Chemistry 2030
"Survey of Organic Chemistry"
Fall Semester 2013
Dr. Rainer Glaser

Examination #2
"Arenes, Electrophilic Aromatic Substitution, Stereochemistry, and Nucleophilic Substitution and Elimination."

Thursday, October 3, 2013, 8:25 - 9:15 am

Name:

Answer Key

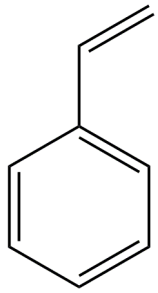
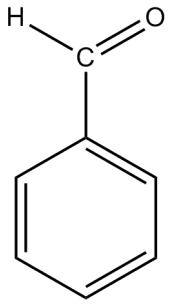
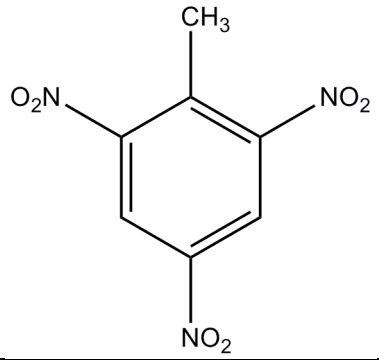
Question 1. Aromatic Compounds – Names, Bonding and Properties	20	
Question 2. Electrophilic Aromatic Substitution	20	
Question 3. Stereoisomers – Chirality & Geometrical Isomers	20	
Question 4. Mechanisms of Nucleophilic Substitution Reactions	20	
Question 5. Reactions of Organic Halides with Nucleophiles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

ALLOWED: Periodic System of the Elements (printed, w/o handwriting on it). Molecular models (you can bring pre-made models). Simple, non-programmable calculator (not really needed).

NOT ALLOWED: Books. Notes. Electronic devices of any kind (other than a simple calculator).

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

(a) Provide abbreviated structural formulas of styrene, benzaldehyde, and TNT. (6 points)

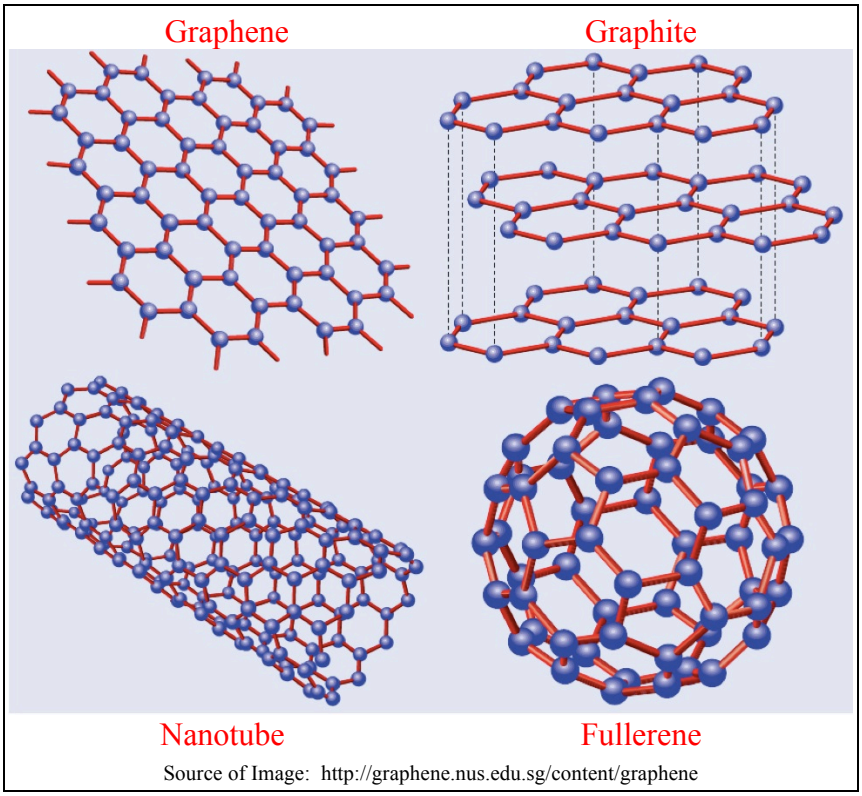
Styrene	**Benzaldehyde**	**TNT, 2,4,6-trinitrotoluene**
		

(b) Consider the structure of **TNT**, i.e., **2,4,6-trinitrotoluene**. The methyl group in position 1 and the nitro group in position 2 are _____ (**ortho**, meta, para) relative to each other. The methyl group in position 1 and the nitro group in position 4 are _____ (ortho, meta, **para**) relative to each other. The nitro groups in positions 2 & 4 are _____ (ortho, **meta**, para) relative to each other. The nitro groups in positions 2 & 6 are _____ (ortho, **meta**, para) relative to each other. (2 points)

(d) **Models** are shown of allotropes of carbon and they show **graphite**, **graphene**, a **fullerene**, and a **nanotube**. Another allotrope of carbon is **diamond** (not shown). Indicate on the image which model shows which allotrope.

