

KEY

high score 89

average 55

low score 22

1

Student Name (first, last):

Student Number:

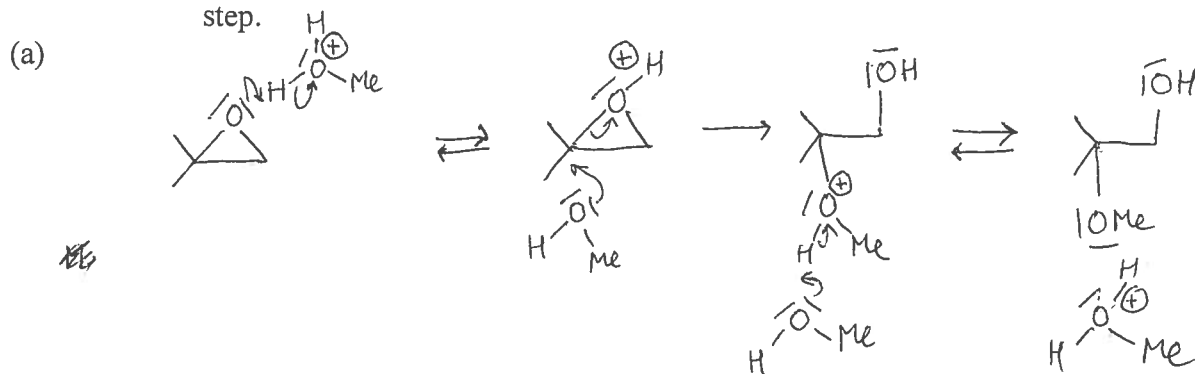
CHEMISTRY 3311
THIRD MIDTERM EXAMINATION

Josef Michl
April 14, 2011

1. (20 points) Check the correct statements only:

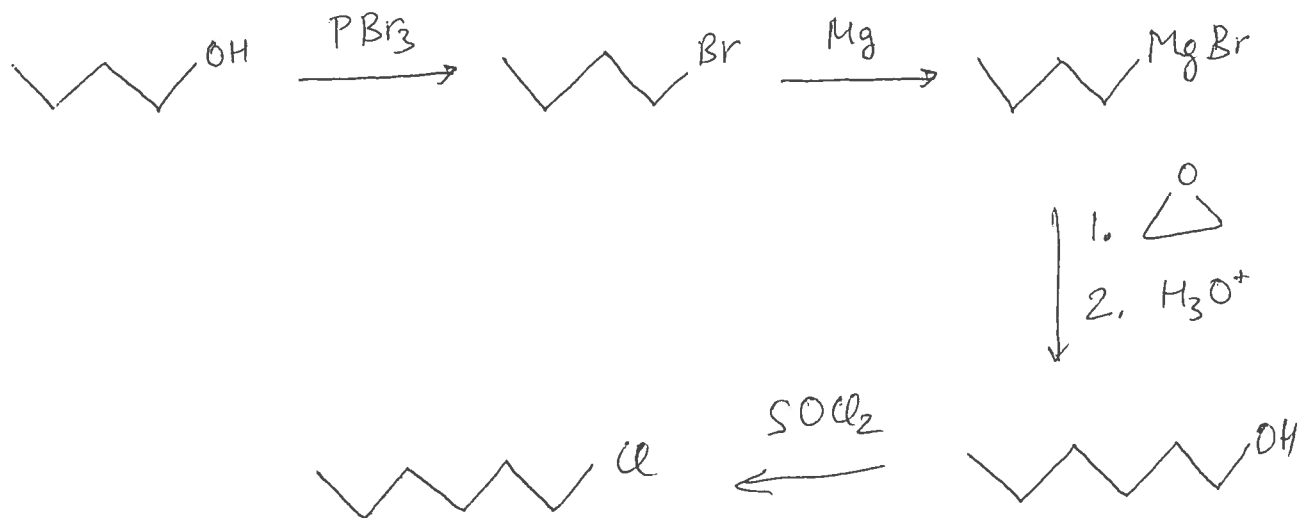
- () At the transition state of an E2 reaction, the proton that is being transferred is not bonded to any atom.
- () A sulfur atom can accommodate twelve valence electrons in its valence shell.
- (X) A secondary alkyl halide reacting with the ethoxide anion often gives a mixture of substitution and elimination products.
- (X) Since KBr is insoluble in acetone, it is possible to effect a reaction of a primary alkyl bromide with KI to give a primary alkyl iodide and KBr in this solvent.
- (X) The reaction rate constant decreases exponentially with increasing free energy of activation.
- () The S_N2 substitution reaction occurs with retention of stereochemistry on the carbon atom on which the substitution takes place.
- (X) Zaitsev's rule states that hydrogen halide elimination from an alkyl halide predominantly yields the most stable of the possible alkenes.
- () Neopentyl halides are particularly reactive in S_N2 substitution reactions.
- () Tertiary alkyl halides are particularly reactive in S_N2 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 stronger nucleophile than iodide, but in dimethylformamide, the opposite is true.
- (X) E2 elimination proceeds preferably in the anti conformation.
- (X) Treatment of chloroform with a strong base yields dichlorocarbene, which can add to alkenes.
- () Sharpless epoxidation uses achiral reagents to convert an achiral allylic alcohol almost entirely to only one of the two possible enantiomers of an epoxide.
- () Primary alcohols are oxidized to aldehydes with CrO₃ only if water is present.
- (X) The two protons of the CH₂ group in ethanol are enantiotopic.
- (X) Thiols react with iodine and base to yield disulfides.
- (X) Conversion of alkenes to epoxides with a peracid is a syn addition.
- () Me₃S⁺ is a stronger methylating agent than Me₃O⁺.
- (X) Hydrogen peroxide oxidizes sulfoxides to sulfones.

