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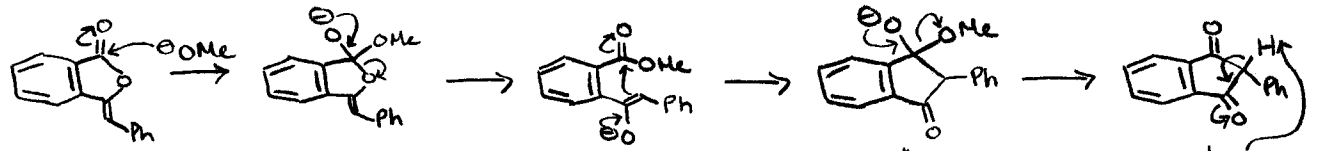
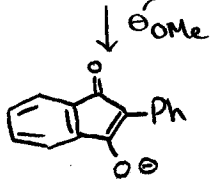
Problem Set 8 Solutions

1a)





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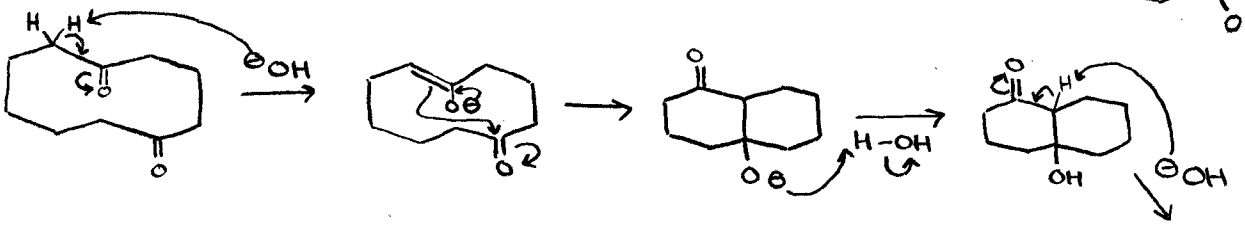
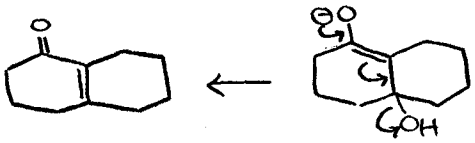
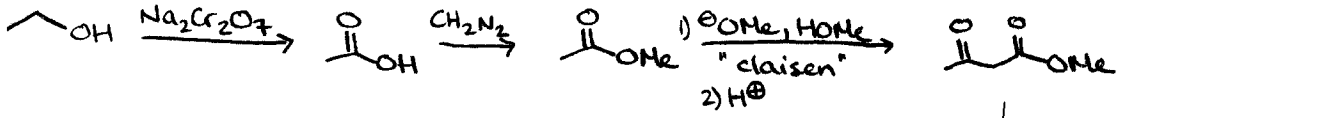
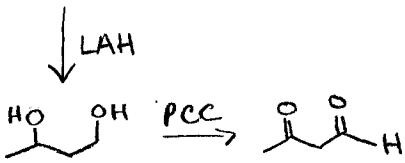


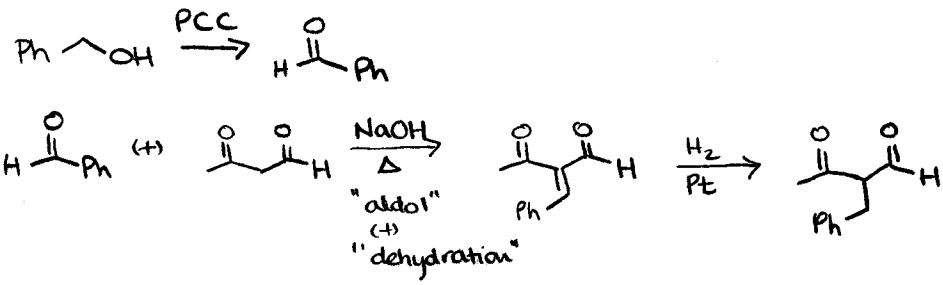
" aldol "
(+)
" dehydration "



2a)