Graphite contains only _6_-membered rings. **Graphene** contain only _6_-membered rings. **Buckyballs** contain _6_-membered rings and _5_-membered rings. **Diamond** contains _6_-membered rings in the _____ (**chair**, boat) conformation.

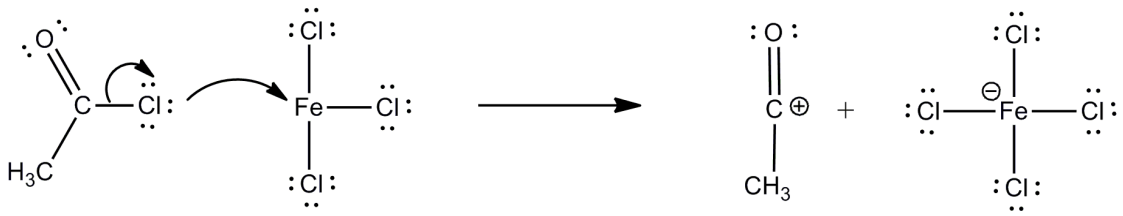
The carbon atoms in diamond are _____ (sp, sp^2, **sp^3**) hybridized. The carbon atoms in graphene and graphite are _____ (sp, **sp^2**, sp^3) hybridized. (12 points)



Source of Image: http://graphene.nus.edu.sg/content/graphene

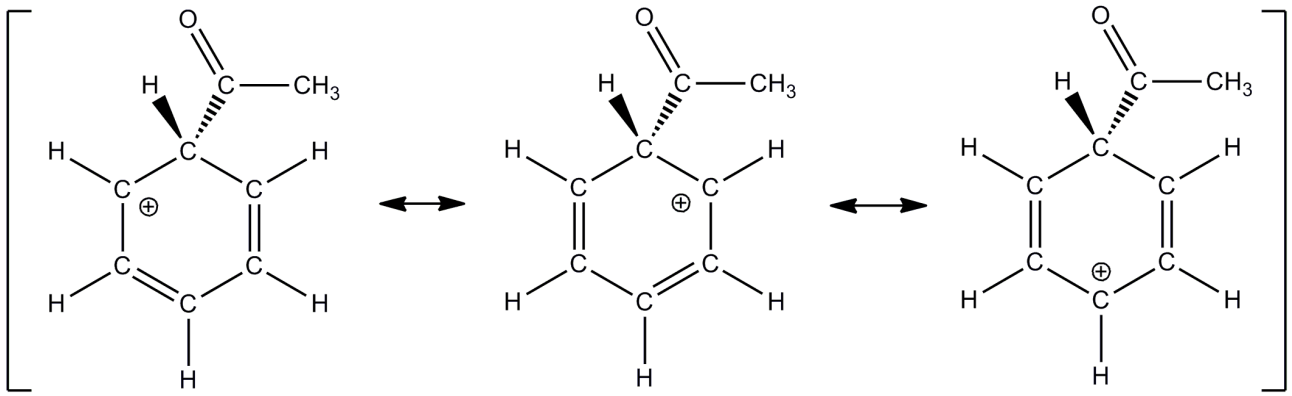
Question 2. Electrophilic Aromatic Substitution. (20 points)

(a) Provide complete structural formulas for the **formation reaction of the electrophile** which is the reactive species in the **Friedel-Crafts Acylation** of benzene to form **acetophenone** by way of electrophilic aromatic substitution. Draw the complete structures of the reagent required ($H_3C–CO–Cl$), of a suitable Lewis acid catalyst, of the electrophile formed, and of the complex formed by the catalyst. (8 points)



You can also use $AlCl_3$ instead of $FeCl_3$.

