ANSWER KEY

Columbia University
Chemistry S3444 Professor Irving J. Borowitz
Summer 1992 -Exam No. 3 THUR Aug 6, 1992
NAME: SUE KROSS & BEN ZION

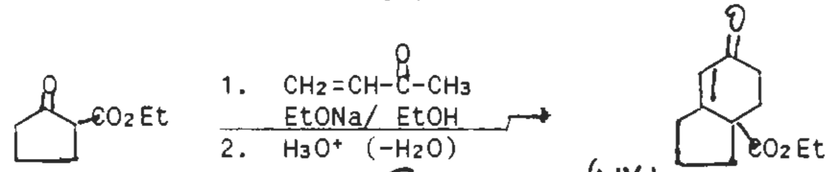
	Question	
(12) 1.		(18) 4.
(22) 2.		(22) 5.
(14) 3.		(12) 6.

Please use a non-red **pen**. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the front of that page. ***Good Luck!***
Note: **Points** appear in ( ) and in margin.

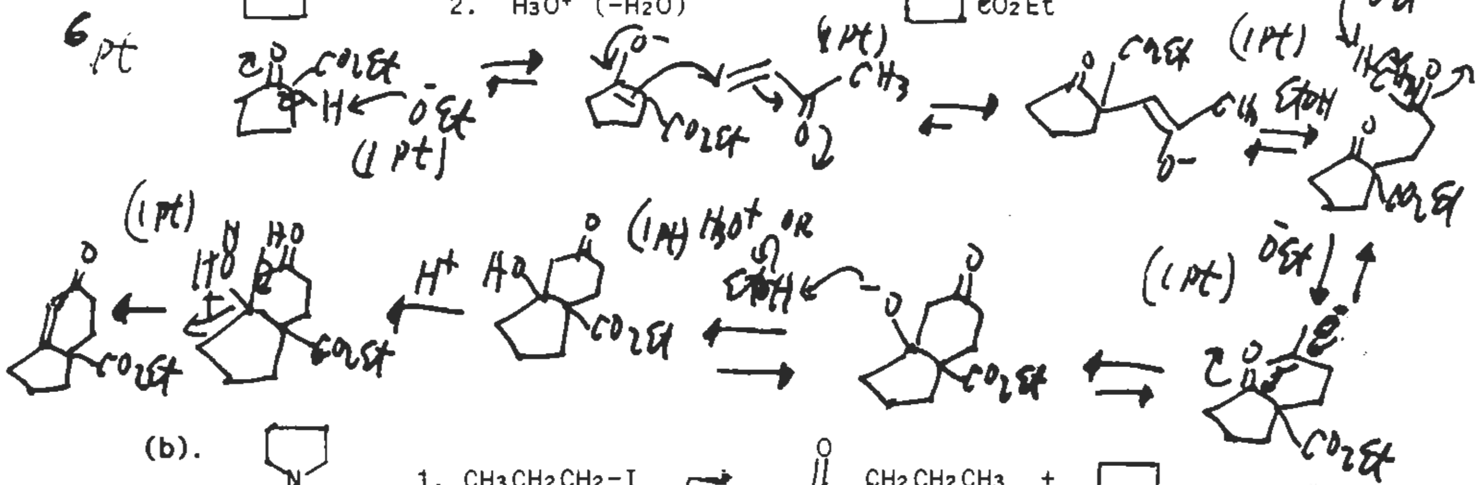
1. Write step-by-step mechanisms for each of the following reactions. Use arrows to show electron flow.

(12)

(a).



6 pt



(b).

