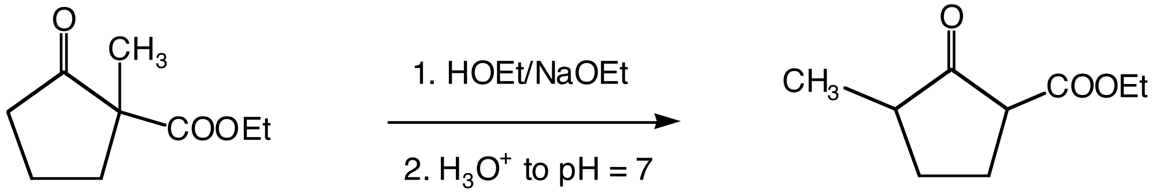
Hour Examination #3, Chemistry 302X - 2006

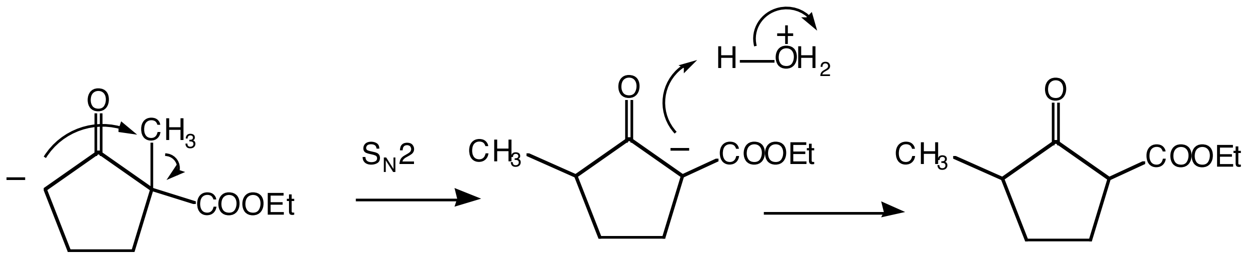
> “Sometimes the straight and narrow path leads to a nasty place.”
>
> Alfred North Whitehead

1 (24 points). Here is a problem you have seen before.



1 **2**

Amy Alonza Stagg suggests a simple S_N2 displacement of the methyl group by the ketone enolate to give, after protonation, **2**.



2

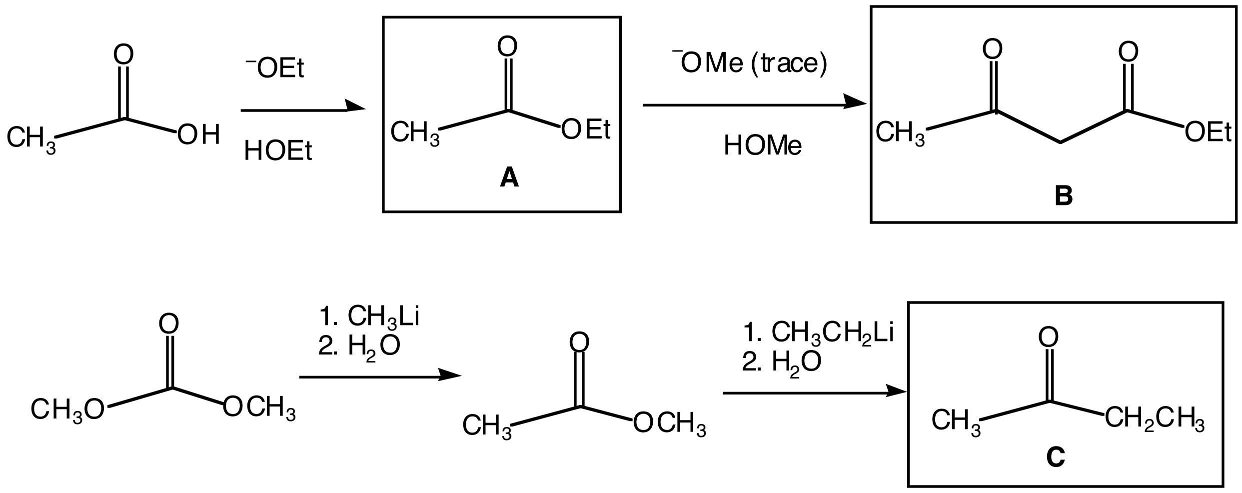
(a) For a start, criticize this seemingly almost trivial mechanism. Why can we be quite sure it’s wrong?

