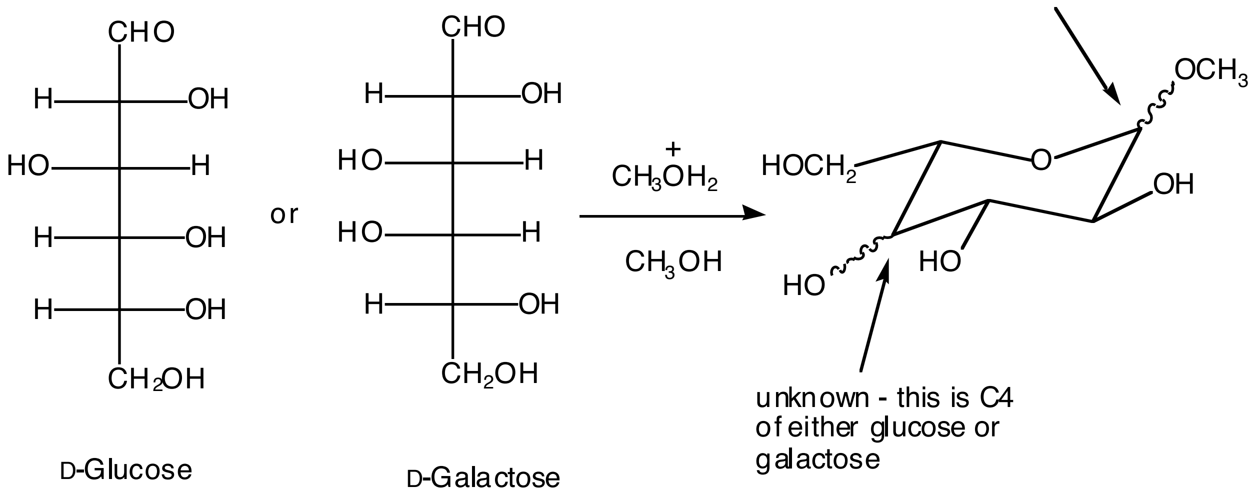
Answers to the Final examination, Chemistry 302X - 2006

1. (a)

unknown - either
α or β

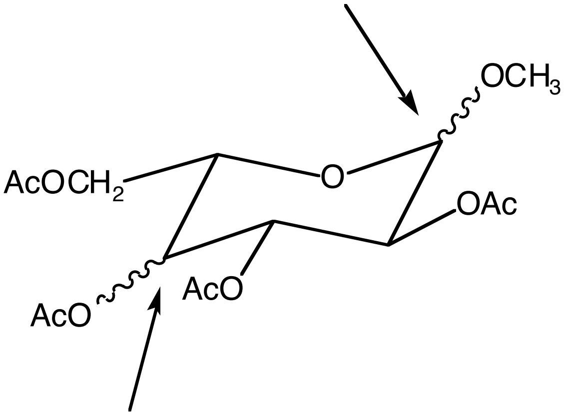


unknown - this is C4
of either glucose or
galactose

(b)

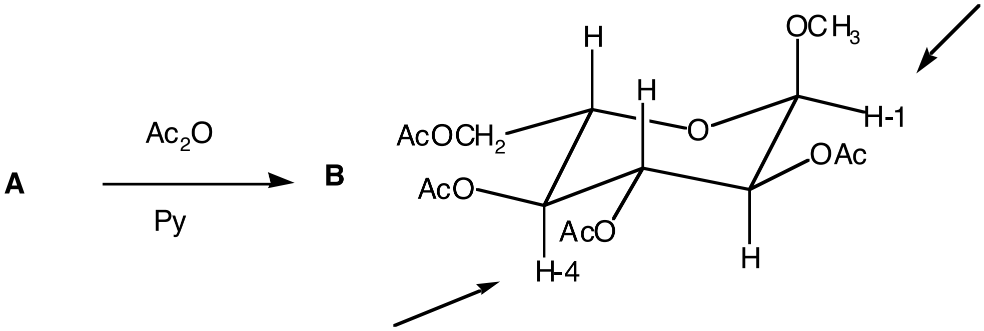
unknown - either
α or β

B



unknown - this is C4
of either glucose or
galactose

(c)



must be equatorial
because of the
small Ax-Eq
coupling --therefore
the OMe is axial,
alpha

must be axial because of
the two large Ax-Ax couplings.
Therefore the OAc on this carbon is equatorial,
and the original sugar must have been glucose

2. a)

Convert butadiene into 1,4-dibromobutane:

1. BH_3 2. $HOOH/HO^-$ 3. HBr

convert acetic acid into ethyl acetate

EtOH/acid cat.

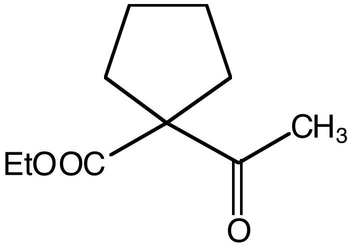
make acetacetic ester through a Claisen condensation of ethyl acetate:

1. full eq. of EtONa 2. pH = 7
(note - you could do the first alkylation with the anion formed before raising the pH to 7)

now alkylate acetoacetic ester twice with 1,4-dibromobutane

1. EtO^- 2. 1,4-dibromobutane (run it twice)

Now you have:



Finally hydrolyze the ester and decarboxylate:

1. H_2O/H_3O^+ 2. heat.

(b)

First add HBr to cyclopentene to give cyclopentyl bromide.

Next make cyclopentyllithium by treating the bromide with Li.