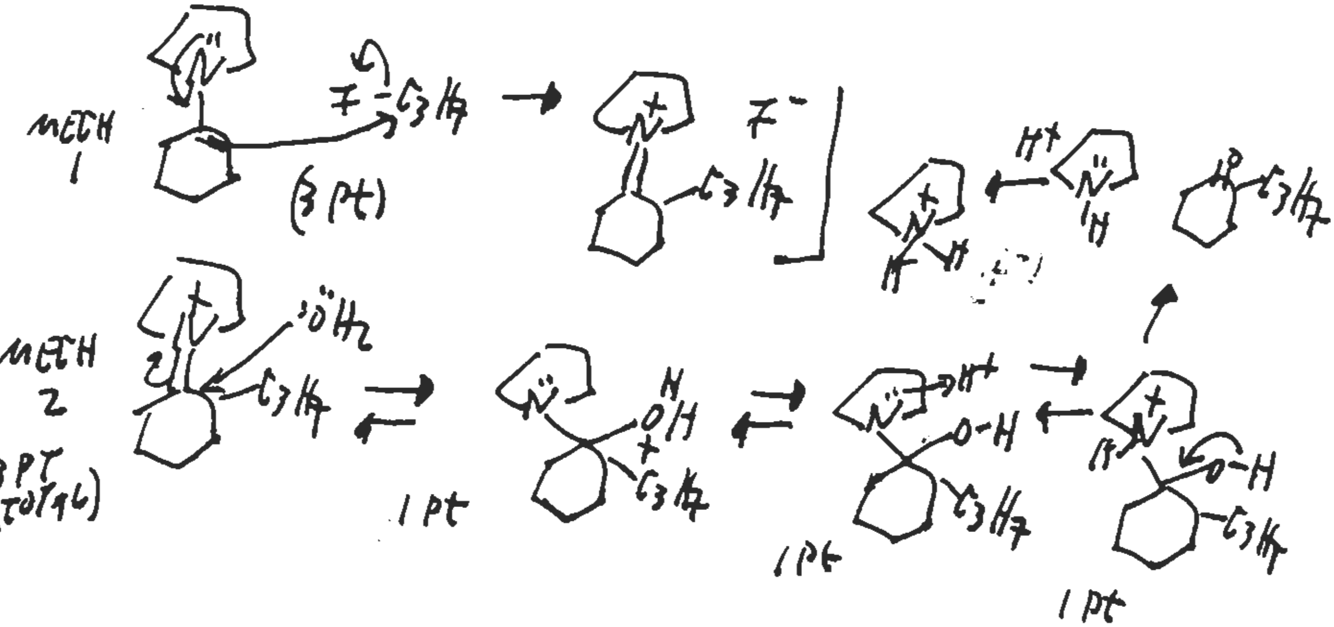
6 pt

NOTE: There are 2 steps here. **Do both mechanisms.**

MECH 1

MECH 2

(3 PT TOTAL)