(b) Draw complete, unabbreviated structural formulas of the three resonance forms of the **sigma-complex** which occurs as an intermediate in the **acetylation of benzene**, i.e., the Friedel-Crafts acylation of benzene with $H_3C–CO–Cl$. (6 points)



(c) Consider the **nitration of nitrobenzene**. The nitro substituent of nitrobenzene is _____ (activating, **deactivating**) and _____ (o/p, **meta**) directing. (2 points)

(d) Consider the **bromination of toluene**. The methyl substituent of toluene is _____ (**activating**, deactivating) and _____ (**o/p**, meta) directing. (2 points)

(e) Consider the **Friedel-Crafts acylation of toluene**. The methyl substituent of toluene is _____ (**activating**, deactivating) and _____ (**o/p**, meta) directing. (2 points)

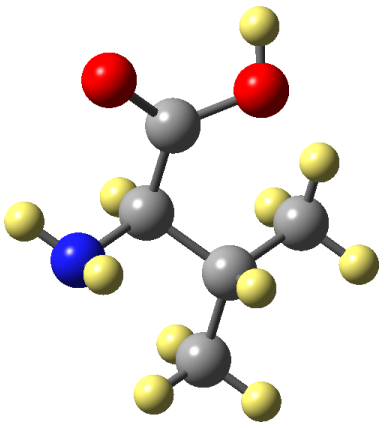
Question 3. Stereoisomers – Chirality & Geometrical Isomers. (20 points)

(a) Two models are shown of the amino acid **valine**, $H_2N–CH(CH(CH_3)_2)–COOH$ (oxygen in red, nitrogen in blue).

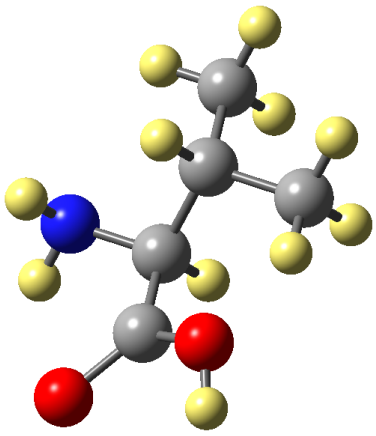
Do the two models show the same molecule or do they show **different** enantiomers?

Provide the "R" **(Model #1)** or "S" **(Model #2)** label for each model. (6 points)

Model #1



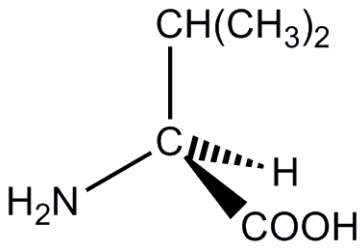
Model #2



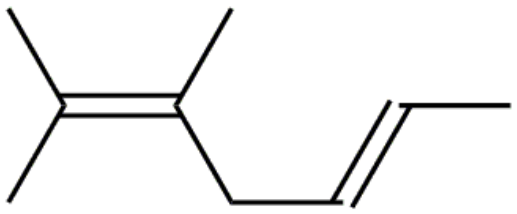
(b) The amino acid **valine** has the structure $H_2N–CH(CH(CH_3)_2)–COOH$ and contains one chiral C atom. Provide the CIP priorities of the four substituents. For the two C-substituents, apply the sequence rule and provide their "lists". (6 points)

Priority of H: **4**
Priority of NH_2: **1**
Priority of $CH(CH_3)_2$: **3** C(**C C H**)
Priority of COOH: **2** C(**O O O**)

(c) Perspective drawing of **(*S*)-enantiomer of valine**. 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 **2,3-dimethylhepta-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*; *Z*,*E*) isomer. (4 points)



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

(a) IUPAC (International Union of Pure and Applied Chemistry) defines "nucleophile (nucleophilic)" as follows: "A nucleophile (or nucleophilic reagent) is a reagent that forms a bond to its reaction partner (the electrophile) by donating both bonding electrons. A 'nucleophilic substitution reaction' is a heterolytic reaction in which the reagent supplying the entering group acts as a nucleophile." For the following questions, circle the one correct answer (2 points each):

Which one of the following is a nucleophile: **NH_3**, $AlCl_3$, NO_2^+.

Which one of the following is the strongest nucleophile: H_3O^+, H_2O, **HO^-**.

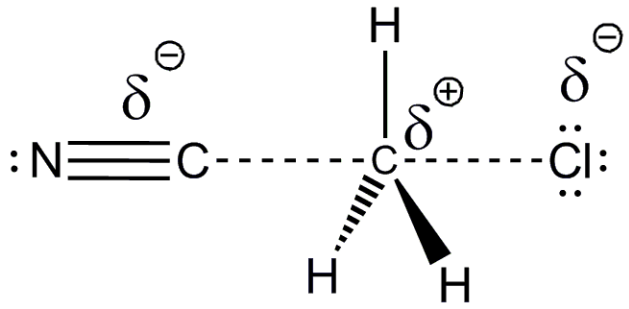
Which one of the following is the stronger nucleophile: **Br^-** or F^-.

Which one of the following is the weaker nucleophile: SH^- or **SO_4H^-**.