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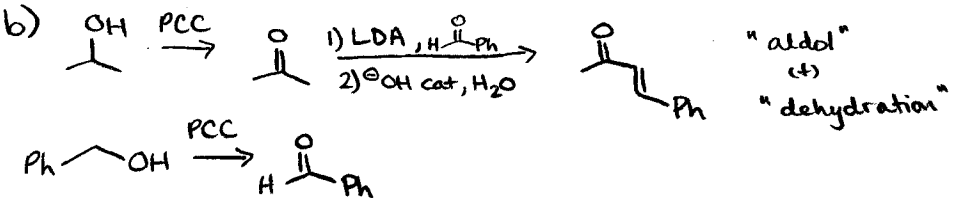
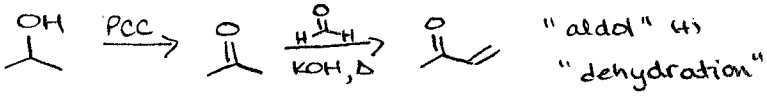
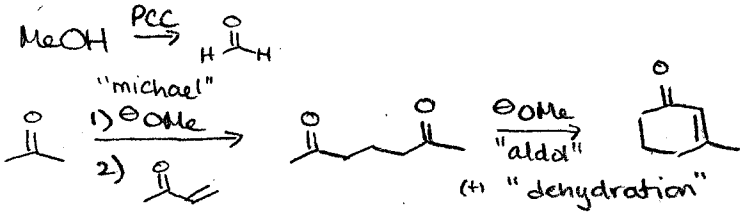


c)





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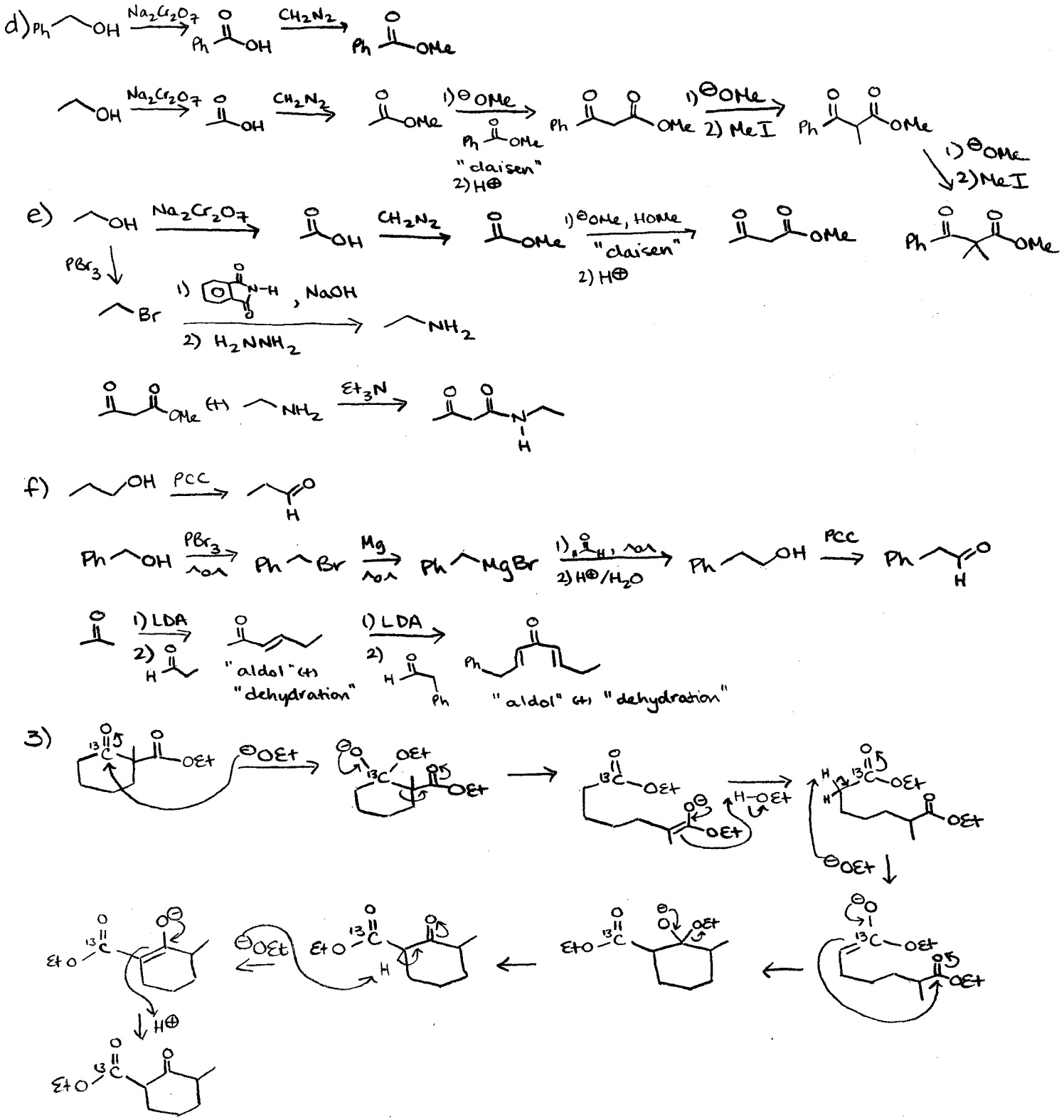