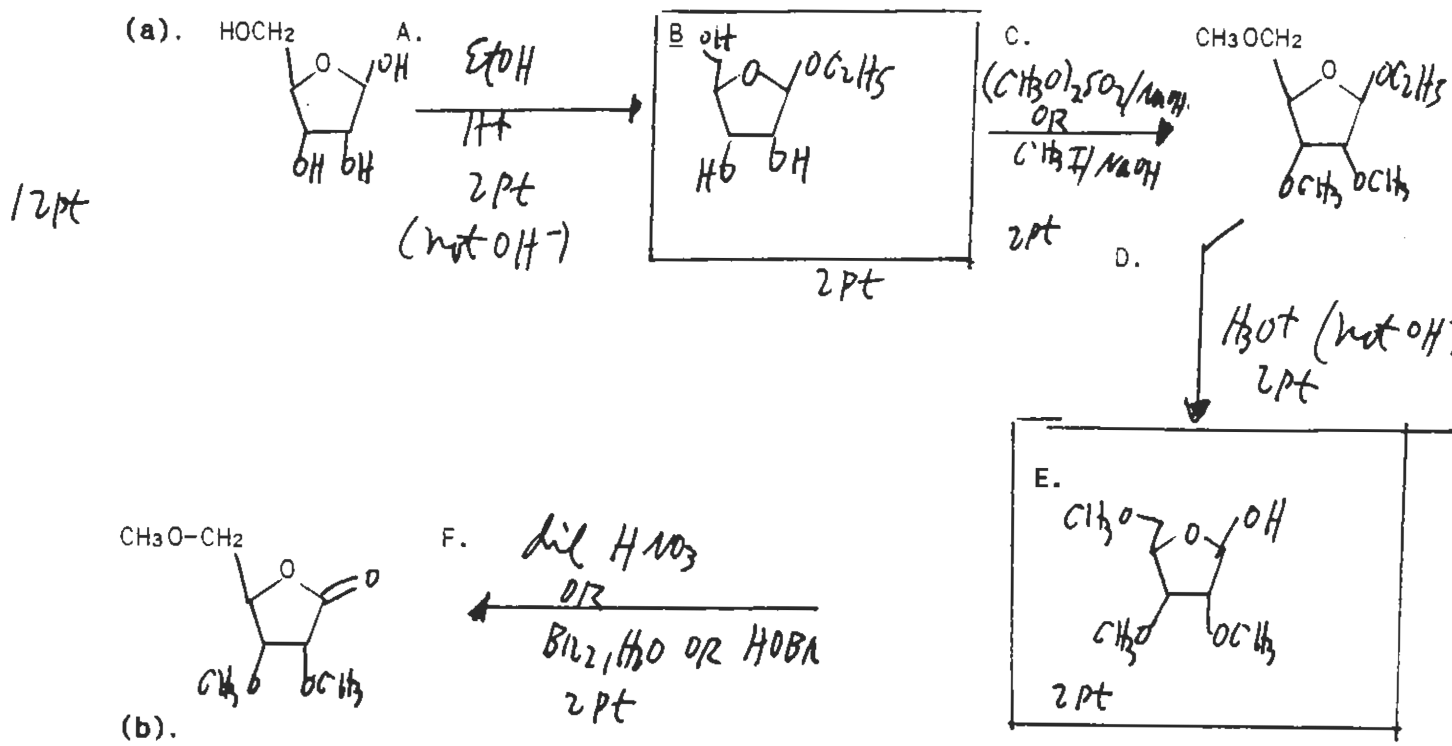


SUGARS NOW ON FINAL EXAM

(22) **2.** Write the structures of the necessary inorganic/ organic reagents or the expected major organic products (**A** to **F**) in each of the following conversions:

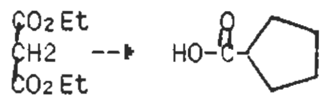
12pt

(a).

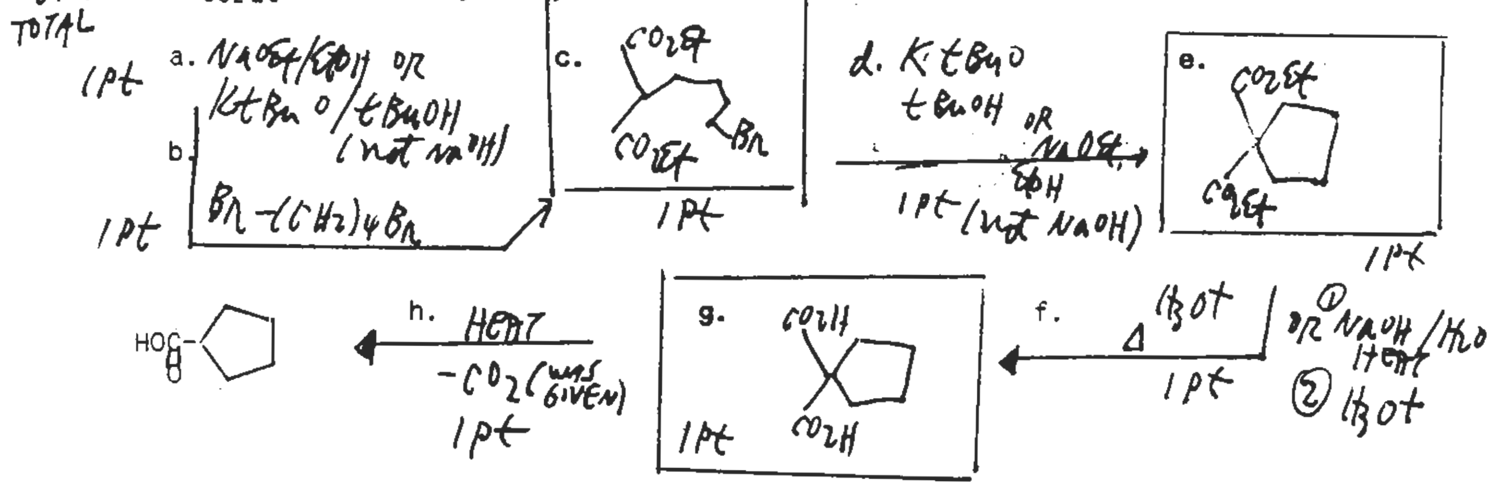


(b).

