

Key

High 197

Ave 116

Low 29

1

Student Name (first, last):

Student Number:

CHEMISTRY 3371
FINAL EXAMINATION

Josef Michl
May 9, 2013

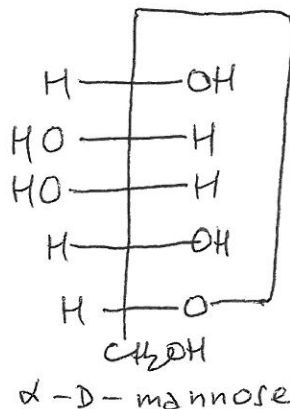
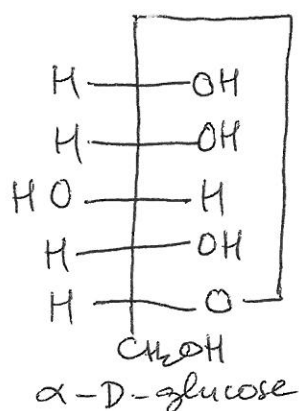
valence els in atom	3	4	5	6	7	8	9	10	11	12
period 4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
period 5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
period 6	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

1. (40 points) Check the correct statements only (make no other marks):

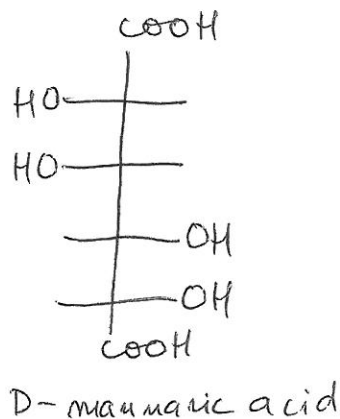
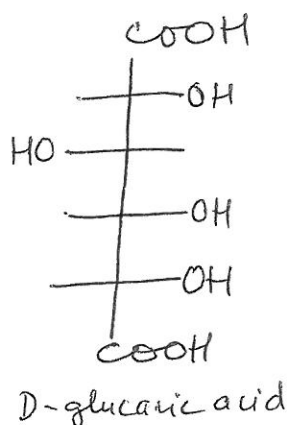
- $\text{Br}_2\text{Pd}(\text{NH}_3)_2$ contains palladium in the oxidation state +4.
- There are 16 electrons in the valence shell of the palladium atom in $\text{Br}_2\text{Pd}(\text{NH}_3)_2$.
- $\text{Br}_2\text{Pd}(\text{NH}_3)_2$ is a d^8 complex of palladium.
- The transition state of a pericyclic reaction contains a linear array of interacting orbitals.
- The 1-cyclopropen-3-yl cation is stabilized by electron delocalization.
- In aqueous solution, formaldehyde is present mostly in the form of its hydrate, methane-1,1-diol.
- Nitration of pyridine-*N*-oxide yields 4-nitropyridine-*N*-oxide.
- Since the $\text{p}K_{a1}$ of glycine is 2.34 and its $\text{p}K_{a2}$ is 9.60, its isoelectric point must be 7.26.
- Aldol reaction of acetaldehyde in aqueous base produces 3-hydroxybutanal.
- Claisen condensation of methyl acetate in the presence of MeONa followed by neutralization with acid affords methyl acetoacetate, $\text{CH}_3\text{COCH}_2\text{COOMe}$.
- α,β -Unsaturated carbonyl compounds undergo carbonyl addition with lithium organocuprates and conjugate addition with organolithium reagents.
- Benzenediazonium chloride reacts with hypophosphorous acid to yield chlorobenzene.
- Curtius rearrangement of an acyl azide RCON_3 yields an alkyl isocyanate $\text{R-N}=\text{C}=\text{O}$ in which the stereochemistry at R has been preserved.
- The central carbon of allene is sp^2 hybridized.
- Under Pd catalysis, bromobenzene can be converted to *N,N*-diethylaniline by reaction with diethylamine and base.
- Saccharose is a reducing sugar.
- Penta-2,3-diene is chiral.
- Suprafacial 1,3-shift of hydrogen is a ground-state allowed sigmatropic process.
- Hydroboration of an alkene is a pericyclic reaction.
- Dichlorocarbene, CCl_2 , has an octet of valence electrons on the carbon atom.
- An orbital is a region of space where an electron is likely to be found.