(b) 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 _____ (front side, **backside**) and a Walden **inversion** occurs. This reaction is fastest for _____ (**primary**, secondary, tertiary) substrates and the penta-coordinate transition state structure is readily accessible.

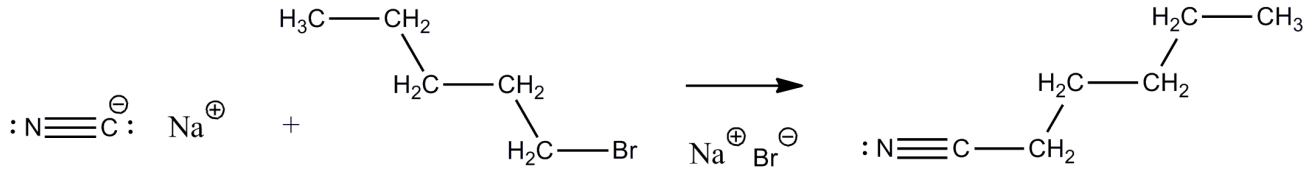
In the transition state structure, the C–L bond is _____ (totally, **partially**, not yet) broken and new C–Nuc bond is _____ (totally, **partially**, not yet) formed. Using dashed lines for partial bonds, provide a perspective drawing of the transition state structure for the **S_N2 reaction of the cyanide nucleophile with the substrate methyl chloride**. Draw the C---Nuc and C---L bonds horizontally in the paper plane and draw one of the C–H bonds also in the paper plane and up.

In the transition state structure the ∠(H–C–H) angles are approximately _____ (90°, 109°, **120°**), the ∠(H–C–CN) angle is approximately _____ (**90°**, 109°, 120°), and the ∠(H–C–Cl) angle is approximately _____ (**90°**, 109°, 120°). (12 points)



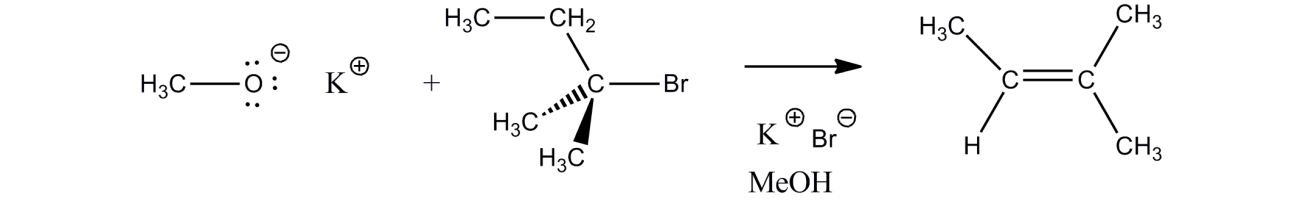
Question 5. Reactions of Organic Halides with Nucleophiles. (20 points)

(a) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **sodium cyanide (Na^+CN^-) with 1-bromopentane**. Name the product. (5 points)

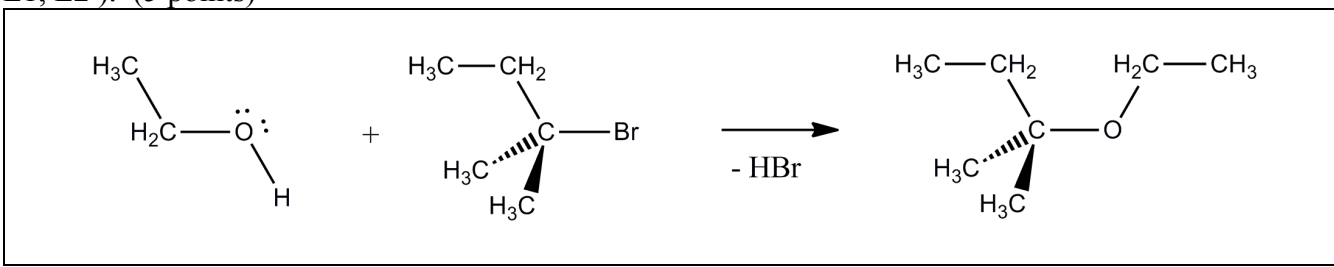


***n*-pentylnitrile, 1-cyanopentane**

(b) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **potassium methoxide with 2-bromo-2-methylbutane**. The substrate is a _____ (primary, secondary, **tertiary**) alkyl bromide. (5 points)



(c) Using abbreviated structural formulas, show the substrate, the reagent, and the major product of the reaction of **ethanol with 2-bromo-2-methylbutane**. The major product is formed by ____ (**S_N1**, S_N2, E1, E2). (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**. Note that the base is very bulky. The major product is formed by ____ (S_N1, S_N2, E1, **E2**). (5 points)