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

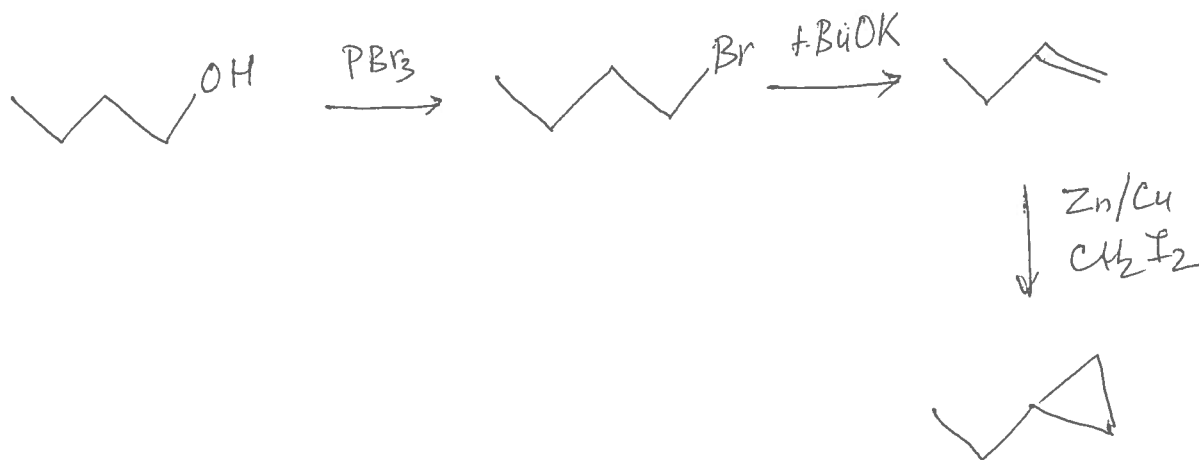


3. (20 pts) Propose reaction sequences that will convert 1-butanol into the following products. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents). The reagents are not allowed to contain more than two carbon atoms in the molecule.