- Fructose is a ketohexose.
- The slowest step in a multistep reaction sequence is called the rate determining step.
- Ribose is an aldohexose.
- 1,3-Cyclobutadiene is aromatic and extremely unreactive.
- An electrostatic potential map (EPM) is a picture of the total electron density on a surface surrounding a molecule, color coded to show areas of negative charge in red and areas of positive charge in blue.
- The mutarotation of D-glucose is due to the equilibration of its anomers.
- Cellulose is a regular polymer of D-glucopyranose units connected by β -1,4-glycosidic linkages.
- Under radical bromination conditions, *p*-bromotoluene is converted to *p*-bromobenzyl bromide.
- Pyrrole is more basic than pyridine.
- Furan reacts with maleic anhydride faster than thiophene does.
- Bromination of benzene followed by nitration produces *m*-bromonitrobenzene.
- A sulfur atom can accommodate twelve electrons in its valence shell.
- Friedel-Crafts acylation requires the use of an equivalent of AlCl_3 , while for Friedel-Crafts alkylation a small (catalytic) amount is sufficient.
- Halogen substituents facilitate electrophilic aromatic substitution.
- Pyrimidine is derived from benzene by replacement of two CH groups in para positions with N.
- In pyrrole, the nitrogen atom provides two electrons to the π -electron system.
- In quinoline, the nitrogen atom provides two electrons to the π -electron system.
- In thiophene, the sulfur atom provides one electron to the π -electron system.
- Under kinetic control, 1,3-dienes add HCl to yield the product of 1,4 addition.

3. (30 pts) (a) Draw Fischer projections of the α anomer of D-glucose, and of its epimer on C2, called α -D-mannose.

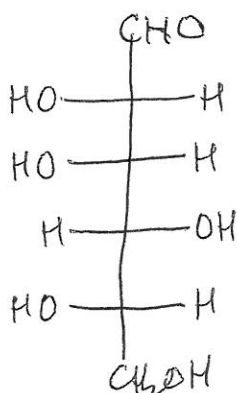


- (b) Oxidation with dilute HNO_3 converts D-glucose into D-glucaric acid and D-mannose into D-mannaric acid. Draw the Fischer projections of these two acids.



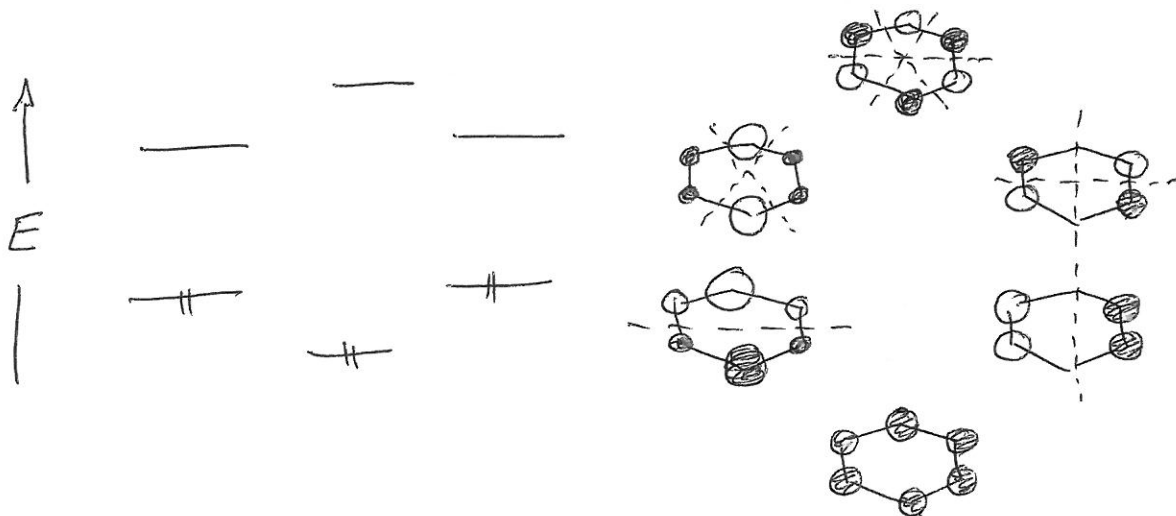
- (c) Draw the Fischer projections of all aldohexoses other than D-glucose whose HNO_3 oxidation yields D-glucaric acid, and of all aldohexoses other than D-mannose whose HNO_3 oxidation yields D-mannaric acid. If there are none, state so.

D-glucaric acid is also formed from



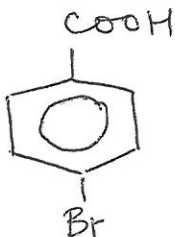
D-mannaric acid is formed from no other aldohexose by oxidation with HNO_3 , only from D-mannose

4. (20 pts) Sketch the form of the six π and π^* molecular orbitals of benzene with their nodal planes and indicate their relative energies on a vertical energy scale.

