

low score 47
average 139
high score 177

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Student Name (first, last):

KEY

Student Number:

CHEMISTRY 3371 (ORG CHEM FOR MAJORS)
FINAL EXAMINATION

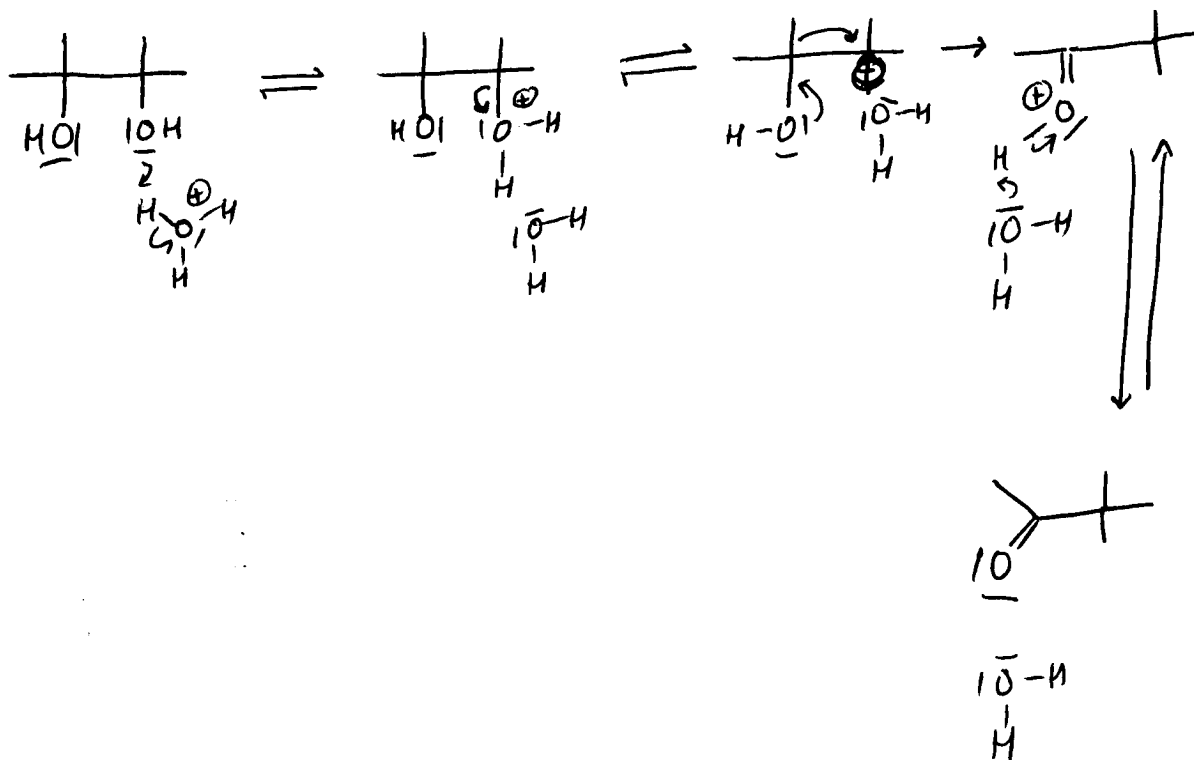
Josef Michl
May 8, 2007

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

- For alanine, $pK_1 = 2.35$ and $pK_2 = 9.87$; therefore, its isoelectric point is 6.11.
- Benzoic acid reacts with lithium aluminum hydride (LAH) to yield benzaldehyde after workup.
- Cellulose is a poly(aminosaccharide).
- Hunsdieker reaction converts silver butanoate into *n*-butyl bromide.
- The Kiliani-Fischer synthesis converts an aldotetrose into a mixture of two aldohexoses.
- Radical polymerization of ethylene yields branched polyethylene.
- Acid hydrolysis of benzonitrile yields benzoic acid.
- The first pK_a of oxalic acid is lower than the pK_a of acetic acid.
- Thiols react with iodine to yield disulfides.
- Treatment of *o*-chlorotoluene with hot NaOH yields a mixture of *o*-cresol and *m*-cresol (cresol is a trivial name for methylphenol).
- Monobromination of ketones by reaction with Br_2 is best done under acidic conditions.
- Propanoic acid reacts with diazomethane to produce methyl propanoate.
- Lithium diethylcuprate reacts with acetyl chloride to yield diethyl ketone.
- Methyl acetate reacts with ammonia to yield acetonitrile in good yield.
- The allene, $C_2H_5ClC=C=CClC_2H_5$, is chiral.
- The reaction of butanoic acid with bromine and a catalytic amount of red phosphorus yields 2-bromobutanoic acid.
- Pyrimidine is 1,3-diazine.
- Heating of 2-naphthol with aqueous ammonium sulfite yields 2-naphthylamine.
- Heating allyl phenyl ether induces Claisen rearrangement.
- Trifluoroacetic acid has a lower pK_a than acetic acid.
- An orbital is a region of space where an electron is likely to be found.
- The most bonding of the six pi molecular orbitals of benzene has a node across two CC bonds.
- Disrotatory ring opening of cyclobutene has an antiaromatic transition state and is forbidden.
- p*-Nitroaniline is a weaker base than *p*-methoxyaniline.
- Low-molecular weight alkyl azides tend to be explosive and dangerous.