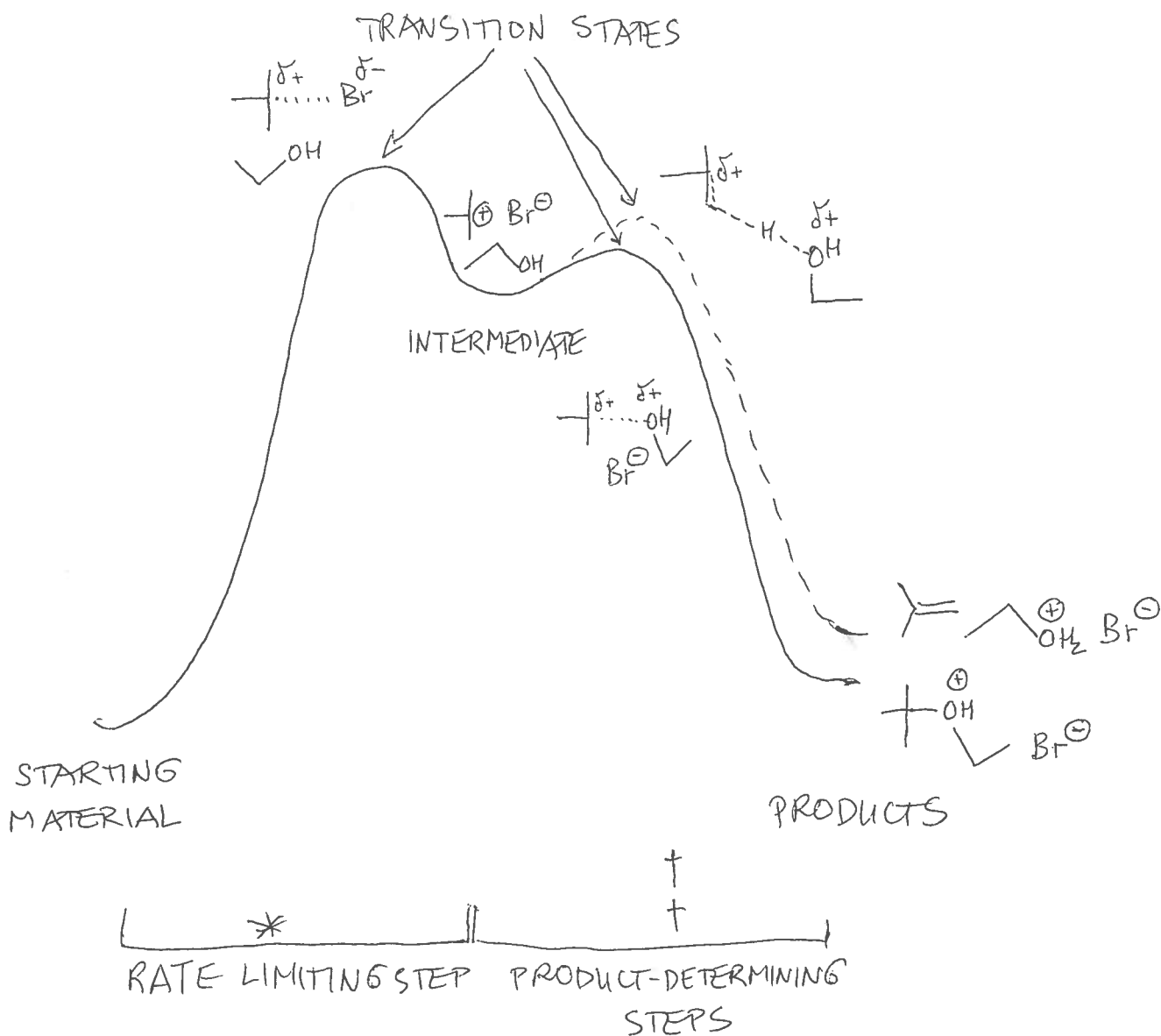
(a) *n*-hexyl chloride



(b) ethylcyclopropane

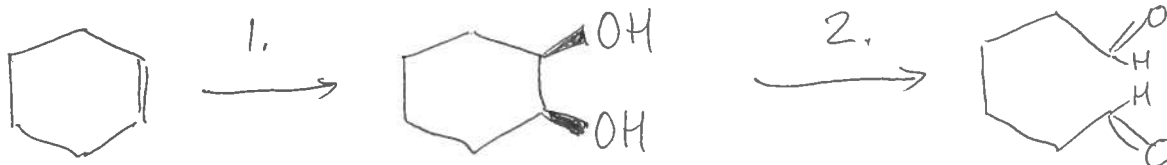


4. (20 pts) Draw the free-energy diagram for the S_N1 -E1 solvolysis reaction of *tert.*-butyl bromide with ethanol. Mark the rate-limiting step with an asterisk and the product-determining steps with crosses. Indicate the location of the starting material, the products, all transition states, and all 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 cyclohexene with the following reagents (do not show mechanisms or curved arrows).

(a) 1. OsO_4 , $(\text{CH}_3)_3\text{NO}$, H_2O , isolate product, treat with 2. H_5IO_6



(b) 1. Br_2 , H_2O , isolate product, treat with 2. NaOH