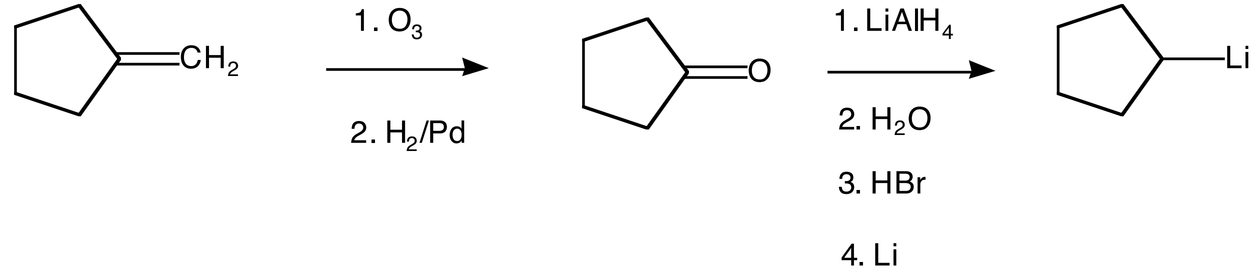
Finally, treat acetic acid with two eq. of cyclopentyllithium, followed by hydrolysis.

(c)

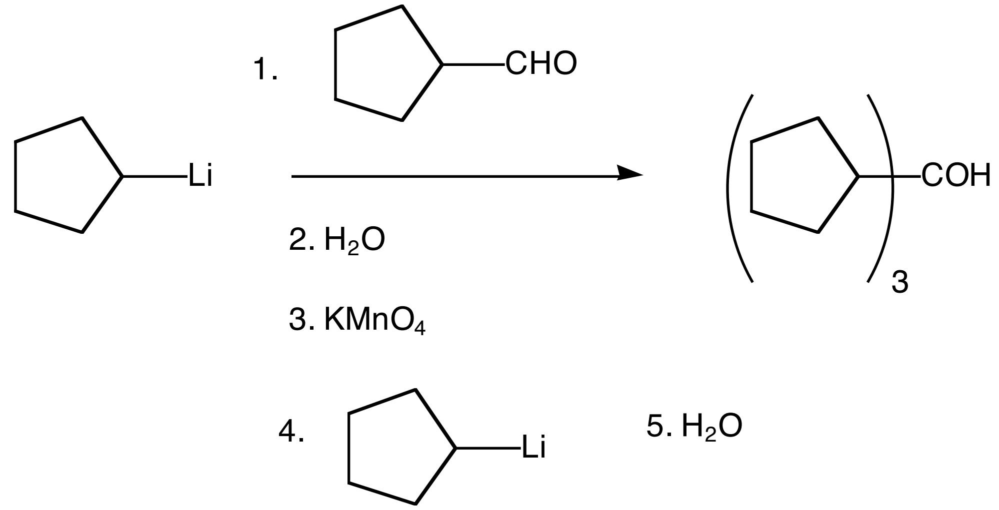
Oxidize the starting alcohol to cyclopentanecarboxaldehyde with CrO_3/pyridine.

Then make the tosylate out of the alcohol with tosyl chloride. Eliminate with $(CH_3)_3C\,O^-$ to give methylenecyclopentane.

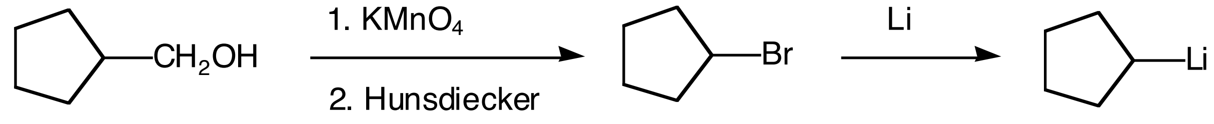
now:



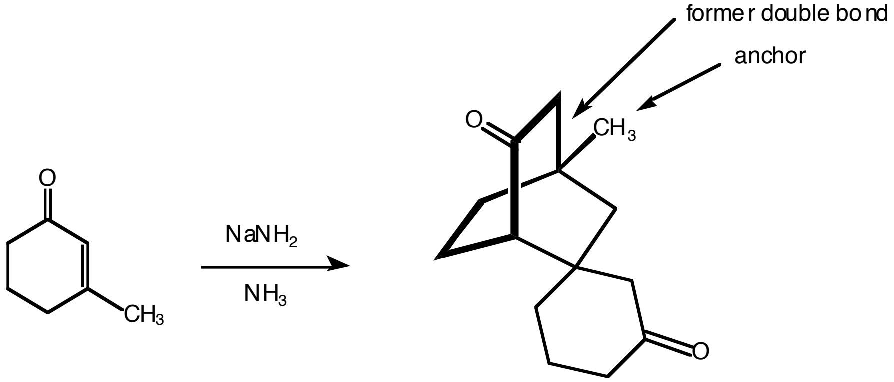
Finally:



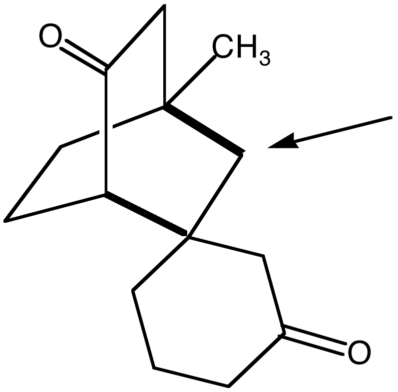
Cyclopentyllithium can be made other ways: here's just one:



3. OK, the problem says “Analyze!” so that’s what we better do. Use the methyl group (mysteriously vanished in one ring) as an anchor. We can identify one residual methyl, and that allows us to fill in one of the reactants and find the location of one of the old double bonds.



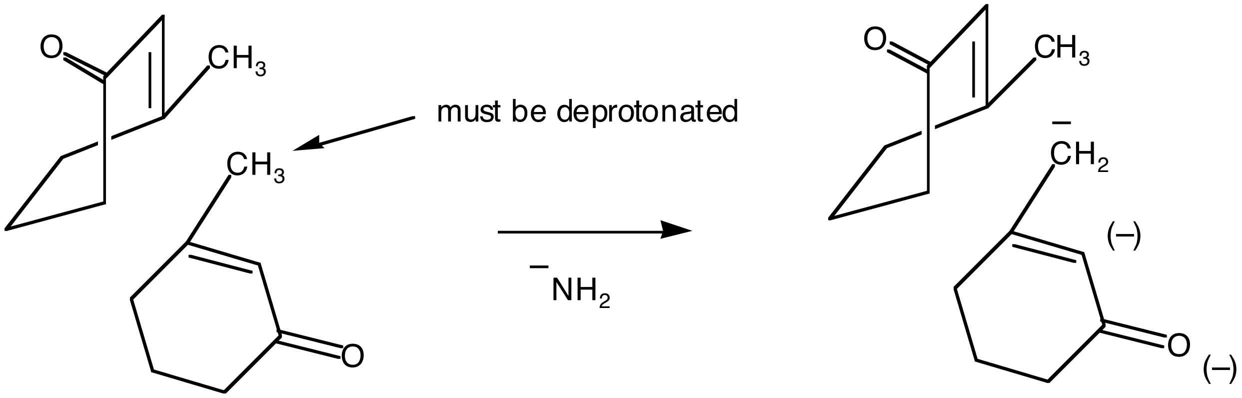
Now we can find the other methyl, and the new bonds that must be made in this reaction. It sure looks like Michael chemistry.