- Under anhydrous conditions, Curtius rearrangement of acyl azides leads to isocyanates.
- Hofmann rule for the direction of elimination quaternary ammonium salt states that the most stable alkene will be formed.
- Benzidine rearrangement converts hydrazobenzene into 4,4'-diaminobiphenyl.

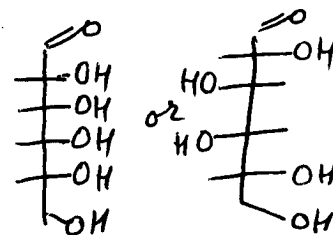
- Cyclobutadiene is antiaromatic and extremely reactive.
- Friedel-Crafts acylation of benzene with acetyl chloride and a catalytic amount of AlCl_3 will proceed to completion.
- Ullmann coupling of *o*-iodonitrobenzene yields *o,o'*-dinitrobiphenyl.
- Phthalic acid cannot be prepared by oxidation of naphthalene.
- Quinhydrone is a 1:1 charge transfer complex of hydroquinone and *p*-benzoquinone.
- Upon treatment with phenylhydrazine, glucose and mannose yield the same osazone.
- The secondary structure of a protein is its linear amino acid sequence.
- Sucrose is a disaccharide containing glucose and ribose.
- Phenolphthalein can be prepared by a condensation of phenol with phthalic anhydride.
- Anthrone predominates in equilibrium with 9-anthranol.
- Pyridine is more basic than pyrrole.
- Intersystem crossing is a process in which a vibrationally excited molecule absorbs a photon.

2. (20 pts) Write a plausible mechanism for the acid-catalyzed rearrangement of pinacol, $(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{OH})(\text{CH}_3)_2$, to pinacone. Include all steps and intermediates and use curved arrows to indicate electron movement in each step.

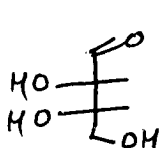


3. (20 pts) D-Aldohexose A is reduced by sodium borohydride to an optically inactive alditol B. Ruff degradation of A gives an aldopentose C, which is oxidized by nitric acid to an optically active saccharic acid D. What are the structures of A - D?

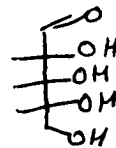
Because the alditol B is inactive, A can only be



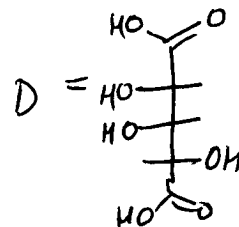
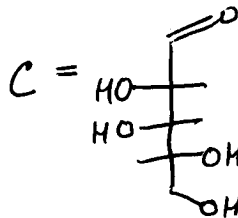
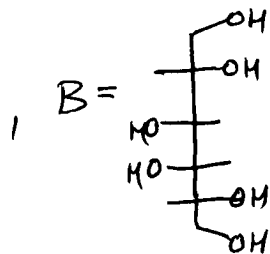
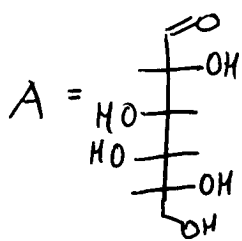
Because the saccharic acid D is active, the aldopentose C derived from A can only be