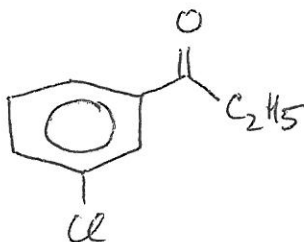


5. (30 pts) Write the structures of all principal organic products of the following reactions after workup. You do not need to show solvents, mechanisms, or curved arrows. Reagents applied concurrently are separated with a comma. Reagents applied after isolation of the product of the preceding step are numbered 1. 2.

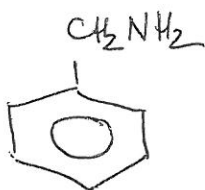
(a) *p*-bromotoluene + KMnO_4 , $100\text{ }^\circ\text{C}$, 4 h \rightarrow



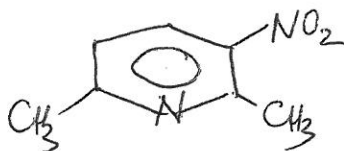
(b) *m*-chlorobenzoyl chloride + lithium diethylcuprate \rightarrow



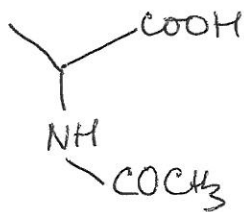
(d) $\text{C}_6\text{H}_5\text{CH}_2\text{CONH}_2 + \text{Br}_2 + \text{NaOH}/\text{H}_2\text{O} \rightarrow$



(e) 2,6-dimethylpyridine + $\text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow$



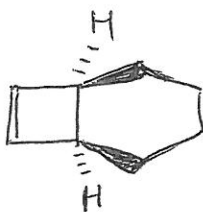
(g) propionic acid + 1. Br_2, P ; 2. excess NH_3 ; 3. acetic anhydride \rightarrow



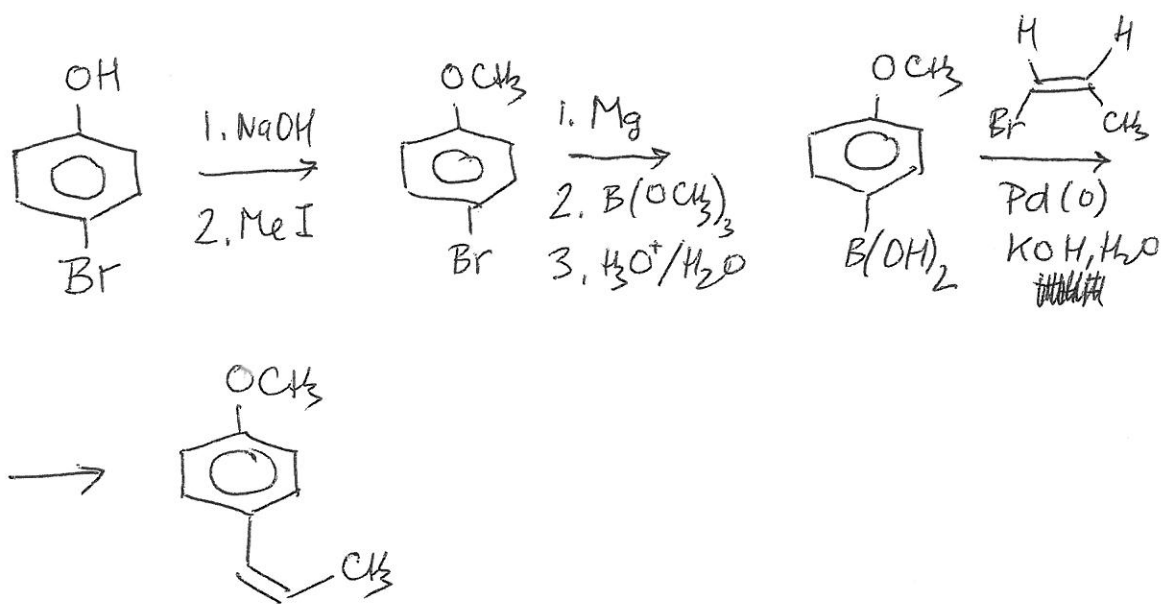
racemic

(h) cycloocta-1,3-diene + light \rightarrow

(show stereochemistry)



6. (25 pts) Propose efficient preparation of *cis*-anethole [(*Z*)-1-methoxy-4-propenylbenzene] from *p*-bromophenol using reagents that contain no more than three carbon atoms in the molecule and relying on Pd-catalyzed Suzuki coupling. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).



7. (30 pts) Starting with Fmoc-protected amino acids and an "insoluble *p*-alkoxybenzyl chloride" resin, outline the solid state (Merrifield) synthesis of L-alanyl-L-proline. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents). You do not need to show the structure of the Fmoc protecting group.