what's left of the other methyl group

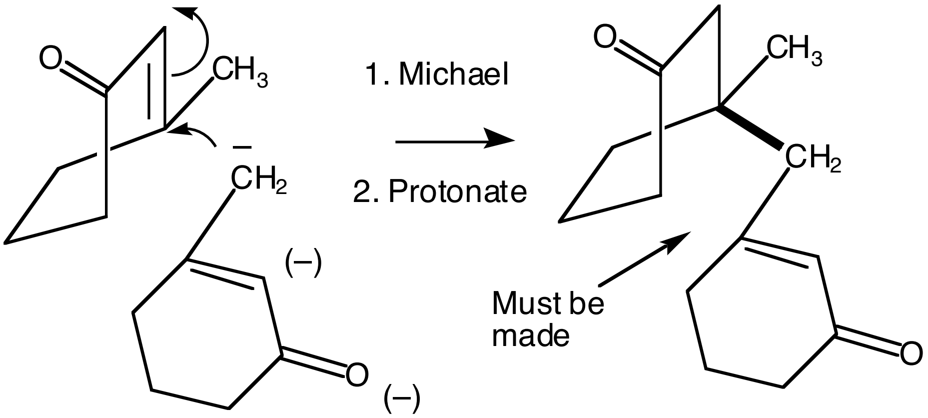
bonds to be made in bold.

If we now line up the two pieces, we can see what must be done, and therefore, how it must be done. One methyl group must be deprotonated to give an anion that does the first Michael:

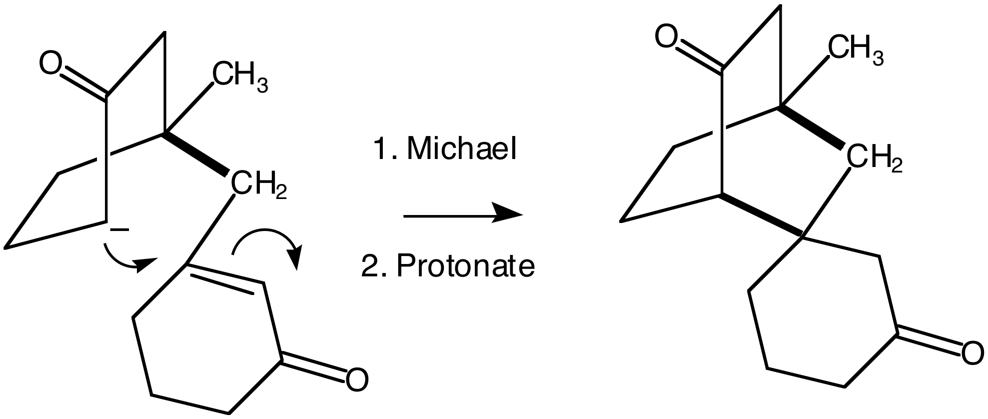


note nice resonance stabilization!

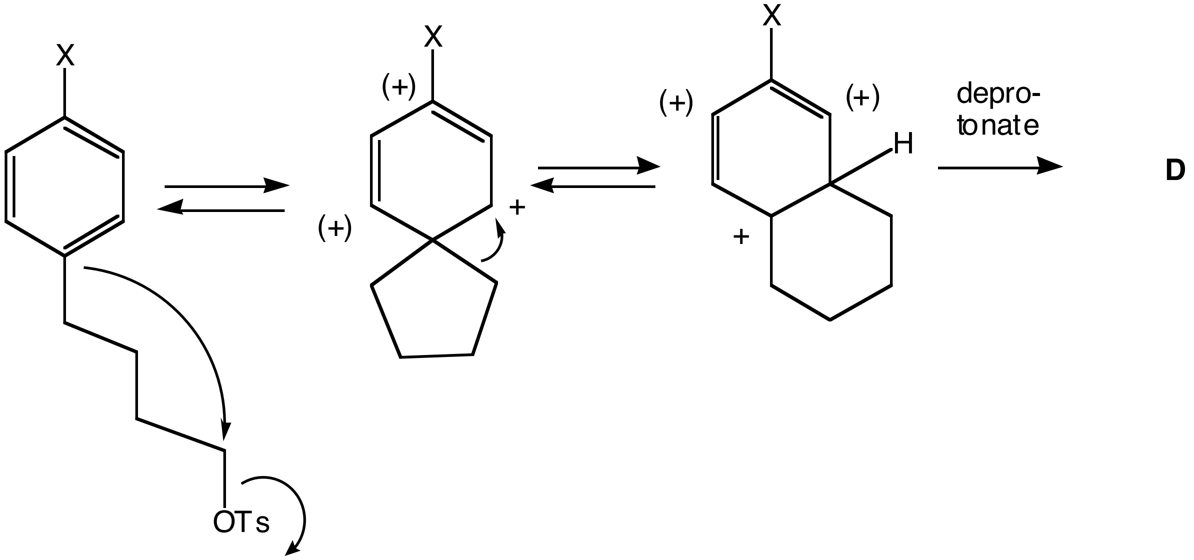
Here’s the first Michael:



Now we can clearly see where the next bond must be constructed - Michael chemistry does the trick again. It’s actually easy when done this way.