8pt TOTAL



Write the structures of needed organic/inorg reagents, and organic intermediate products (**a** to **h**):



(c). Intramolecular cyclization reactions, such as the Dieckmann condensation of a diester to prepare a β-ketoester, are best carried out in very dilute solutions of the compound to be cyclized. Why is this so? (circle one correct answer).

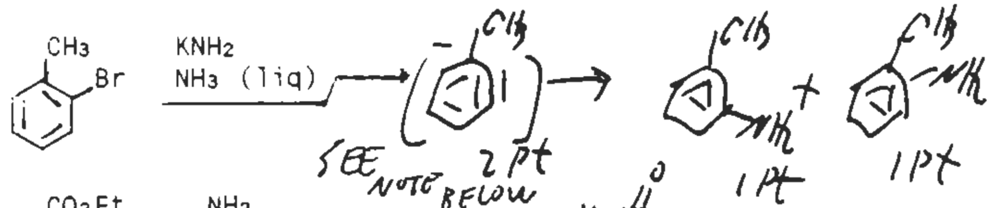
2pt

1. It is then possible to use less base.
2. The reagents used are generally expensive.
3. A smaller amount of the compound to be cyclized can be used.
4. Intermolecular condensation is minimized at low concentration.
5. The concentration factor is not important.

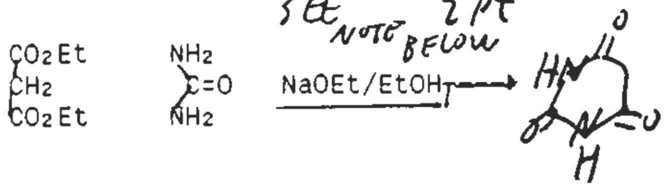
(14) 3. Write the structures of the major organic product(s) and/ or reagents and intermediate products for each of the following conversions:

3pt a.

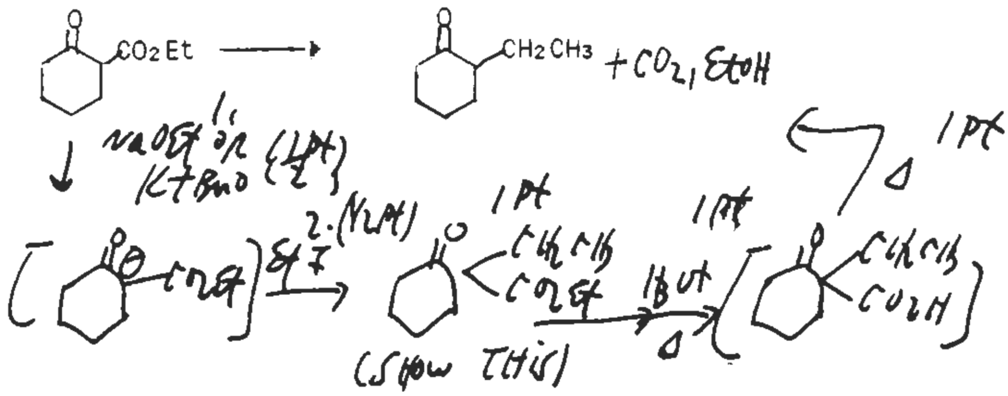
4pt b.



3pt c.



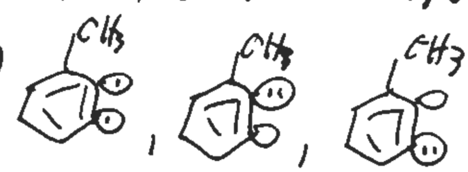
4pt d.



SCRAP

TO GRADERS:  CAN ALSO BE WRITTEN AS:

(METHYL BENZYNE)



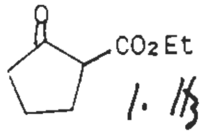
P.3

NOTE TO GRADER/STUDENT: CHECK WITH FJB

(18) **4.** Write a chemical reaction or a test which differentiates the members of each of the following pairs of compounds. Write the structures of all major organic/inorganic products that form. **For a test, write also what you see** FOR BOTH CPDS.