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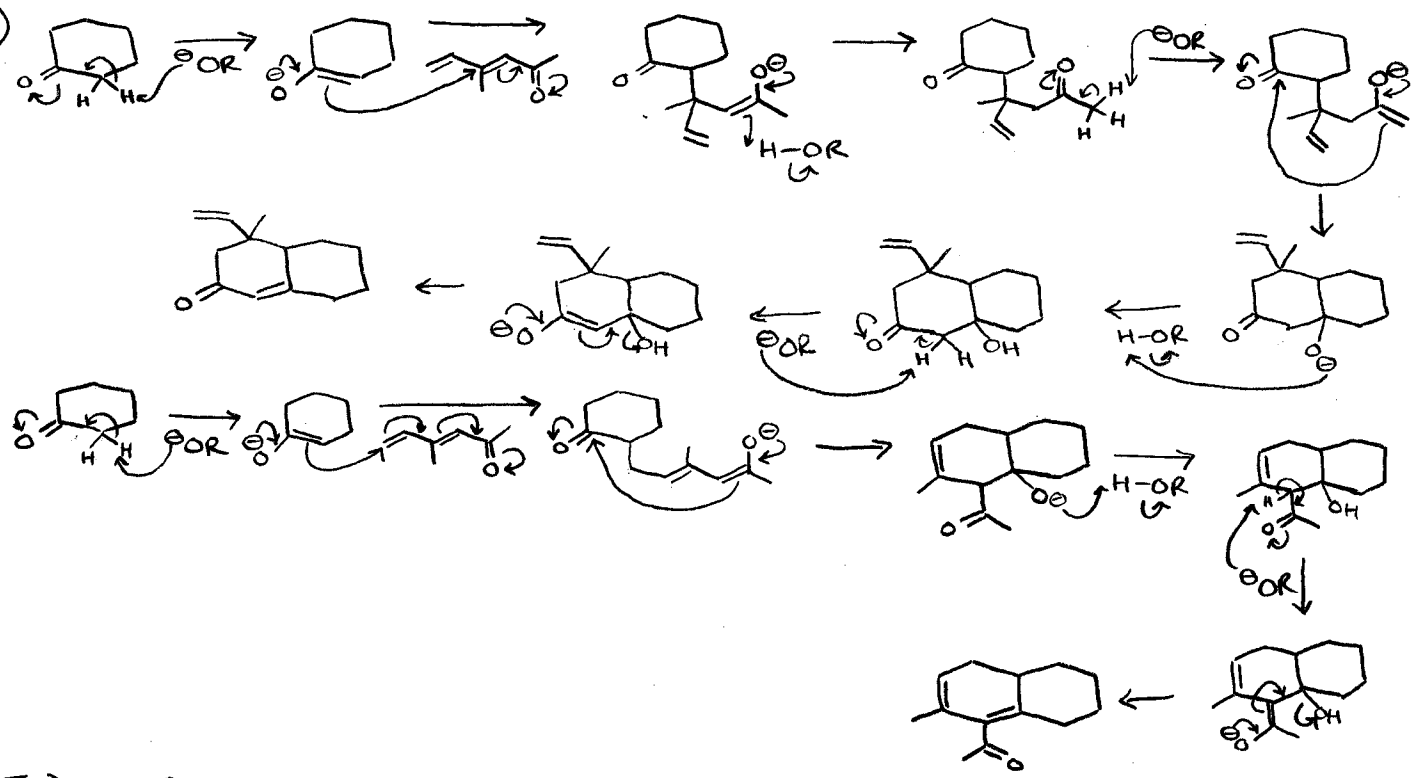
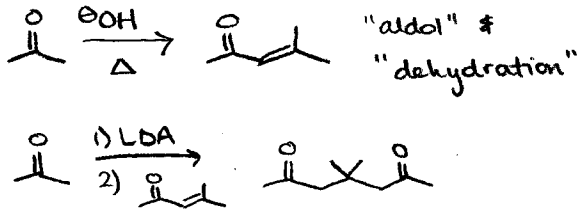
4)



