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

Student Number:

CHEMISTRY 3371

THIRD MIDTERM EXAMINATION

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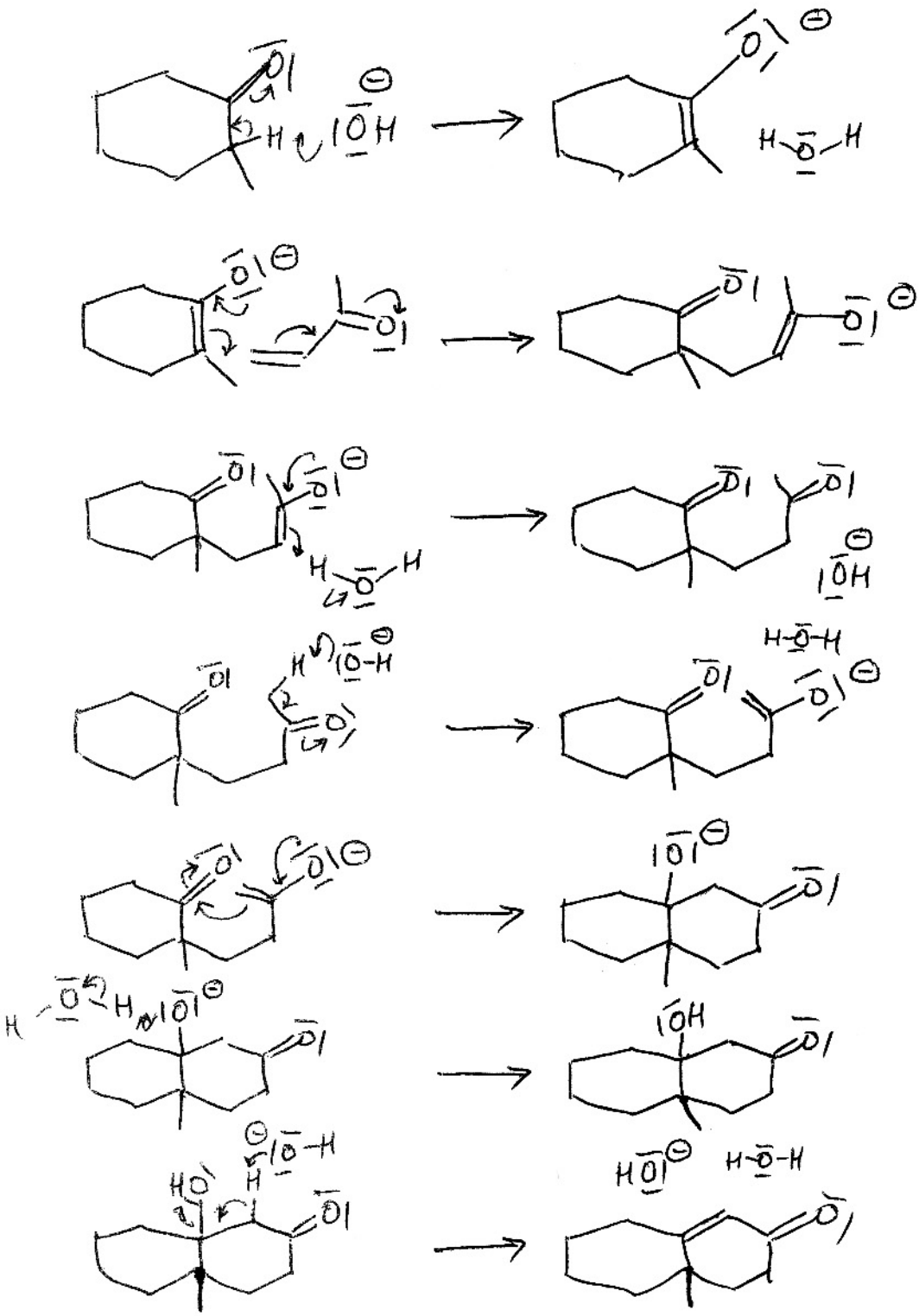
1. (20 points) Check the correct statements only (make no other marks):