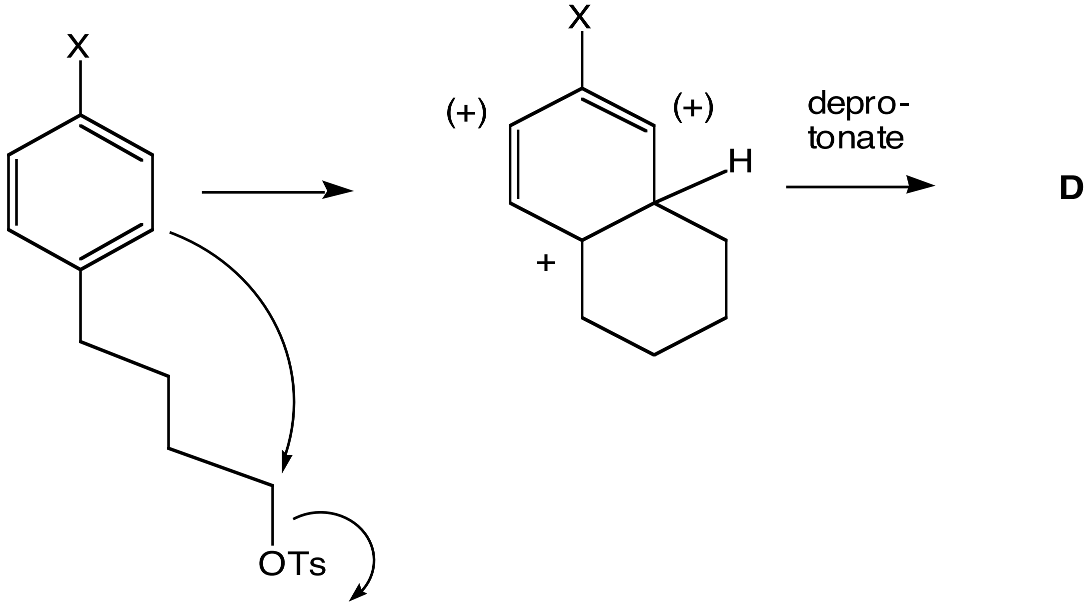


4. Here is one mechanism in which the phenyl group participates to give a five-membered ring. Note that when X = methyl it stabilizes this intermediate, but when X - nitro it destabilizes it, exactly as happens in aromatic substitution (which this reaction is).



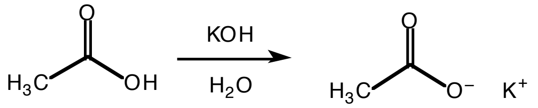
Ring expansion is followed by deprotonation and re-aromatization.

Alternatively, we could form the six-membered ring directly through participation through the ortho position (aromatic substitution meta to X). When X = nitro this route will be favored for all the reasons that nitro aromatics substitute meta, not ortho/para.

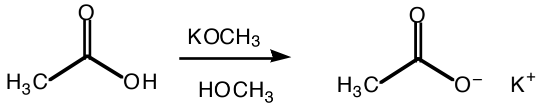


5.

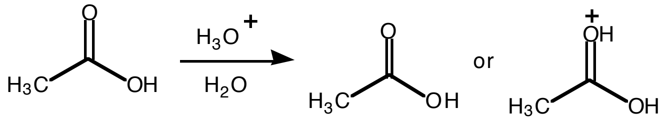
(a)



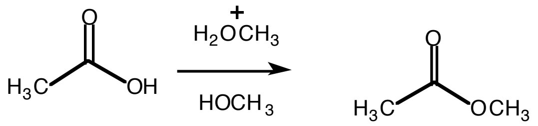
(b)



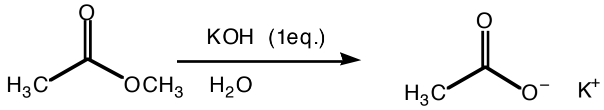
(c)



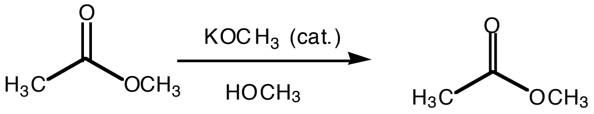
(d)



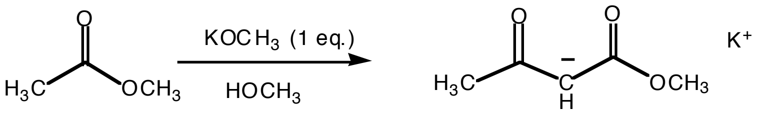
(e)



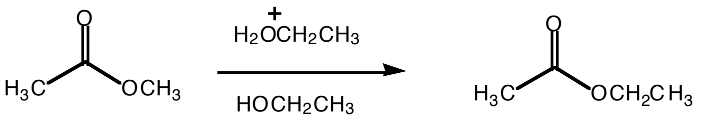
(f)



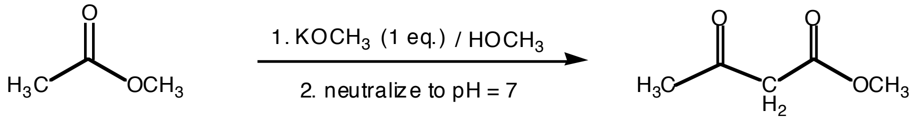
(g)



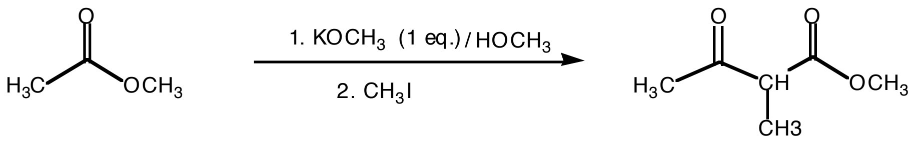
(h)



(i)