5a)



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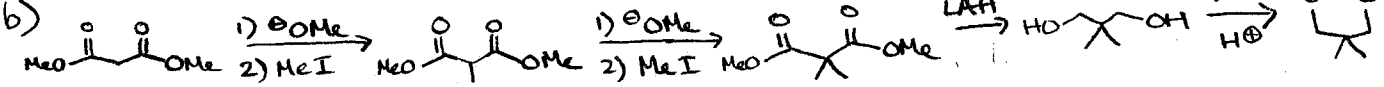

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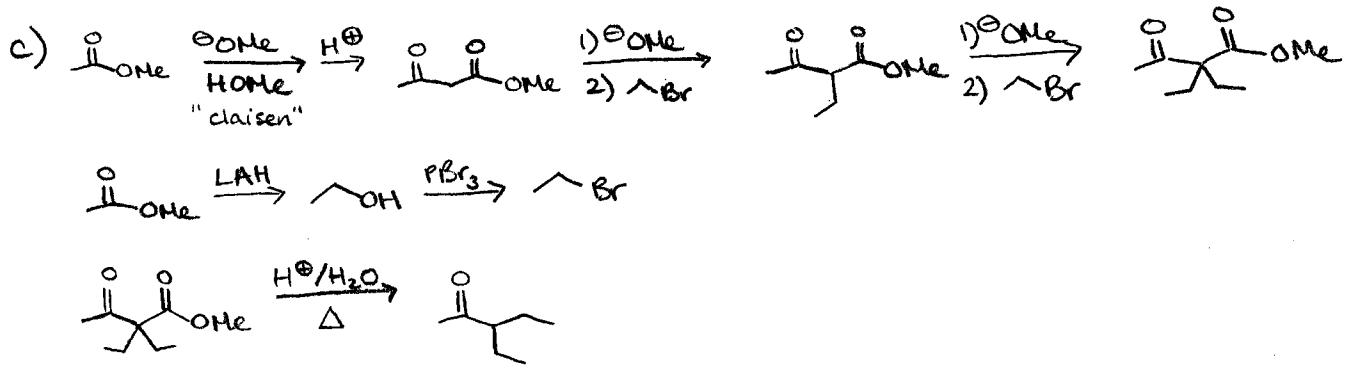
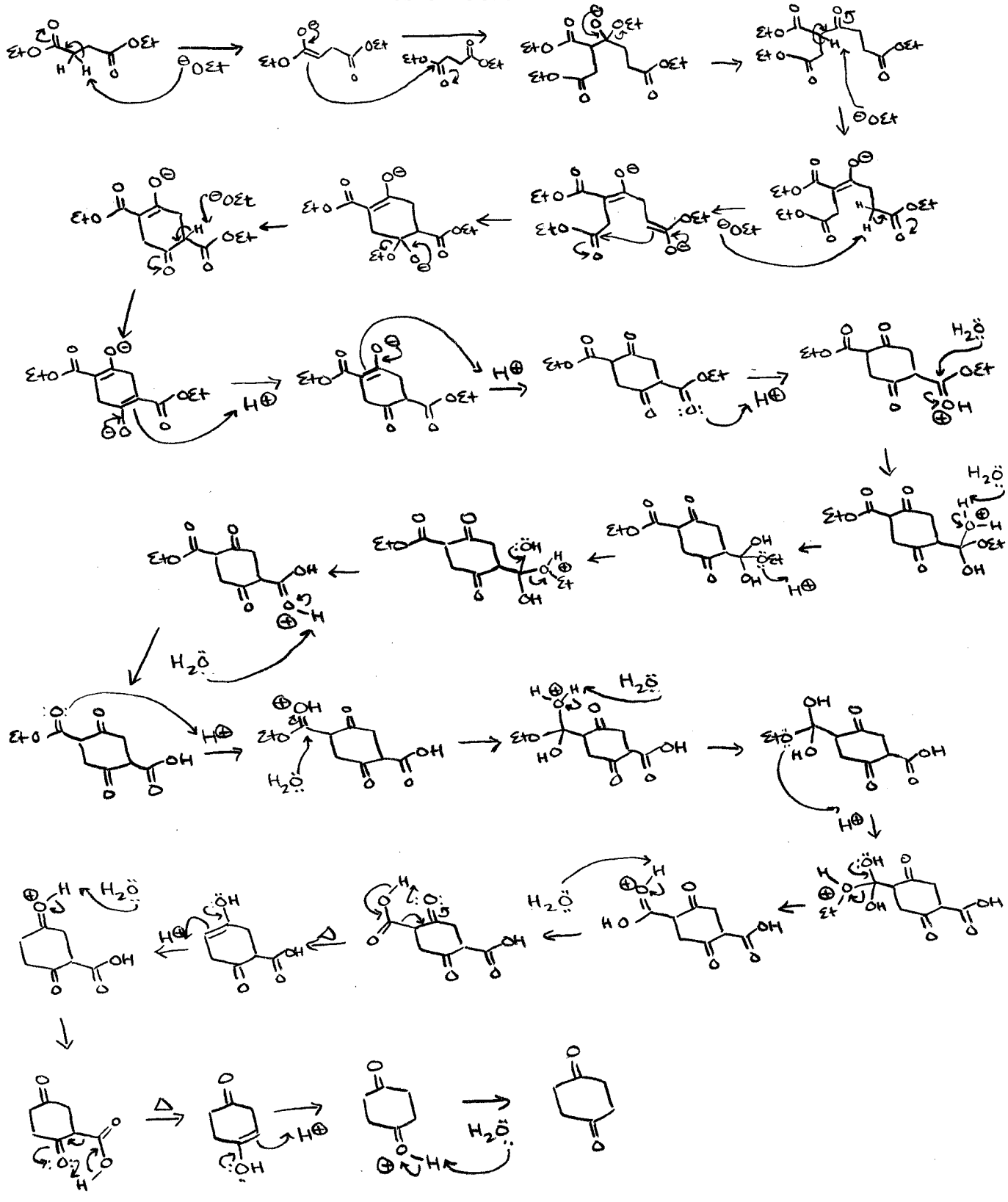