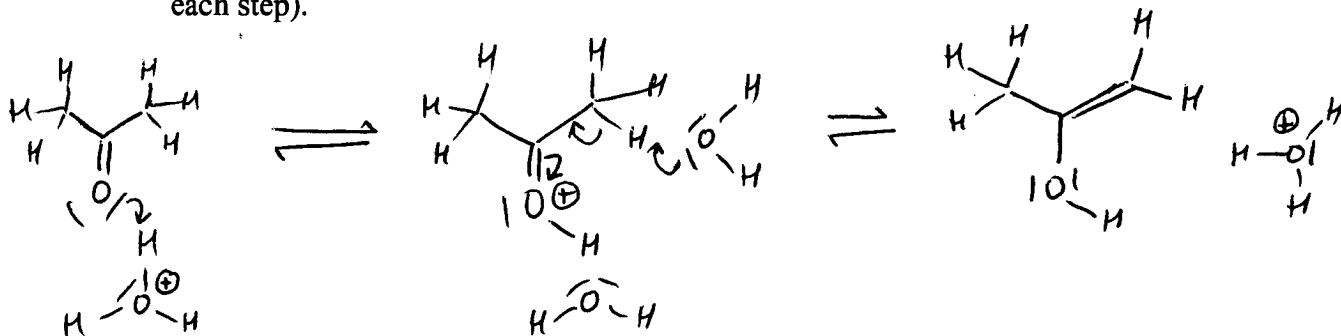
and not



Therefore,

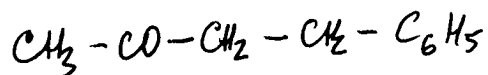


4. (20 pts) Write a plausible mechanism for the acid-catalyzed enolization of acetone (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

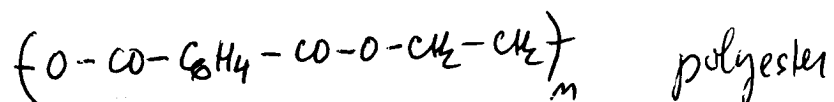


5. (40 pts) Write the structures of all principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

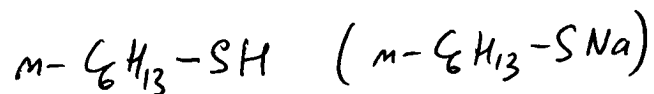
(a) $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5 + 1. \text{C}_2\text{H}_5\text{ONa}/\text{C}_2\text{H}_5\text{OH}, 2. \text{C}_6\text{H}_5\text{CH}_2\text{Br}, \text{isolate}, 3. \text{HCl}/\text{H}_2\text{O}, \text{heat} \rightarrow$



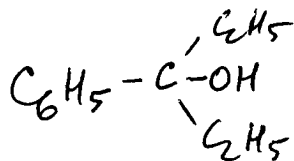
(b) $p\text{-CH}_3\text{OOC}-\text{C}_6\text{H}_4\text{-COOCH}_3 + \text{HOCH}_2\text{CH}_2\text{OH}, \text{heat}, \text{distill away volatile material} \rightarrow$



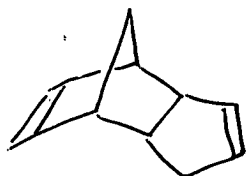
(c) $m\text{-C}_6\text{H}_{13}\text{Br} + 1. \text{S}=\text{C}(\text{NH}_2)_2 \text{ (thiourea)}, 2. \text{NaOH}/\text{H}_2\text{O} \rightarrow$



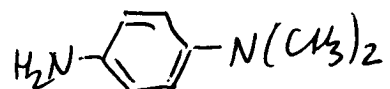
(d) $\text{C}_6\text{H}_5\text{-CO-OCH}_3 + 1. \text{C}_2\text{H}_5\text{MgI} \text{ (excess)}, 2. \text{H}^+ \rightarrow$