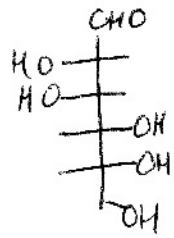
( ) Ninhydrin reacts with aqueous solutions of α-amino acids to give an intense green color.
( ) The tertiary structure of a protein is its linear amino acid sequence.
( ) Sucrose is a disaccharide containing two units of glucose.
(X) In the first step of Strecker synthesis of an α-amino acid an aldehyde reacts with HCN and NH_3.
( ) The first pK_a of malonic acid is higher than the pK_a of acetic acid.
( ) Thiols react with iodine to yield alkanesulfonic acids.
( ) Aromatic sulfonation is not a reversible process.
(X) The products of the Edman degradation of glycylalanine are N-phenylthiohydantoin and alanine.
(X) Upon treatment with phenylhydrazine, glucose and mannose yield the same osazone.
(X) Sodium periodate oxidizes dialkyl sulfides to dialkyl sulfoxides but not to sulfones.
(X) Starch is a polysaccharide.
( ) The *tert.*-butoxycarbonyl group protecting an amine is removed by catalytic hydrogenation.
(X) The Kiliani-Fischer synthesis converts an aldohexose into a mixture of two aldoheptoses.
( ) Periodic acid oxidizes glycolaldehyde, $HOCH_2CHO$, into two equivalents of formaldehyde.
(X) Dicyclohexylcarbodiimide (DCC) is a reagent in the Merrifield (solid state) peptide synthesis.
( ) The common form of naturally occurring alanine is a D amino acid.
(X) For glycine, $pK_1 = 2.35$ and $pK_2 = 9.78$; therefore, its isoelectric point is 6.065.
( ) Cellulose is a poly(aminosaccharide).
(X) A trimethylsilyl substituent in β position stabilizes a carbocation.
(X) Silicones are polymers containing a repeated -SiR'R"-O- unit in the backbone.

2. (16 pts) Show the mechanism of Robinson annulation: 2-methylcyclohexanone + methyl vinyl ketone + KOH in ethanol Include all steps and intermediates and use curved arrows to indicate electron movement in each step.



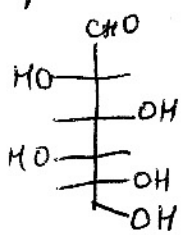
3. (12 pts) Ruff degradation of two D-aldohexoses, A and B, gives the same D-aldopentose, which is reduced by sodium borohydride to an optically active alditol. Interchange of the CHO and CH_2OH groups in B by a complicated reaction sequence ultimately converts B into itself. Write the structure of A and circle it.

1. A and B are epimers (differ by stereochemistry on C2)
2. The only D-aldohexoses that convert into themselves upon exchange of CHO and CH_2OH groups are



1

and



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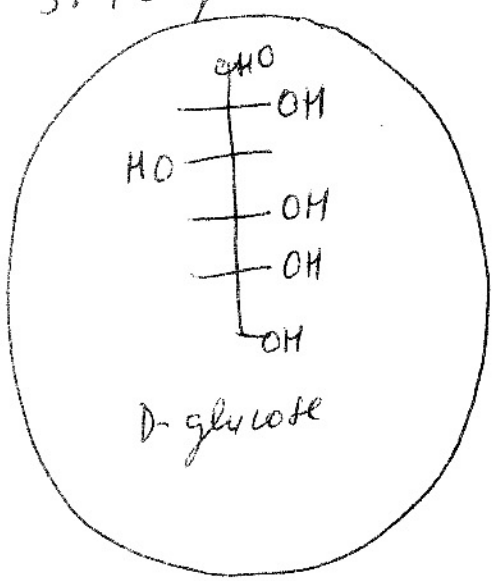
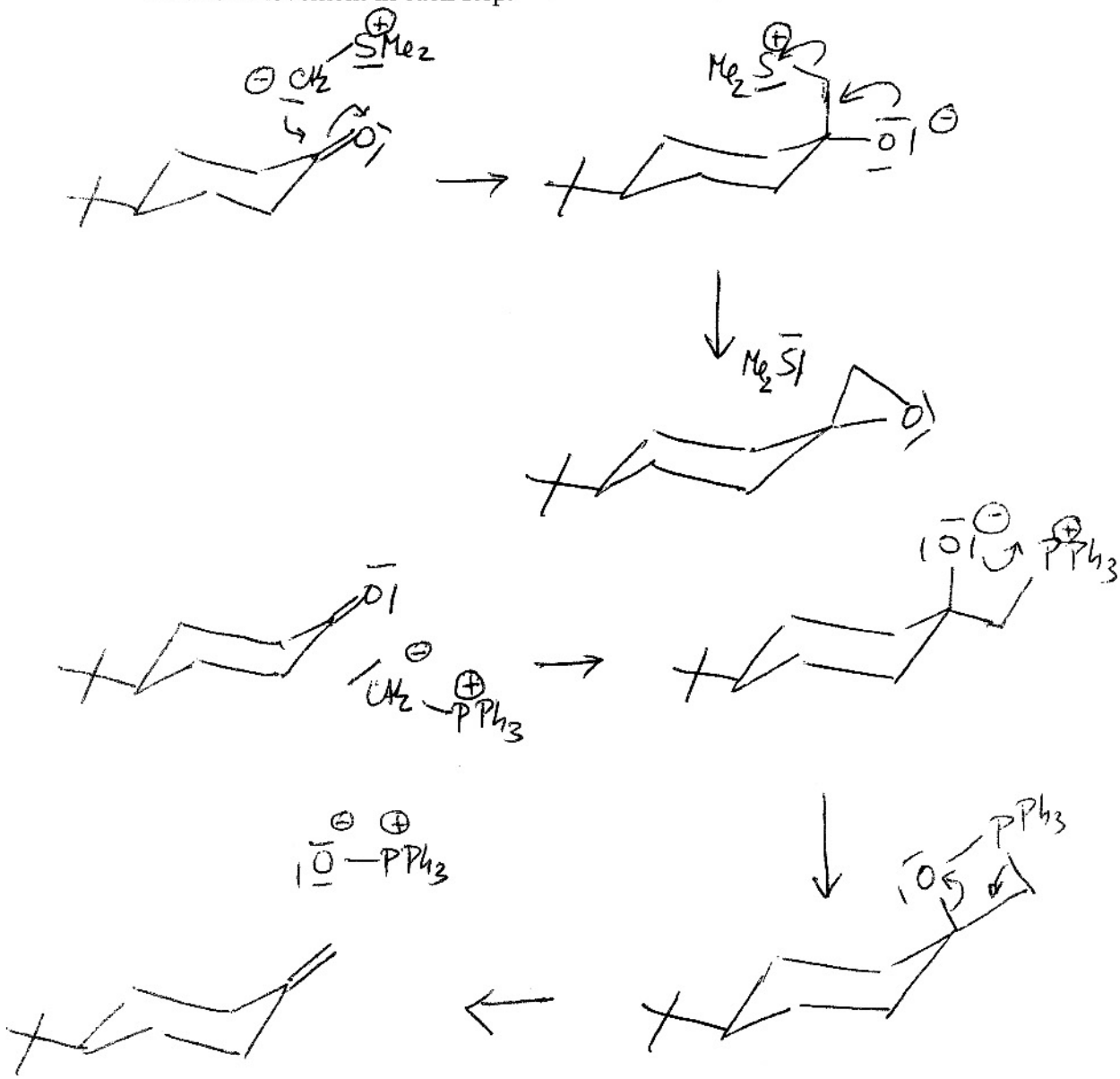
3. Ruff degradation followed by reduction to alditol will yield an optically active alditol from 1 but not from 2.
4. Therefore B is 1.
5. Therefore A is the epimer of 1:



