***Student Name* (first, last):** KEY

***Social Security Number*:**

***TA Name*:**

CHEMISTRY 3311 (100)
THIRD MIDTERM EXAMINATION

Josef Michl
November 18, 2004

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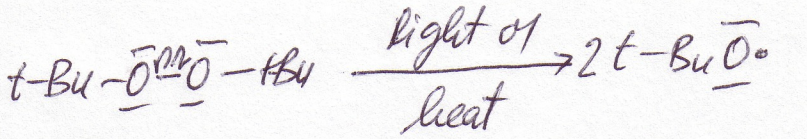
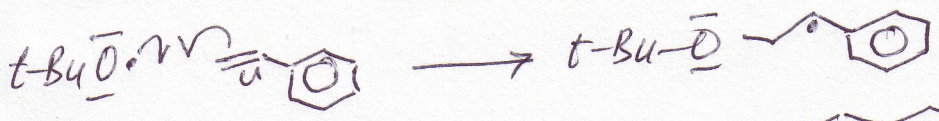
1. (20 points) Check the correct statements only and make no marks at the incorrect statements:

(✓) The S_N1 mechanism is favored for substitution on tertiary carbons and disfavored at primary carbons.
( ) The S_N2 mechanism is favored for substitution on tertiary carbons and disfavored at primary carbons.
(✓) The E1 mechanism of elimination requires a polar solvent.
(✓) The E2 mechanism of elimination requires a strong base.
( ) The reaction of an alkyl halide with an alkali cyanide to give a nitrile is known as the Williamson ether synthesis.
( ) Thionyl chloride converts primary alcohols into aldehydes.
(✓) Disulfides are often prepared by oxidation of thiols.
(✓) The conversion of an alkyl halide to a primary amine via an *N*-alkylphthalimide is known as the Gabriel synthesis.
(✓) Phosphoranes can be produced by deprotonation of alkyltriphenylphosphonium salts with a strong base.
(✓) According to Markovnikov's rule, the addition of hydrogen chloride to an alkene will place the proton on the less substituted carbon and the chloride on the more substituted carbon of the double bond.

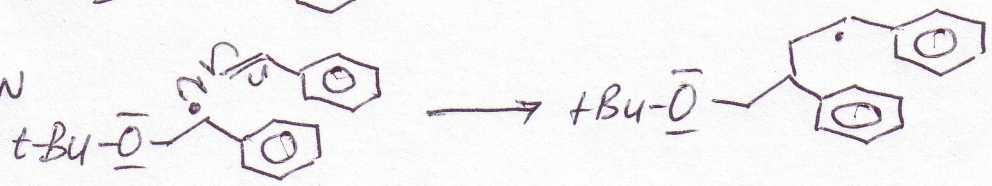
2. (13 pts) Write the mechanism of free-radical polymerization of styrene (vinylbenzene) under UV irradiation with di-t-butyl peroxide as the initiator. Show all reaction steps and structure of the organic product and of all intermediates, if any. Use curved arrows to indicate how electrons move in the individual elementary reaction steps (be careful to use "fishhook" and/or ordinary arrows properly). Label reaction steps or groups of reaction steps with names, if they have any.

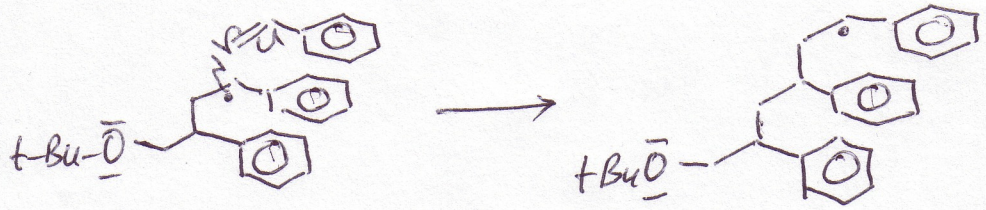
INITIATION





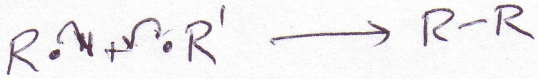
PROPAGATION





etc.

