KEY

HIGH 92

***Student Name* (first, last):** ALE 69

Student Number: LOW 22

CHEMISTRY 3371

THIRD MIDTERM EXAMINATION

Josef Michl

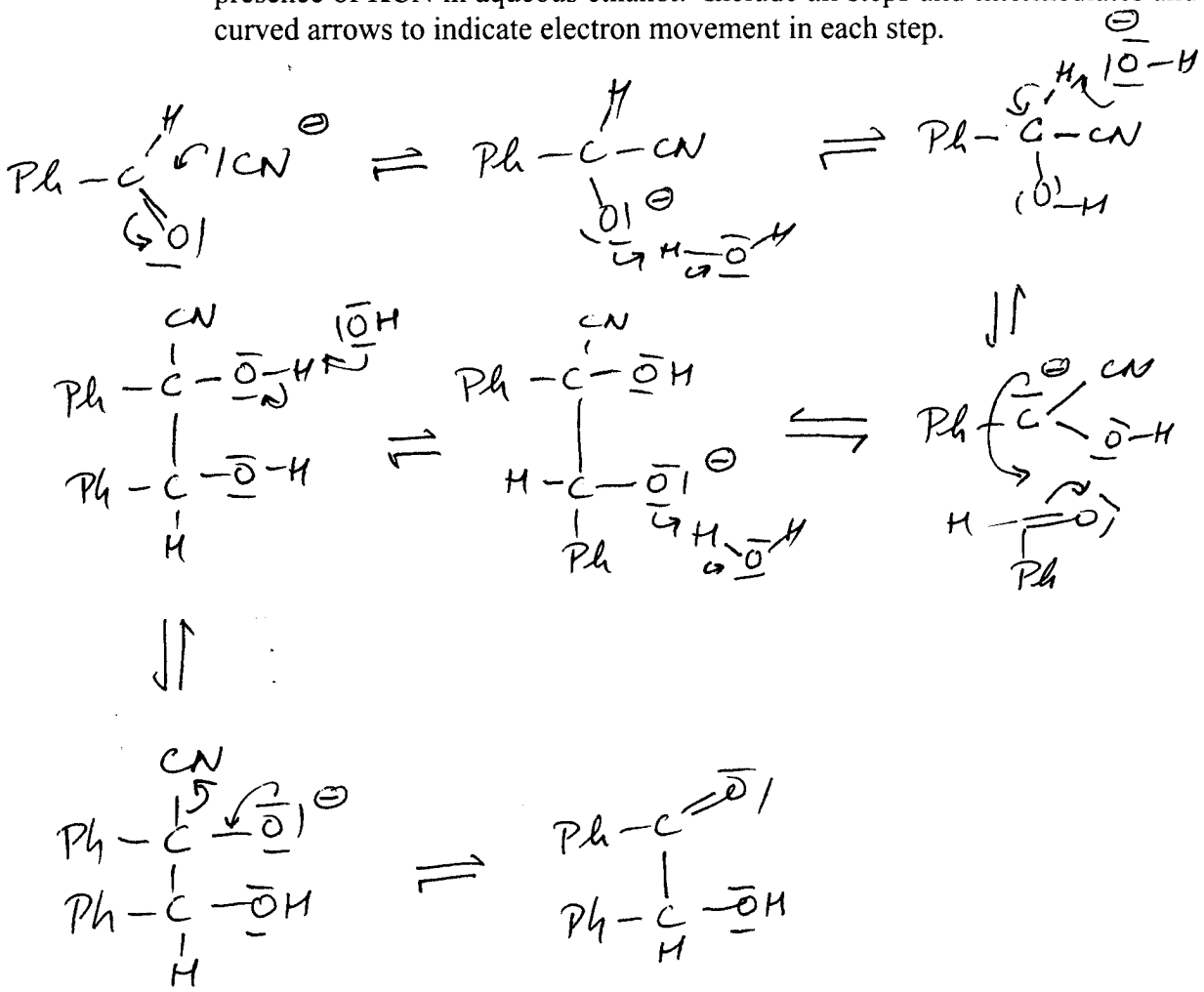
April 19, 2007

---

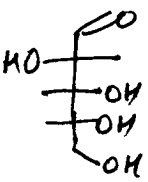
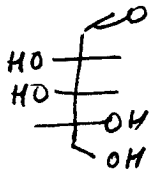
1. (20 points) Check the correct statements only (make no other marks):

( ) For alanine, $pK_1 = 2.35$ and $pK_2 = 9.87$; therefore, its isoelectric point is 12.22.
(✓) Chitin is a poly(aminosaccharide).
(✓) Cellulose is a polysaccharide.
(✓) The benzyloxycarbonyl group protecting an amine is removed by catalytic hydrogenation.
(✓) The Kiliani-Fischer synthesis converts an aldopentose into a mixture of two aldohexoses.
(✓) Periodic acid oxidizes ethylene glycol into two equivalents of formaldehyde.
(✓) In the first step of Strecker synthesis of an α-amino acid an aldehyde reacts with HCN and NH_3.
( ) The first pK_a of oxalic acid is higher than the pK_a of acetic acid.
(✓) Thiols react with iodine to yield disulfides.
( ) Sodium periodate oxidizes dialkyl sulfides to dialkyl sulfones.
( ) Dicyclohexylcarbodiimide activates an amino group for later coupling with a carboxyl.
(✓) Unlike nitration, aromatic sulfonation is a reversible process.
(✓) Conversion of a vicinal diol to a ketone by treatment with acid is called pinacol rearrangement.
(✓) Benzyl chloroformate is made by treatment of benzyl alcohol with phosgene.
(✓) Phthalic acid can be prepared by oxidation of naphthalene.
(✓) Alanine is transformed into ethyl ester by treating its solution in ethanol with anhydrous HCl.
( ) Upon treatment with phenylhydrazine, glucose and mannose yield different osazones.
(✓) The primary structure of a protein is its linear amino acid sequence.
(✓) Sucrose is a disaccharide containing glucose and fructose.
(✓) The common form of naturally occurring alanine is an L amino acid.