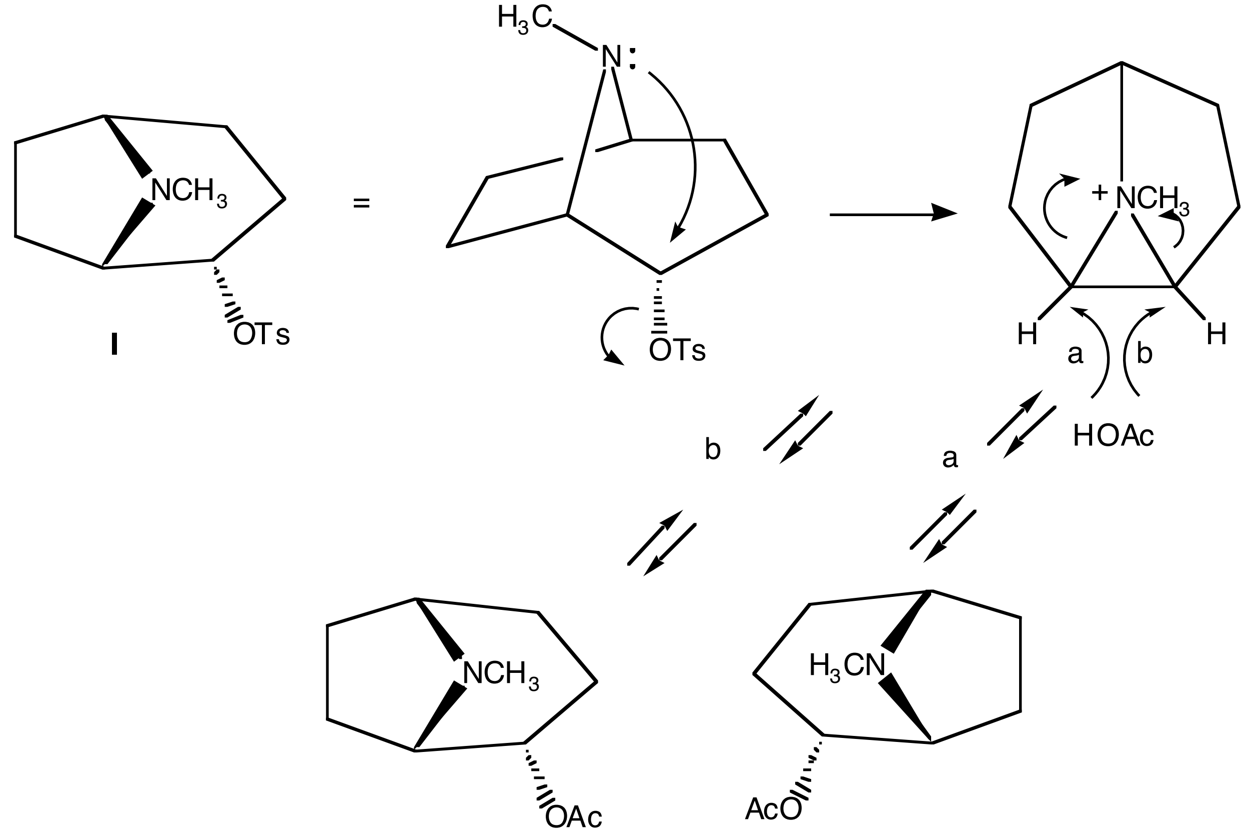


(j)



6. (a) The reaction begins with an intramolecular S_N2 displacement of tosylate by the nitrogen. That displacement is impossible for **J**, as it would be a front-side S_N2 reaction. Thus, **I** reacts faster than **J**.

The intermediate formed is achiral, so it must open to give racemic product. The two enantiomers are formed through equivalent pathways a and b. This second S_N2 reaction also goes with inversion, so the overall result is retention.