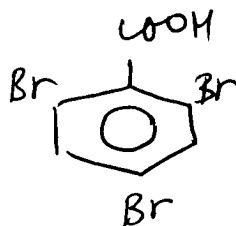
(e) cyclopentadiene, room temperature →



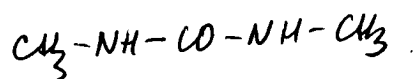
(f) $C_6H_5N(CH_3)_2 + 1. NaNO_2, HCl, \text{isolate}, 2. H_2/\text{cat} \rightarrow$



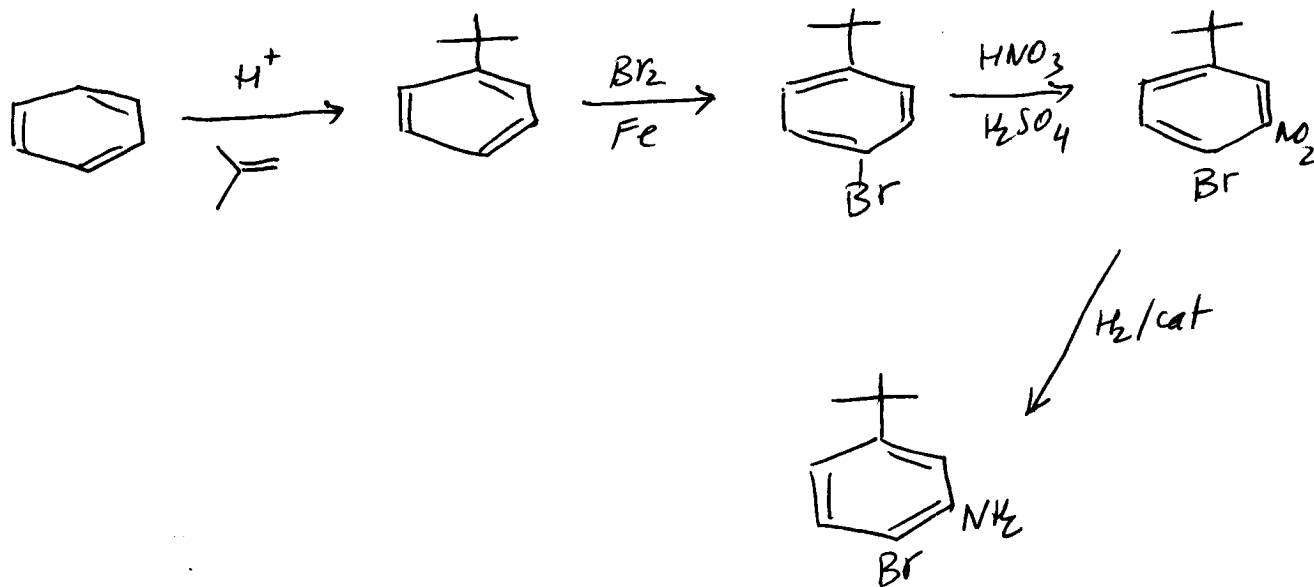
(g) $m\text{-}H_2N\text{-}C_6H_4\text{-}COOH + 1. Br_2 \text{ (excess)}, \text{isolate}, 2. NaNO_2, H_2SO_4, H_2O, 0^\circ C, 3. H_3PO_2 \rightarrow$