4. (10 pts) Draw the structure of 4-*tert*-butylcyclohexanone and show the mechanisms of its reactions with (a) the sulfonium ylide Me_2S^+-CH_2^- and (b) the phosphonium ylide Ph_3P^+-CH_2^-. Include all steps and intermediates and use curved arrows to indicate electron movement in each step.

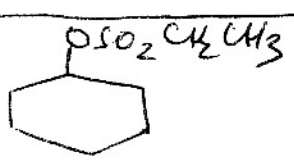


5. (30 pts) Write the structures of all principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.

(a) 1. CH_3CH_2Br + $NaHSO_3$, 2. PCl_5, 3. cyclohexanol, pyridine ➜

1. $CH_3CH_2SO_3Na$

2. $CH_3CH_2SO_2Cl$

3. 

(b) 1. $CH_3COCH_2COOC_2H_5$ + C_2H_5ONa/C_2H_5OH, 2. *n*-C_4H_9Br, 3. conc. HCl, heat ➜

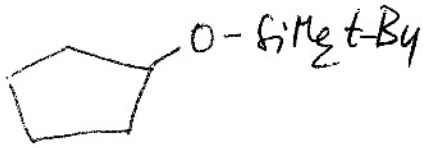
1. $CH_3COCHNaCOOC_2H_5$

2. $CH_3COCH(C_4H_9)COOC_2H_5$

3. $CH_3COCH_2C_4H_9$

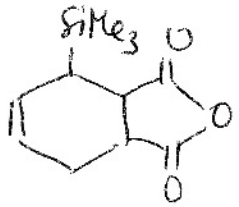
(c) 1. *tert*-BuLi (1 equiv) + Me_2SiCl_2 (1 equiv), 2. cyclopentanol, imidazole ➜

1. $t\text{-}Bu\text{-}SiMe_2Cl$

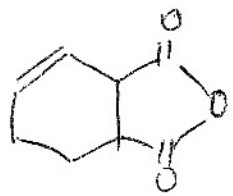
2. 

(d) 1. CH_2=CH-CH=CH-$SiMe_3$ + maleic anhydride, heat, 2. *p*-TsOH, heat ➜

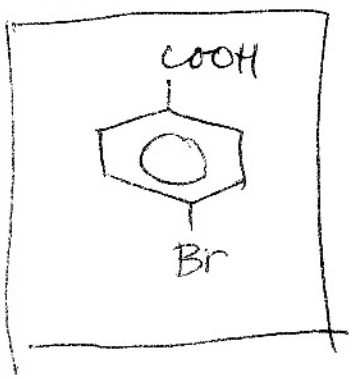
1.



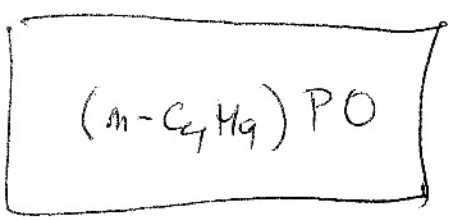
2.



(e) *p*-(trimethylsilyl)benzoic acid + Br_2 ➜



(f) (n-C_4H_9)$_3$P + air ➜



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