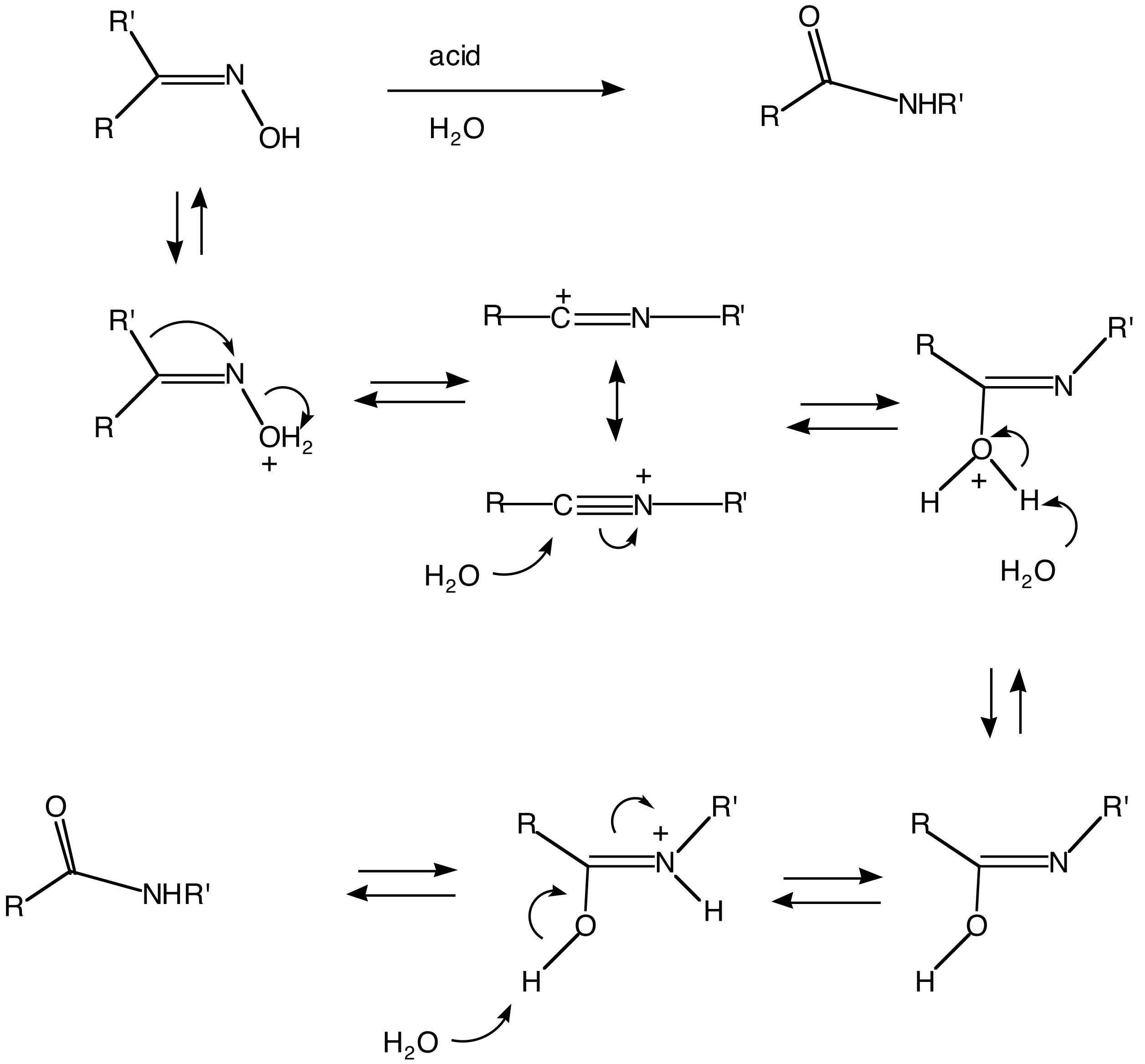


6. (b)

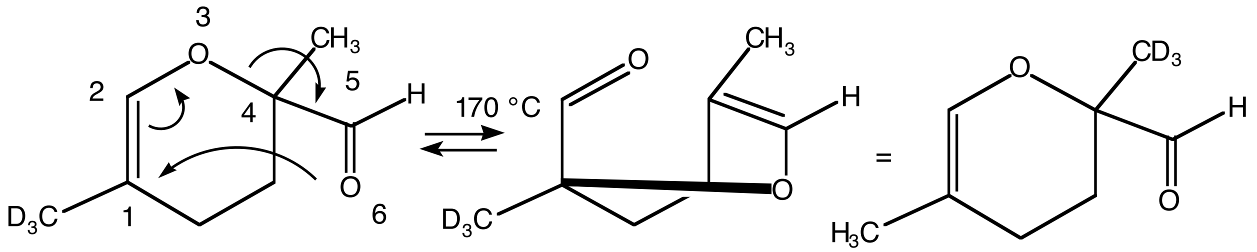
Observation 1: Yes it is.

Observation 2: No it isn’t. There is no reason that R can’t also migrate in this mechanism.

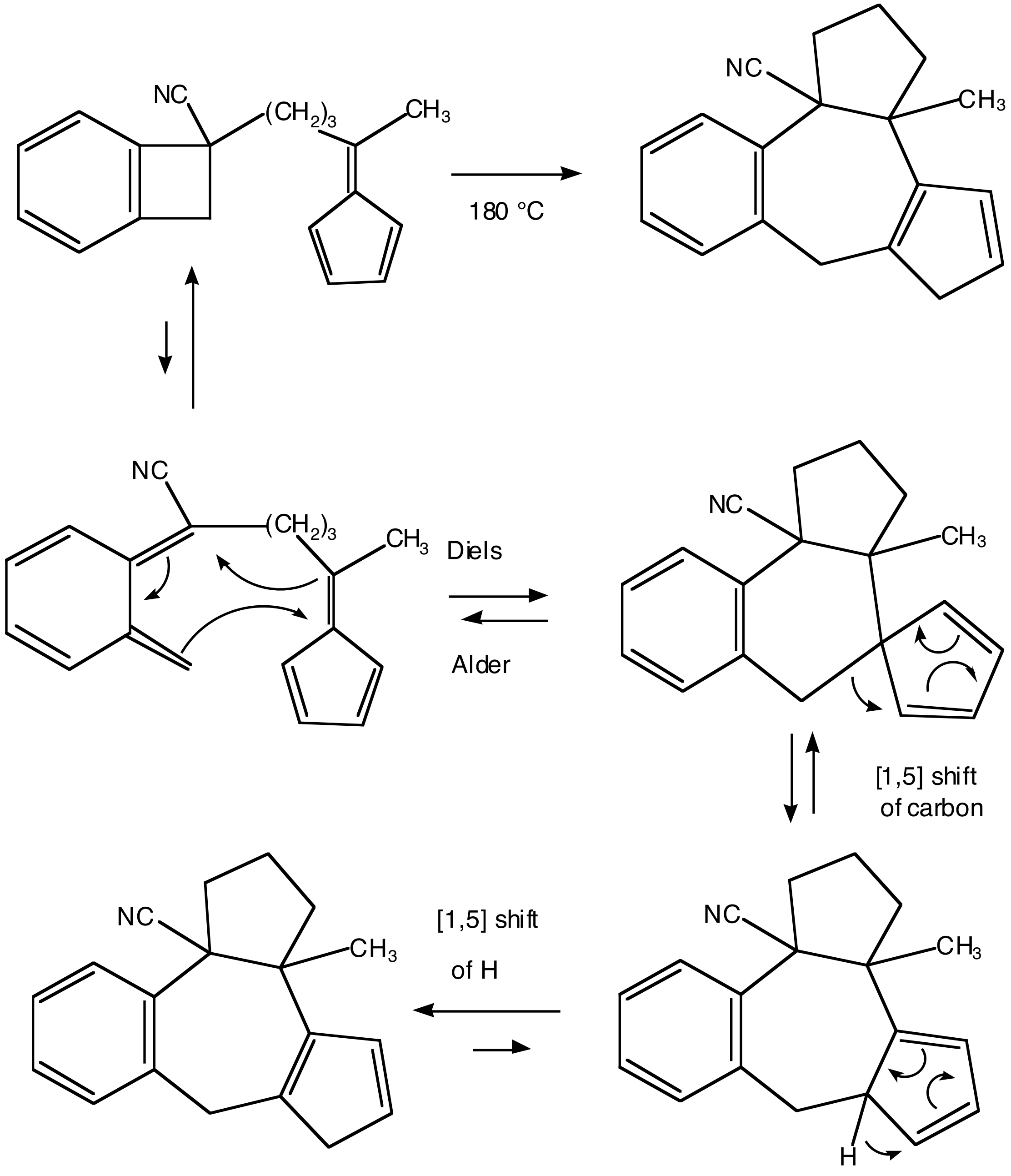
The real mechanism involves an intramolecular S_N2 reaction in which the migrating anti group, here R’, displaces the leaving group.