(b) Now, provide Amy with two alternative mechanisms. Hint: There are two archetypal reactions of carbonyl compounds in base. Each begins one of the possible mechanisms.

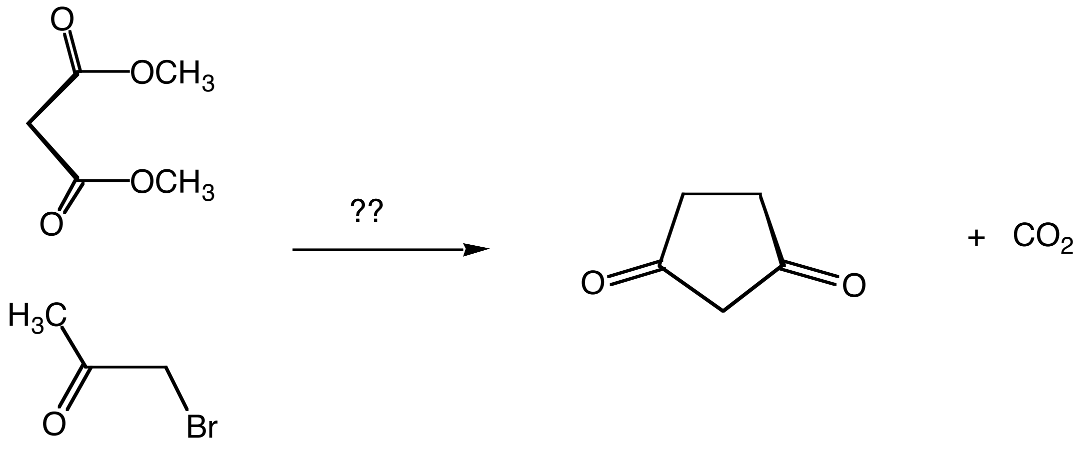
(c) Finally, suggest an experiment that would tell which mechanism is operating. You may assume an ability to make any labeled compound necessary.

2 (17 points). The following synthetic scheme was devised by Henry Gingrich's favorite student, I. B. Verständnislos. It contains several errors. Show what products really would be formed in each of the four reactions below, and provide correct routes to the three boxed products, **A**, **B**, and **C**.

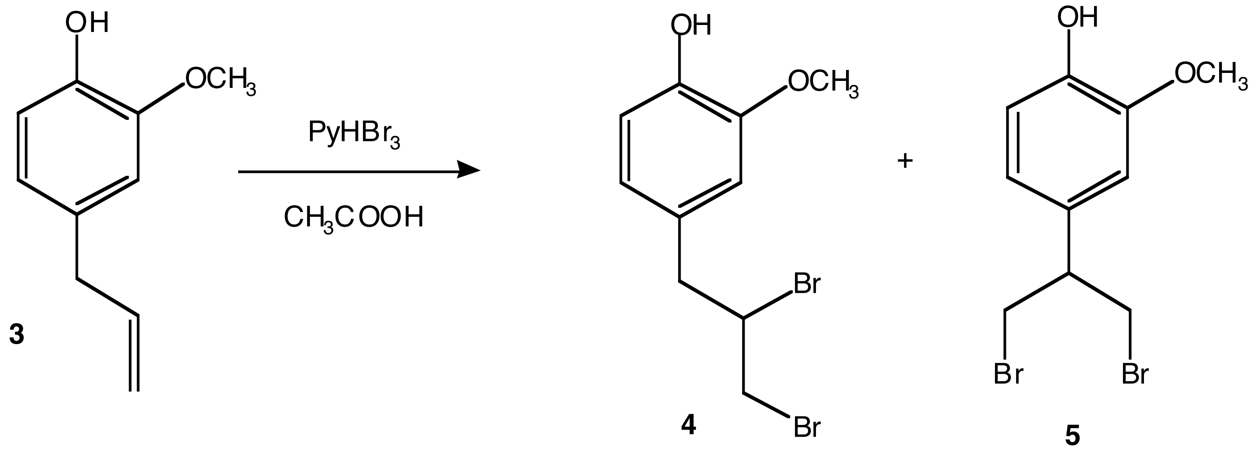
For a 2 point bonus, find a route to the unboxed product from dimethyl carbonate.