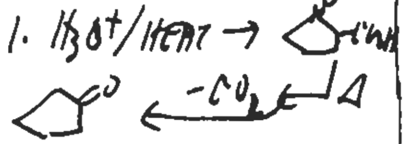
ANY ONE OF FOLLOWING:

(a).



(6pt)

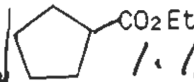
1. H_3O^+/HEAT → $-CO_2$, Δ



2. NaOEt/EtOH → NO FURTHER RXN; (1) H_3O^+ →

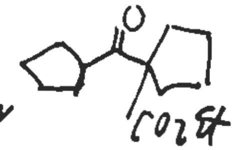
3. 2,4-DNPH → YELLOW PPT

4. $NaBH_4$ →



1. H_3O^+/HEAT → + EtOH; no CO_2 EVOLVED

2. NaOEt/EtOH, CLAISEN CONDENSATION



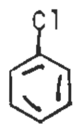
3. 2,4-DNPH: no RXN

4. $NaBH_4$: no RXN

ALSO OTHER RXNS WHICH DISTINGUISH ESTERS FROM KETONES ARE O.K. (KETALIZATION, WITTIG, ETC.)

(b).

ANY ONE:

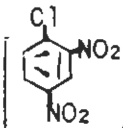


(6pt)

1. NO RXN WITH MOST NUCLEOPHILES

2. No RXN WITH REDUCING AGENTS

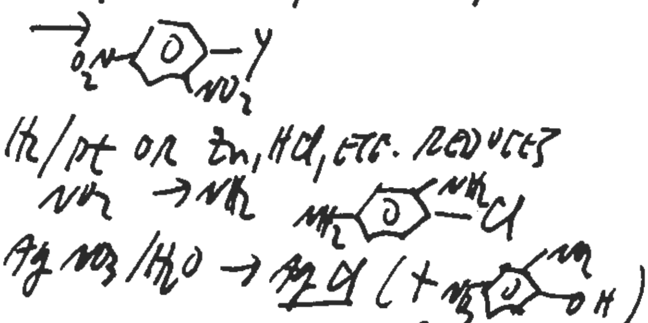
3. No RXN WITH $AgNO_3$



1. ANY WEAK NUCLEOPHILE RS⁻, ROH, RNH_2, H_2O, R_3P, CN^- ≡ Y →

2. H_2/Pt OR Zn, HCl, ETC. REDUCES NO_2 → NH_2

3. $AgNO_3$/H_2O → AgCl (+) (CAN BE OMITTED) NO PENALTY



(c).

ANY ONE:

(6pt)

HC=O
HC–OH
HC–OH
CH₂–OH

1. HIO_4: 3 MOLES CONSUMED → H–C(=O)–OH 3 MOLES + 1 mole $H_2C=O$

2. dil HNO_3 → di ACID CO_2H–CHOH–CHOH–CO_2H (MESO-TARTARIC) not necessary TO IDENTIFY

3. Br_2, H_2O → CO_2H–CHOH–CHOH–CH_2OH

4. EXCESS ΦNH–NH_2/H^+ → COLORED OSAZONE: HC=N–NHΦ, C=N–NHΦ, CHOH, CH_2OH

5. RUFF DEGRAD. CO_2H–CHOH–CHOH–CH_2OH, H_2O_2/Fe^{3+} → H–C=O, HCOH, CH_2OH

HC=O
CH₂CH₂CH₃

1. HIO_4: no RXN

2. dil HNO_3 → H_3C–C–C–CO_2H

3. Br_2, H_2O PROBABLY OXIDIZES

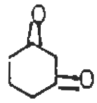
4. NH_2–NHΦ (EXCESS) → H–C=N–NHΦ, C–C–CH_3 PHENYLHYDRAZONE (COLORLESS)

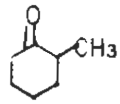
5. RUFF DEGRAD. on C–C–C–CO_2H → ? PRODUCTS (ALKANES MAYBE but NO ALDEHYDES OR SUGARS)

NOTE: SUGARS NOW ON FINAL

(22) **5a.** 2-Methylcyclohexane-1,3-dione (**M**) can be synthesized from (circle correct answer):

