

Student Name (first, last):

Student Number:

CHEMISTRY 3311
THIRD MIDTERM EXAMINATION

Josef Michl
April 17, 2012

1. (20 points) Check the correct statements only and make no other marks:

- A two-step treatment of an alkene with 1. OsO_4 followed by 2. H_5IO_6 gives the same product as ozonolysis followed by a treatment with dimethyl sulfide.
- Reaction rate constants increase exponentially with decreasing free energy of activation.
- The $\text{S}_{\text{N}}1$ substitution reaction always occurs with inversion of stereochemistry on the carbon atom on which the substitution takes place.
- Sharpless epoxidation uses achiral reagents to convert an achiral allylic alcohol almost entirely to only one of the two possible enantiomers of an epoxide.
- CrO_3 oxidizes primary alcohols to carboxylic acids if water is present.
- Zaitsev's rule states that hydrogen halide elimination from an alkyl halide predominantly yields the least stable of the possible alkenes.
- Tertiary alkyl halides are particularly reactive in $\text{S}_{\text{N}}2$ substitution reactions.
- Since the acetate anion and the azide anion have similar basicity, they must have similar nucleophilicity as well.
- In methanol, fluoride is a weaker nucleophile than iodide, but in dimethylformamide, the opposite is true.
- E2 elimination cannot occur when the leaving group and the proton are anti to each other.
- (*S*)-2-chloro-2-deuterioethyl methyl sulfide reacts with water to yield (*R*)-2-hydroxy-2-deuterioethyl methyl sulfide.
- It follows from isotope effect studies that in the transition state of an E2 reaction, the proton that is being transferred is not bonded to any atom.
- A sulfur atom can accommodate twelve valence electrons in its valence shell.
- A secondary alkyl halide reacting with the hydroxide anion in ethanol solvent often gives a mixture of substitution and elimination products.
- Although they are primary, neopentyl halides are very unreactive in $\text{S}_{\text{N}}2$ substitution reactions.
- The two protons of the CH_2 group in ethanol are diastereotopic.
- Thiols react with iodine and base to yield sulfones.
- Conversion of alkenes to mercurinium cations with mercury(II) acetate is a syn addition.
- Me_3S^+ is a weaker methylating agent than Me_3O^+ .

() Hydrogen peroxide can be used to oxidize sulfides to sulfoxides.

2. (20 pts) Write plausible mechanisms for the (a) acid catalyzed and (b) base catalyzed addition of ethanol to 2,2-dimethyloxirane (isobutylene oxide). Include all steps and intermediates and use proper curved arrows to indicate electron movement in each step.

(a)

(b)

3. (20 pts) Propose reaction sequences that will convert 1-pentanol into the following products. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents). The reagents are not allowed to contain more than two carbon atoms in the molecule.

(a) *n*-heptyl bromide

(b) 1,1-dichloro-2-propylcyclopropane

4. (20 pts) Draw the free-energy diagram for the solvolysis of *tert.*-butyl chloride in methanol, including both S_N1 and E1 paths in the same diagram. Mark the rate-limiting step with an asterisk and the product-determining steps with crosses. Indicate the location of the starting material, the products, all transition states, and all intermediates in the diagram, and use chemical formulas to show their structures.

5. (20 pts) Write the structures (including stereochemistry where applicable) of the principal organic product in each step of the two-step reactions of cyclopentene with the following reagents (do not show mechanisms or curved arrows).

(a) 1. *m*-Chloroperbenzoic acid, isolate product, treat with 2. lithium dimethylcuprate

(b) 1. Br₂, H₂O, isolate product, treat with 2. NaOH