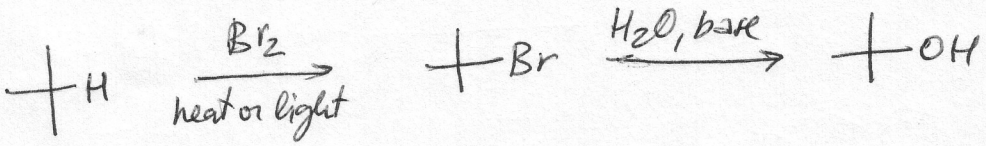
TERMINATION



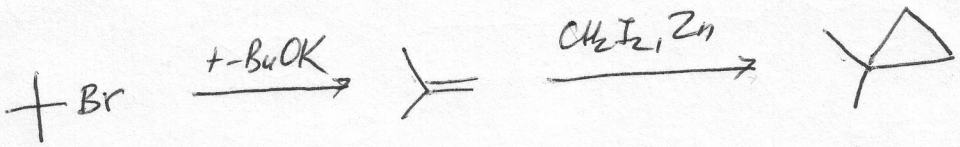
R, R': one of the above radicals

3. (30 pts) Propose an efficient synthesis of each of the following compounds, starting with isobutane $(CH_3)_3CH$ and any reagents whose molecule contains no more than two carbon atoms. Specify all reagents used, but do not specify mechanisms. If you have already described the preparation of a compound and use it again later, you do not need to describe its preparation again.

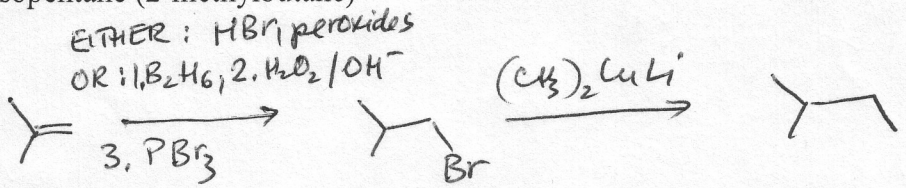
(a) *t*-butyl alcohol



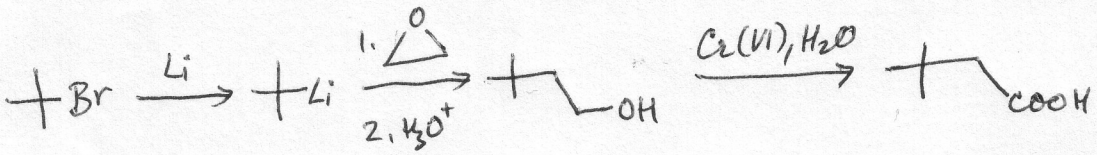
(b) 1,1-dimethylcyclopropane



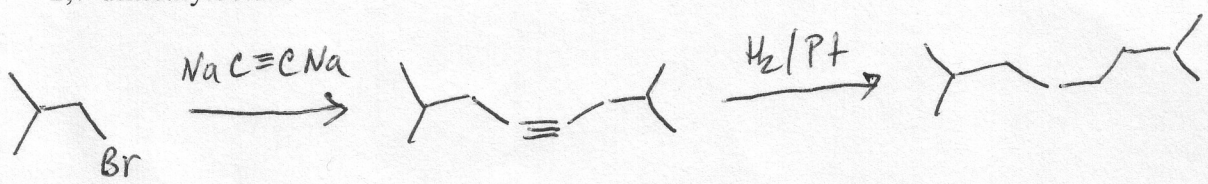
(c) isopentane (2-methylbutane)



(d) 3,3-dimethylbutanoic acid



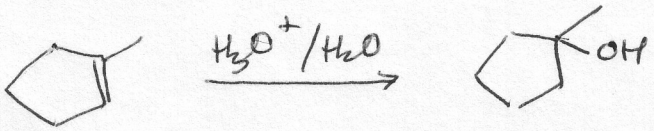
(e) 2,7-dimethyloctane



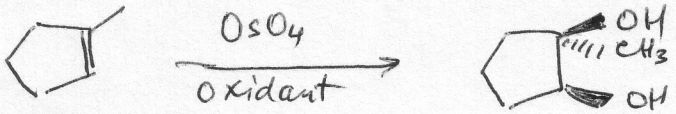
4. (21 pts) Write the reagents you would use to convert the starting materials given into the products shown. Specify the solvent only if its use is critical since other solvents would not work. You do not need to specify mechanisms.