Problem Set 8 Solutions

(6)



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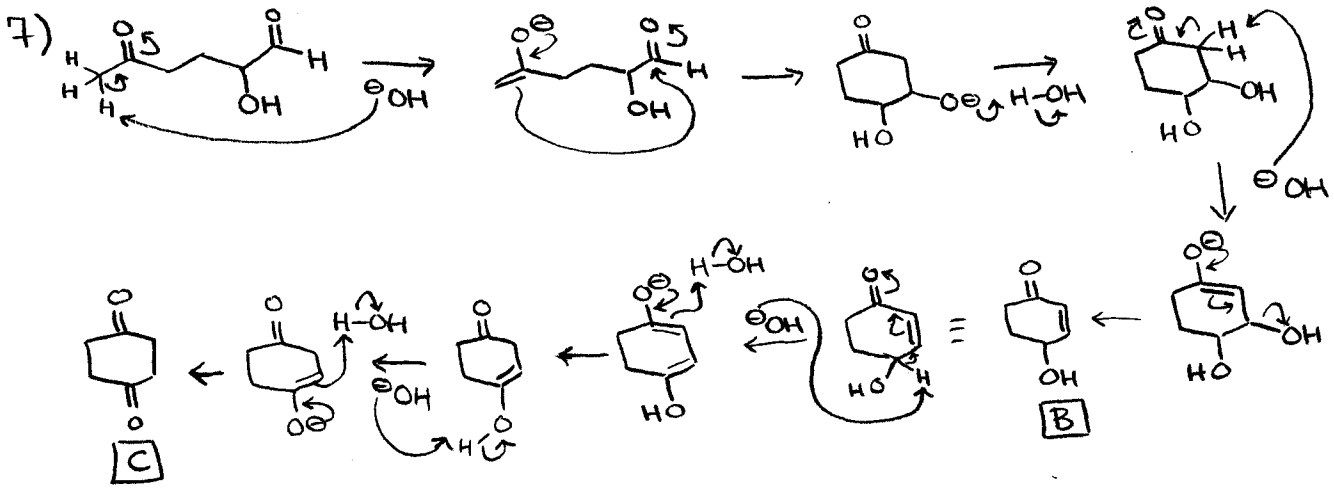
7)