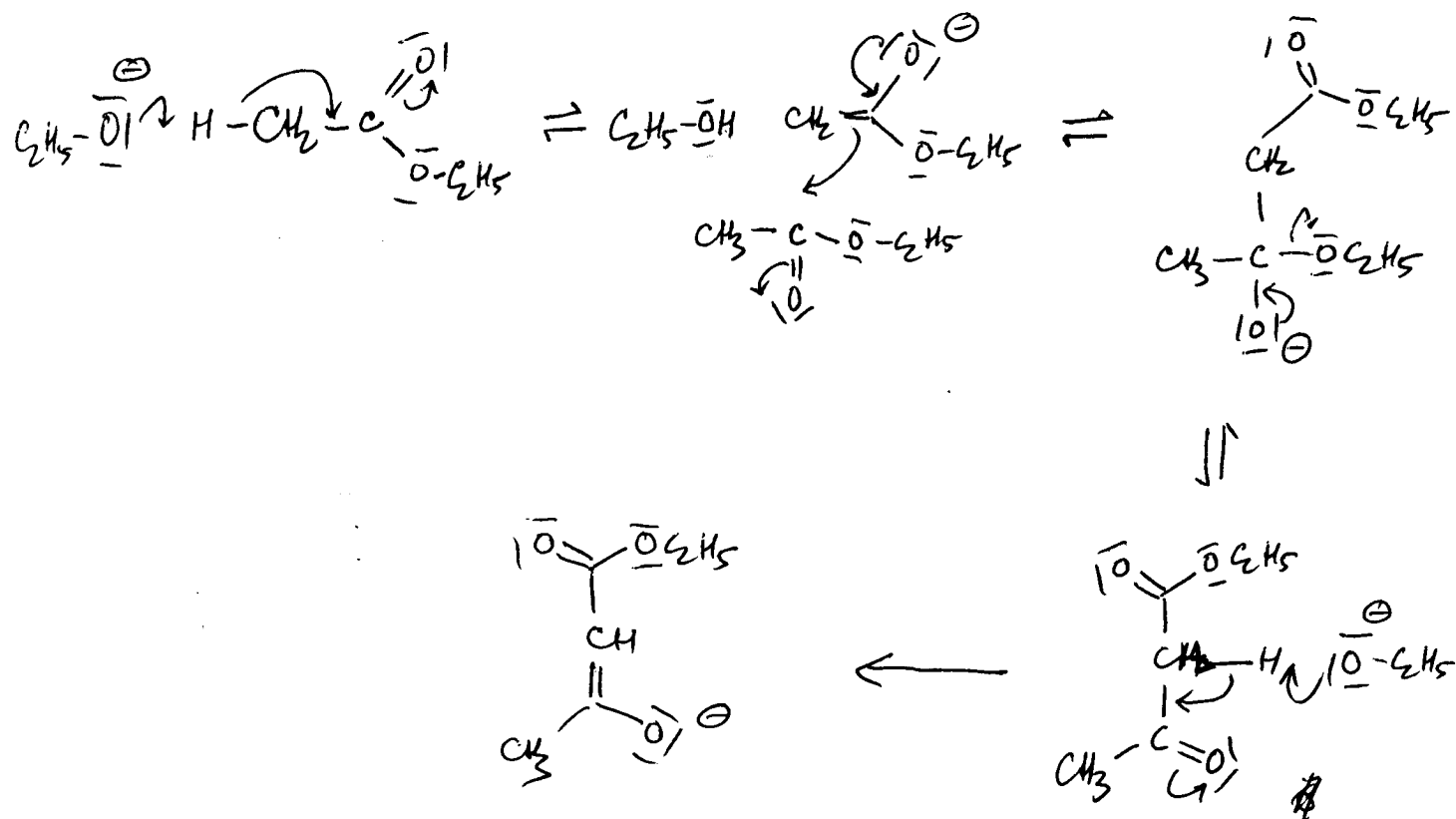
(h) $CH_3Br + 1. KNCO, 2. CH_3NH_2 \rightarrow$



6. (20 pts) Propose an efficient synthesis of 2-bromo-5-*tert*-butylaniline from benzene and reagents that do not contain more than four carbon atoms in the molecule. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).



7. (20 pts) Write a plausible mechanism for the Claisen condensation of ethyl acetate in the presence of one full equivalent of sodium ethoxide in ethanol (include all steps and intermediates and use curved arrows to indicate electron movement in each step).



8. (20 pts) Write a plausible mechanism for the monosulfonation of naphthalene with H_2SO_4 at 160°C (show all steps and intermediates, including products that form temporarily, and use curved arrows to indicate electron movement in each step).