1-Methylcyclopentene into:

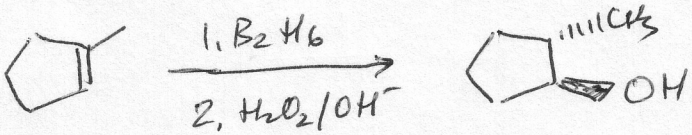
(a) 1-Hydroxy-1-methylcyclopentane



(b) *cis*-1,2-Dihydroxy-1-methylcyclopentane (hydroxy groups cis to each other, racemic)

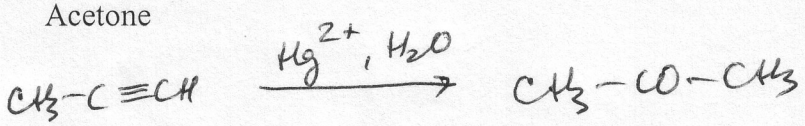


(c) *trans*-2-Hydroxy-1-methylcyclopentane (racemic)

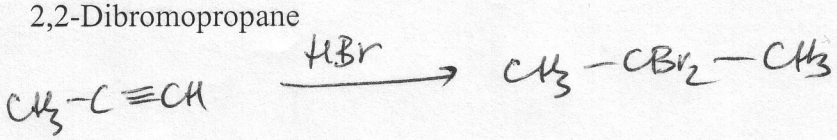


Propyne into

(d) Acetone

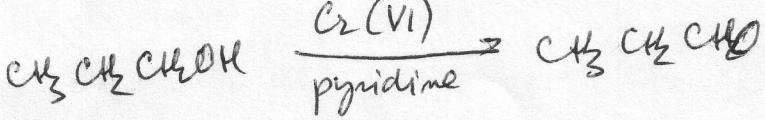


(e) 2,2-Dibromopropane

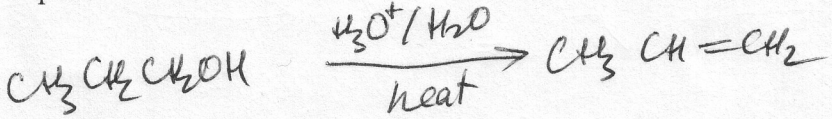


1-Propanol into

(f) Propanal

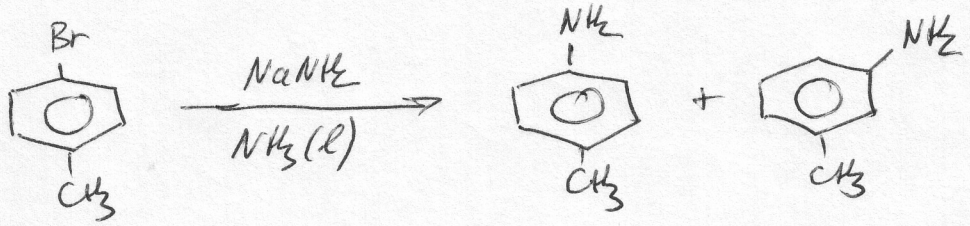


(g) Propene

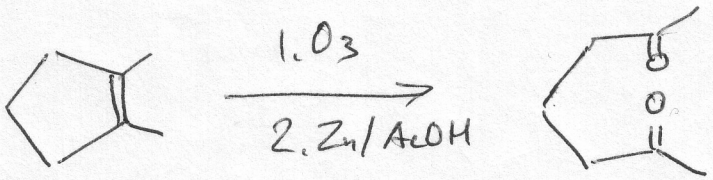


5. (16 pts) Fully specify (including stereochemistry if applicable) all the principal organic products of the following reactions (do not write the mechanism).

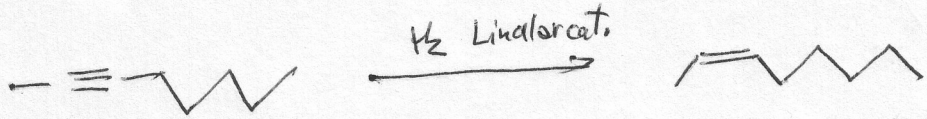
(a) *p*-Bromotoluene and $NaNH_2$ in liquid ammonia solvent.



(b) 1,2-Dimethylcyclopentene and ozone, then zinc and acetic acid.



(c) 2-Octyne and hydrogen gas over a Pd catalyst on $BaSO_4$ poisoned with quinoline (Lindlar catalyst).



(d) 2-Octyne and sodium metal in liquid ammonia and a little methanol.