2. (12 pts) Write a plausible mechanism for the formation of benzoin from benzaldehyde in the presence of KCN in aqueous ethanol. Include all steps and intermediates and use curved arrows to indicate electron movement in each step.

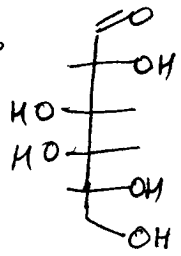
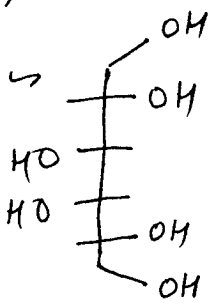


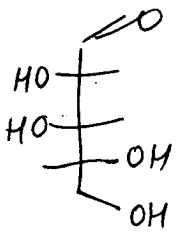
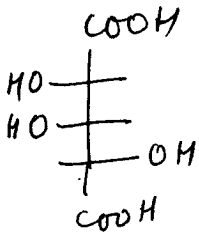
3. (16 pts) D-Aldohexose A is reduced by sodium borohydride to an optically inactive alditol B. Ruff degradation of A gives an aldopentose C, which is oxidized by nitric acid to an optically active saccharic acid D. What are the structures of A - D? Hint: remember the Fischer proof of glucose structure.

A. C could be  or  ; the other two aldopentoses would give inactive saccharic acids

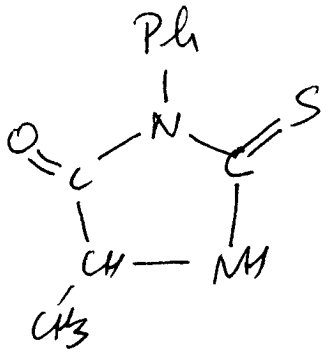
B. The aldopentose on the left is excluded since both aldohexoses from which it could be produced by Ruff degradation would give optically active alditols upon reduction

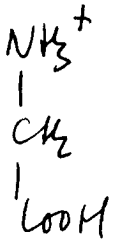
C. Two aldohexoses yield the aldopentose on the right by Ruff degradation, but one of them would yield an active alditol upon reduction, so

A must be  and then B is  and

C is  and D is 

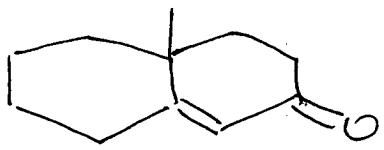
4. (10 pts) Draw the structures of the products of the Edman degradation of alanylglycine (treatment with phenyl isothiocyanate followed by treatment with anhydrous HCl in an organic solvent). No mechanisms, no curved arrows are needed.



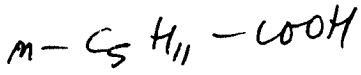


5. (30 pts) Write the structures of all principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

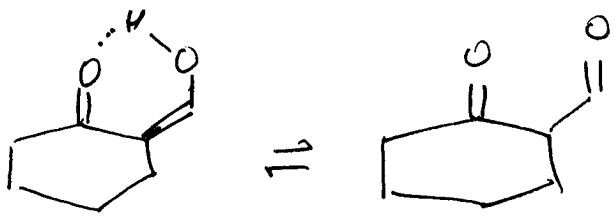
(a) Robinson annulation: 2-methylcyclohexanone + methyl vinyl ketone + KOH in ethanol ➜



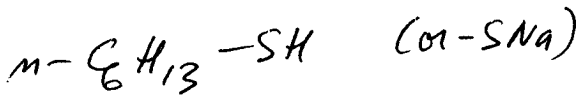
(b) $CH_2(COOC_2H_5)_2$ + 1. C_2H_5ONa/C_2H_5OH, 2. *n*-C_4H_9Br, isolate product, 3. conc. HCl, heat ➜



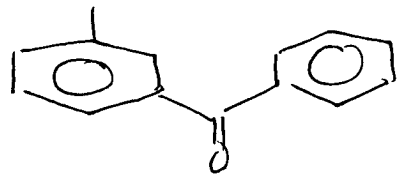
(c) cyclohexanone and $HCOOC_2H_5$ + 1. $NaOC_2H_5/C_2H_5OH$, 2.H_3O ➜



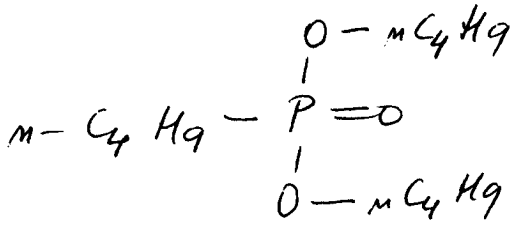
(d) n-$C_6H_{13}Br$ + 1. $S{=}C(NH_2)_2$ (thiourea), 2. $NaOH/H_2O$ ➜



(e) m-(trimethylsilyl)toluene + benzoyl chloride ➜



(f) (n-$C_4H_9O)_3P$ + n-C_4H_9Br (trace) ➜



6. (12 pts) Draw the Fischer, Haworth, and realistic (chair conformation) representations of the α anomer of D-glucopyranose.