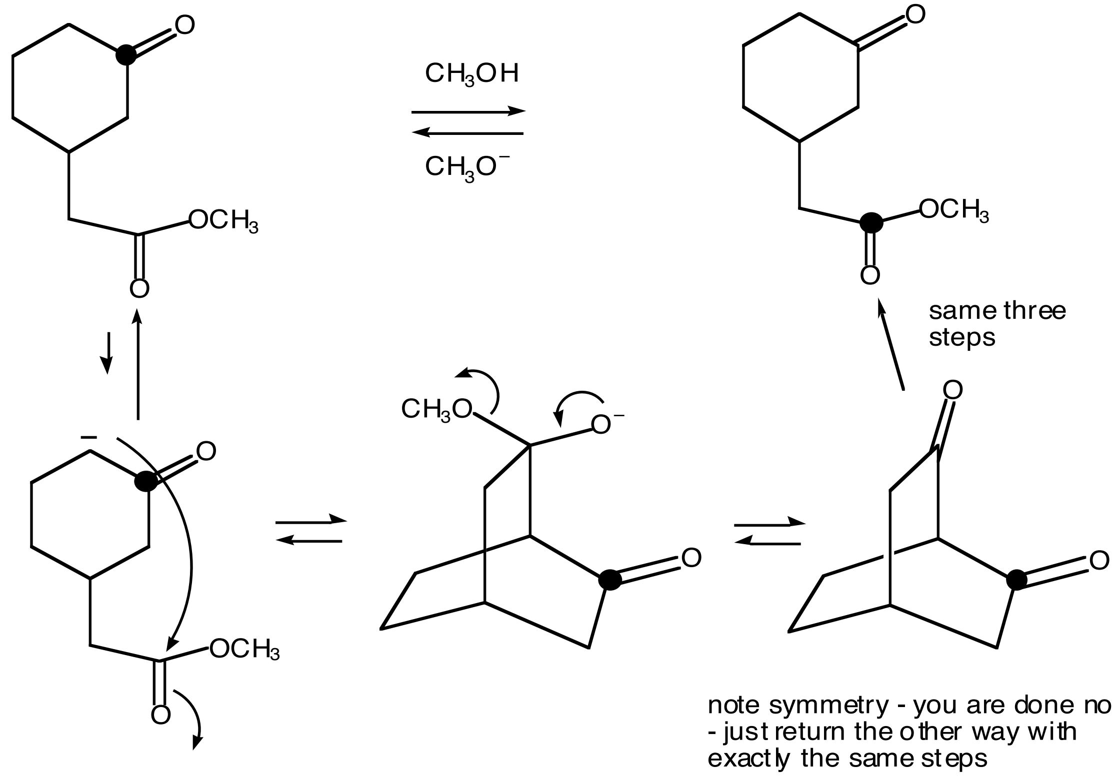
7. (a). It is just a Cope-like rearrangement. Make 1-6, break 3-4.



(b)



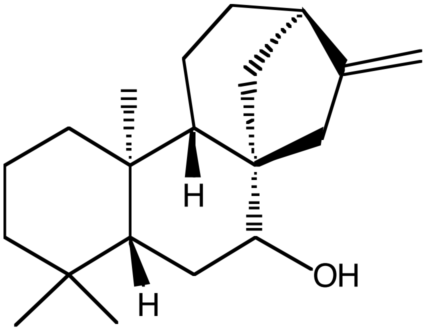
8b. This problem must be a “symmetrize” problem - there is no way for that label to move otherwise. The ring carbonyl must become the ester carbonyl and vice versa. It’s addition-elimination, no big deal:



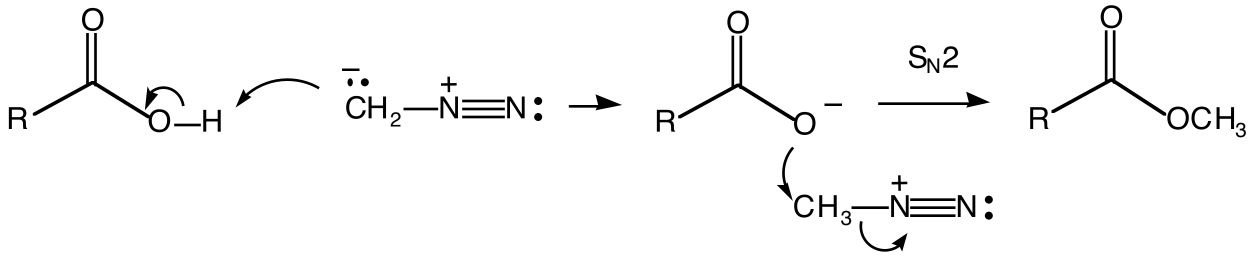
same three steps

note symmetry - you are done now
- just return the other way with
exactly the same steps

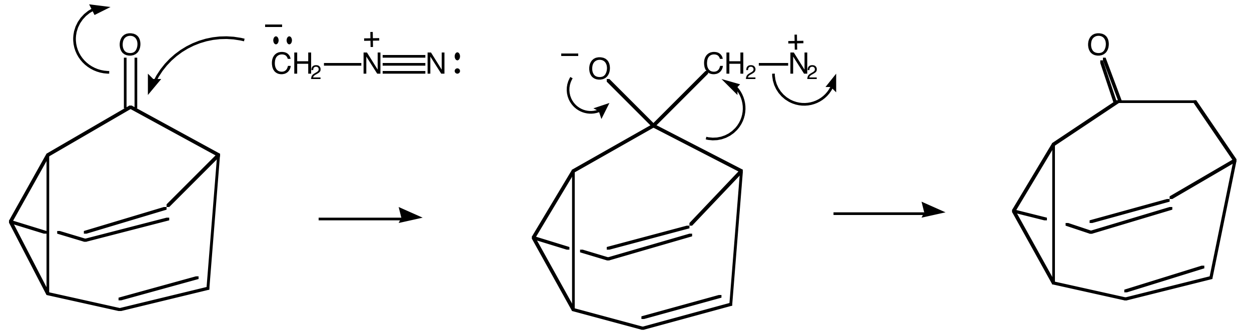
8a. By the way, Here’s Kaurene:



9. (a) Acids are called acids because they are acidic. So, the first step is deprotonation. An S_N2 reaction follows:



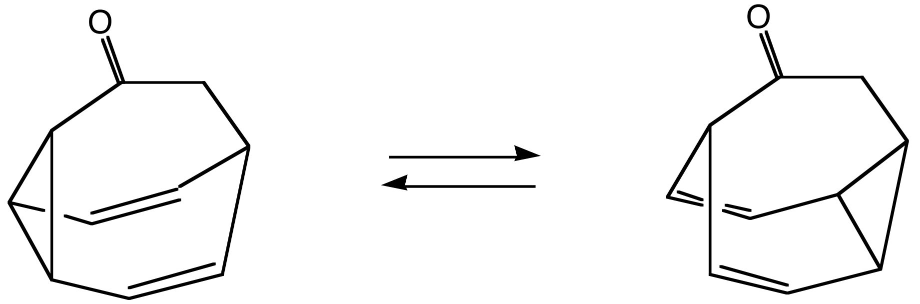
(b) Diazomethane is not only a Brönsted base, as in part (a), but a Lewis base as well. So, it adds to the carbonyl group. Ring expansion with loss of nitrogen gives the product.



F

G

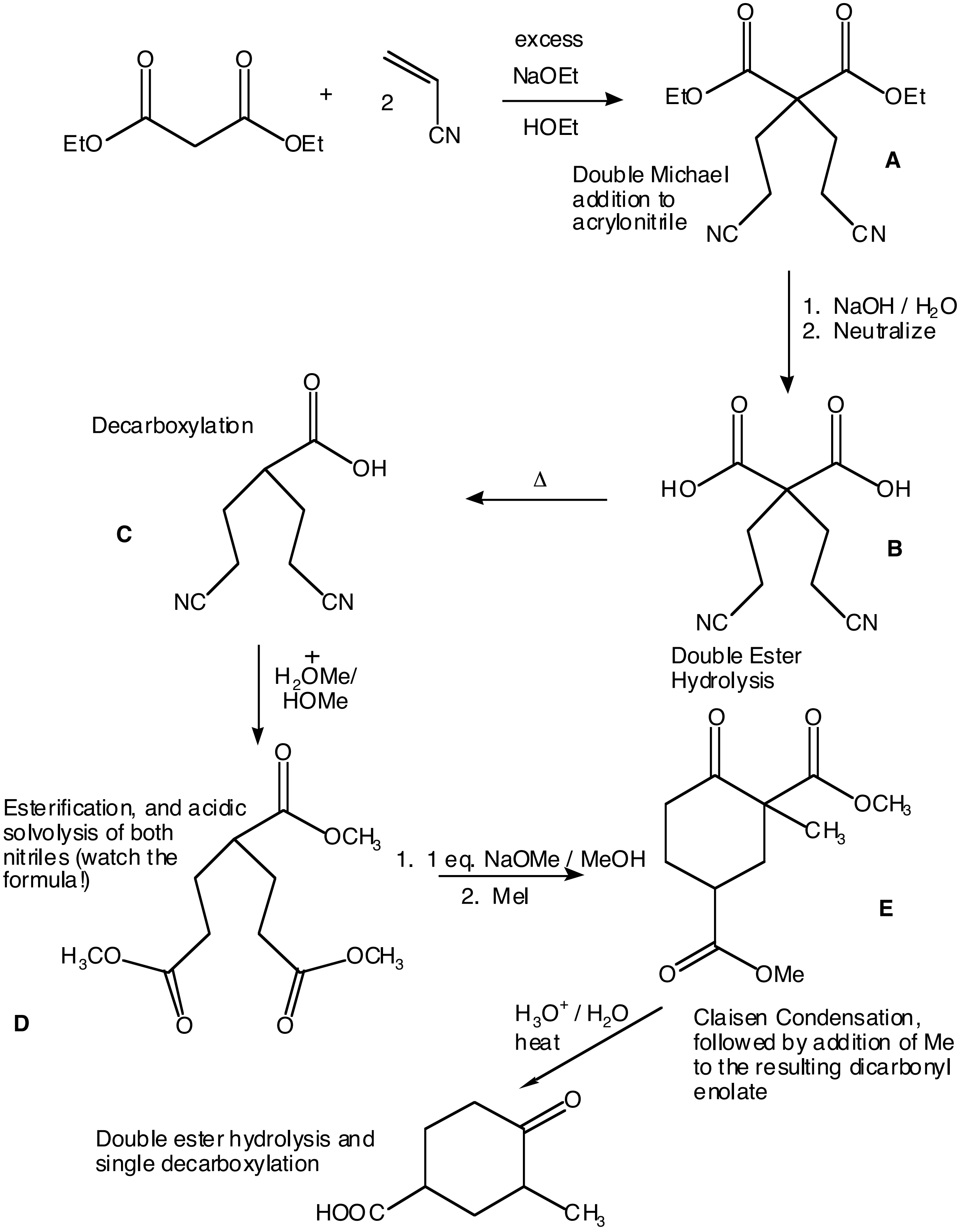
(c) The Cope rearrangement equilibrates the two! Whatever you get, you get from either ring expansion.



F

H

10.



Double Michael addition to acrylonitrile

Double Ester Hydrolysis

Decarboxylation

Esterification, and acidic solvolysis of both nitriles (watch the formula!)

Claisen Condensation, followed by addition of Me to the resulting dicarbonyl enolate

Double ester hydrolysis and single decarboxylation