3 (21 points). Use the indicated starting materials to build a synthesis of the product, 1,3-cyclopentanedione. You must use the starting molecules, and may add useful reagents as needed. Hint: Think about the order of steps.



4 (18 points). When **3** is treated with $PyHBr_3$ in acetic acid (of course, you recall that this mixture is the source of Br_2 you used in lab!), two dibromides, **4** and **5**, are formed. Write a mechanism that accounts for the formation of both of these products.

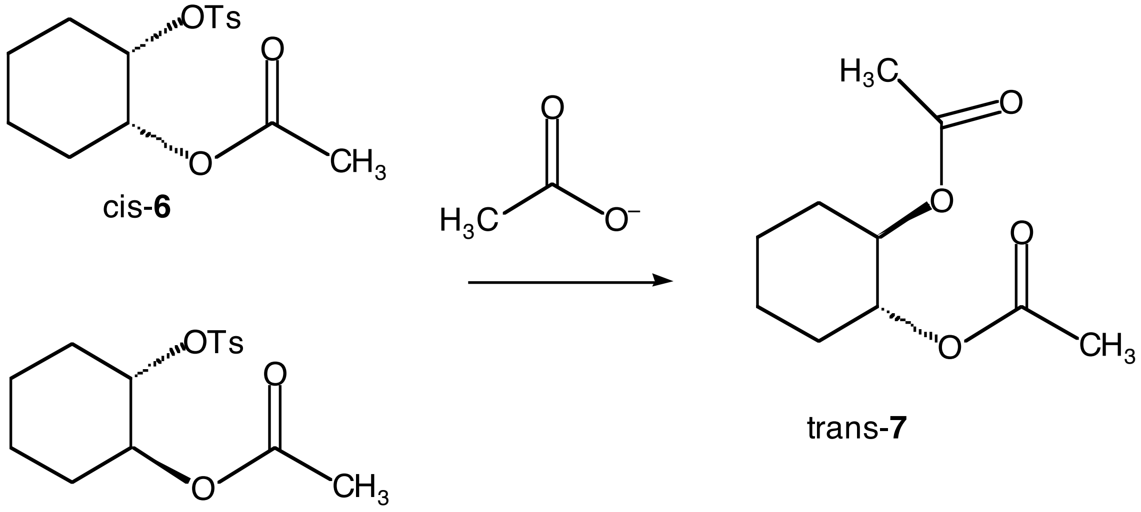


DO ONLY ONE (1) OF THE FOLLOWING TWO (2) QUESTIONS

Each is worth 20 points

5. Both the cis diastereomer, cis-**6** and the trans diastereomer trans-**6** give the trans product trans-**7**, but the details of the reactions are very different.

(a) trans-**6** reacts 670 times faster than cis-**6**.
(b) Product **7** is optically active when formed from optically active cis-**6** but is racemic when formed from optically active trans-**6**.
(c) When the reaction is run in the presence of ethyl alcohol, a new achiral product (**8**) of the formula $C_{10}H_{18}O_3$ can be isolated from the reaction of trans-**6** but not from the reaction of cis-**6**. Compound **8** shows a mere seven signals in its ^{13}C NMR spectrum.



cis-**6**

trans-**7**

trans-**6**

Explain carefully, giving a mechanism for both reactions and a structure for **8**. Please deal explicitly with the questions of rate and optical activity.

6. Years ago, in a large town in Germany, there were four bottles, each of which contained one of the four possible L-aldopentoses, **A**, **B**, **C**, and **D**.

(a) What are the four possibilities? Draw them in Fischer projection.

Two of these isomers, **A** and **B**, give meso diacids when treated with **E**.

(b) which isomers share **A** and **B**, and what is **E**?

Compound **A** gives a meso diacid when treated with 1. $NH_2OH/CH_3O^- Na^+$
2. Ac_2O, heat 3. $CH_3O^- Na^+$, followed by HNO_3.
Compound **B** gives an optically active diacid when treated with 1. $NH_2OH/CH_3O^- Na^+$
2. Ac_2O, heat 3. $CH_3O^- Na^+$, followed by HNO_3.

(c) Write Fischer projections for **A** and **B** - make sure you label them clearly.

Compound **C** gives L-glucose (and L-mannose) when treated under Killiani-Fischer conditions.

(d) Draw a Fischer projection for **C**.

"I pledge that I have not violated the Honour Code on this examination."