2pt

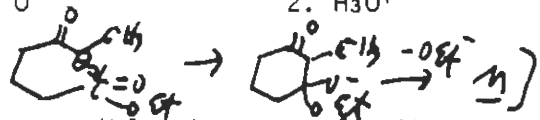
1.  1. CH_3MgBr 2. H_3O^+ →

2.  $KMnO_4$, $NaOH/H_2O$ →

3. $CH_3CH_2C(=O)CH_2CH(CH_3)CH_2CO_2Et$ 1. NaOEt 2. H_3O^+ →

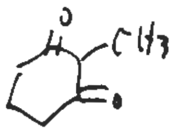
(4.) $CH_3CH_2C(=O)CH_2CH_2CH_2CO_2Et$ 1. NaOEt 2. H_3O^+ →

5. None of the above.

[NOTE: VIA  M]

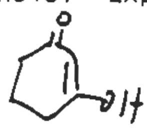
(b). Write the structure for **M** based on its name.

2pt



(c). Write a possible structure for the mono enol of **M**. Is this structure expected to be more stable than are MOST ORDINARY enols? Explain your answer.

(4pt)

1pt  STRUCTURE

MORE STABLE (1pt)

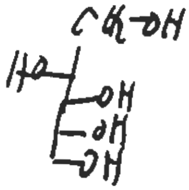
BECAUSE: CONJUGATED O=C–C=C SYSTEM (2pt)

(d). Which of the following sugars will not lose their optical (O.A.) activity after the described reaction occurs. Explain and write the structures of the expected major organic product(s): FOR ALL 3 RXNS.

3pt **1.**
HC=O
HO–CH
HC–OH
HC–OH
CH₂–OH

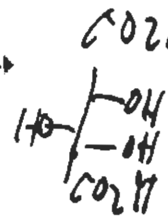
NaBH₄, H₂O →

WILL NOT LOSE O.A.



2. (3pt)
HC=O
HC–OH
HOCH
HC–OH
CH₂–OH

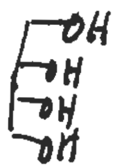
dil. HNO_3 →



WILL LOSE O.A.

3pt **3.**
HC=O
HC–OH
HC–OH
CH₂–OH

$NaBH_4$, H_2O →



WILL LOSE O.A.

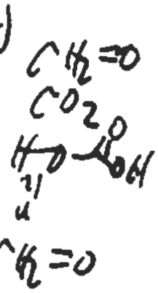
5(e). In the reaction of HIO_4 with sorbose (**S**), how many moles of HIO_4 are consumed? Also write the structures and number of moles of each expected product.

5pt

CH₂–OH **S**
C=O
HO–CH
HC–OH
HO–CH
CH₂–OH

HIO_4, H_2O →

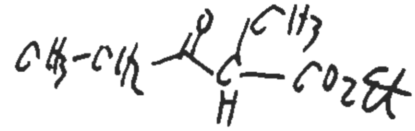
5 MOLES HIO_4 (1pt)



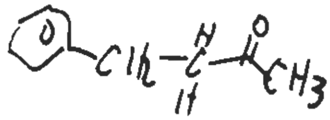
SO: 2 MOLES $H_2C=O$
3 " HCO_2H
1 MOLE CO_2 } 4pt

12
( ) **6.** Write the structures of the expected major organic product(s) or the necessary inorganic/ organic reagents for each of the following conversions:

3pt

(a). $CH_3CH_2CO_2Et$ + $CH_3CH_2CO_2Et$ —— 1. NaOEt/ EtOH; 2. H_3O^+ ——→ 

3 pt

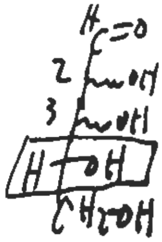
(b). $CH_2=CH-C(=O)-CH_3$ —— 1. Ph2CuLi; 2. H_3O^+ ——→ 

Write a structure for :

(c). a D-aldopentose

3pt

ONE OF FOLLOWING



C_2 OH CAN BE "D" OR "L"
C_3 OH " " "

ETC.

(d). a non-reducing sugar or sugar derivative

(3 pt) ANY SUGAR ACETAL /KETAL

NOT HEMIACETAL 

NOT ALDEHYDE-CONTAINING SUGAR
NOT HOCH2-C(=O)-C-C CONTAINING