic chemistry. In most cases, the nucleophile Nuc^- attacks the carbon that carries the leaving group L from the backside and a __**Walden**__ inversion occurs. This works really well for _____ (**primary**, secondary, tertiary) substrates and the penta-coordinate transition state structure is readily accessible. In the transition state structure, the C–L bond is partially broken and new C–Nuc bond is partially formed. Using dashed lines for partial bonds, provide a perspective drawing of the transition state structure for the **S_N2 reaction of bromide nucleophile with substrate propyl chloride**. Draw the C---Nuc and C---L bonds horizontally in the paper plane and draw the C–C_2H_5 bond also in the paper plane. (10 points)



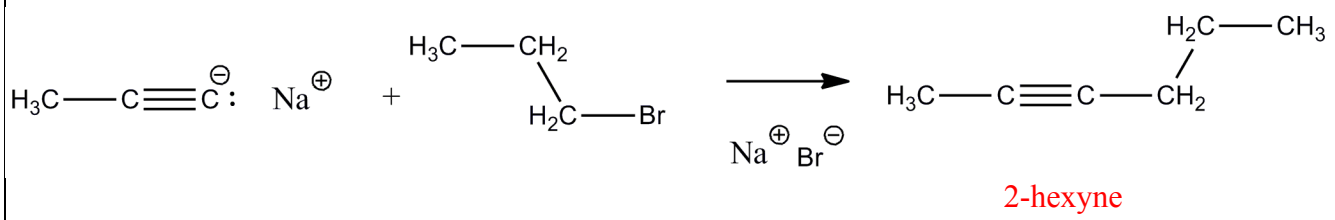
(b) Reactions in which the solvent also is the nucleophilic reagent are called "solvolysis reactions." If the solvent is water, then the solvolysis reaction is a "hydrolysis reaction." The reaction of the tertiary "triflate" (a triflate is an alkyl trifluoromethanesulfonate) $(H_3C)_3C–O–SO_2–CF_3$ with water HOH is an example of such a reaction and it forms the product _____***tert*-butanol**_____ (provide acceptable name of product). This hydrolysis reaction involves a _____ (**weak**, strong) nucleophile and will proceed via the ____ (**S_N1**, S_N2, E1, E2) mechanism. The reaction will be faster in _____ (**more**, less) polar solvents. In the space below, explain why $F_3C–SO_3^-$ is an excellent leaving group. You may want to show resonance forms of $F_3C–SO_3^-$ to make your argument. (10 points)



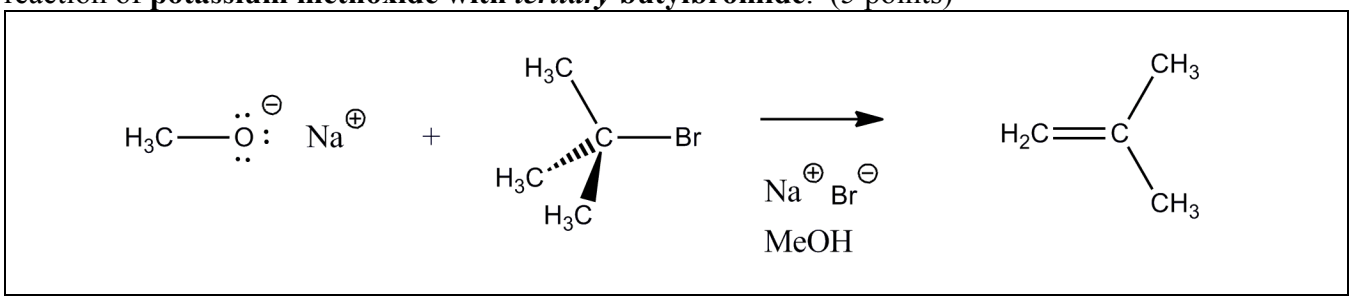
The negative charge is delocalized over three O-atoms.
In addition, the CF_3 group exerts a strong electron-withdrawing, inductive effect.

Question 5. Reactions of Organic Halides with Nucleophiles. (20 points)

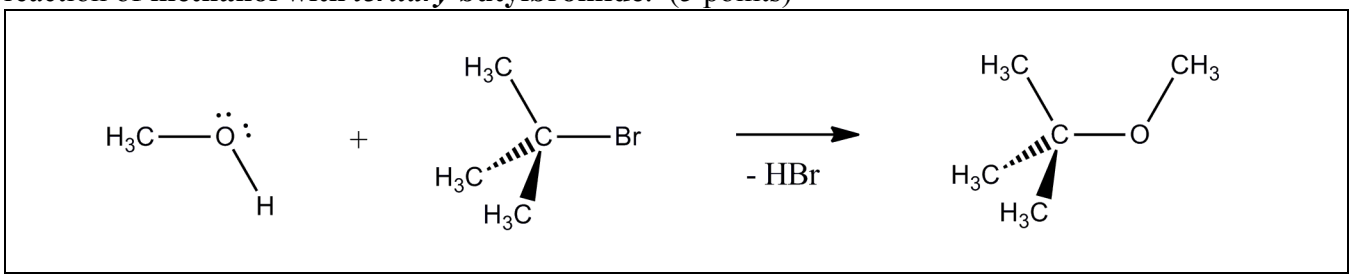
(a) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **sodium acetylide of propyne, $H_3C\text{-}C{\equiv}C^-Na^+$ with 1-bromopropane**. Name the product. (5 points)



(b) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **potassium methoxide with *tertiary* butylbromide**. (5 points)



(c) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **methanol with *tertiary* butylbromide**. (5 points)



(d) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **$(H_3C)_3C{-}O^-\ K^+$ with 2-bromopentane**. (5 points)