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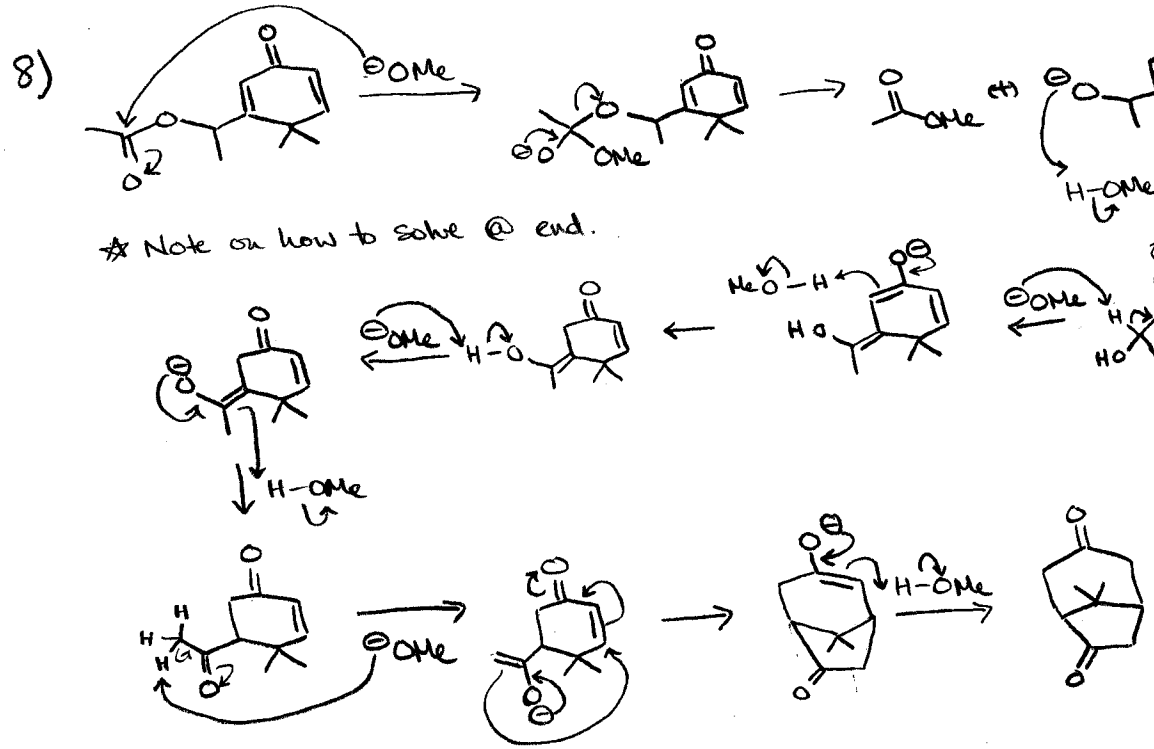
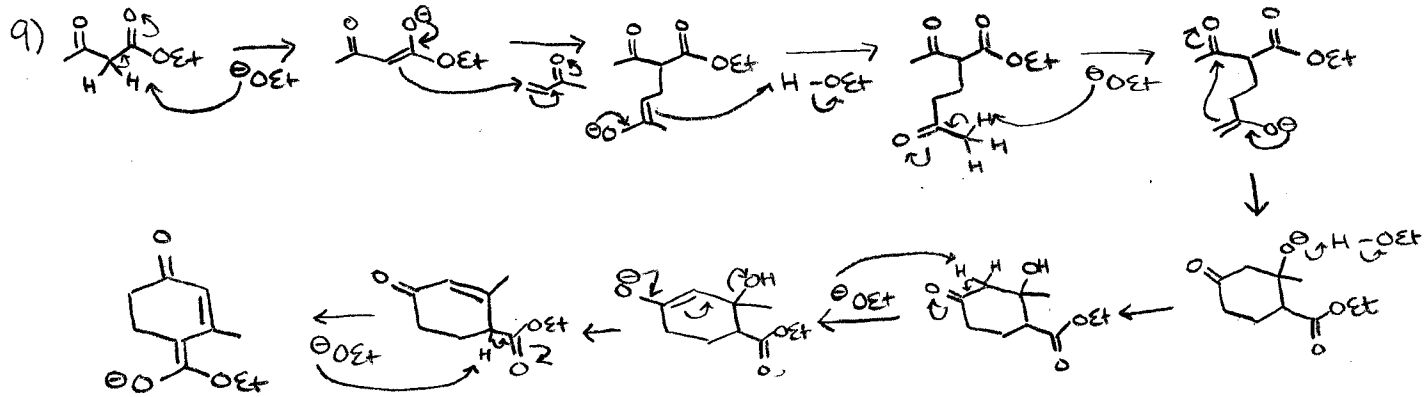


* Note on how to solve @ end.

9)



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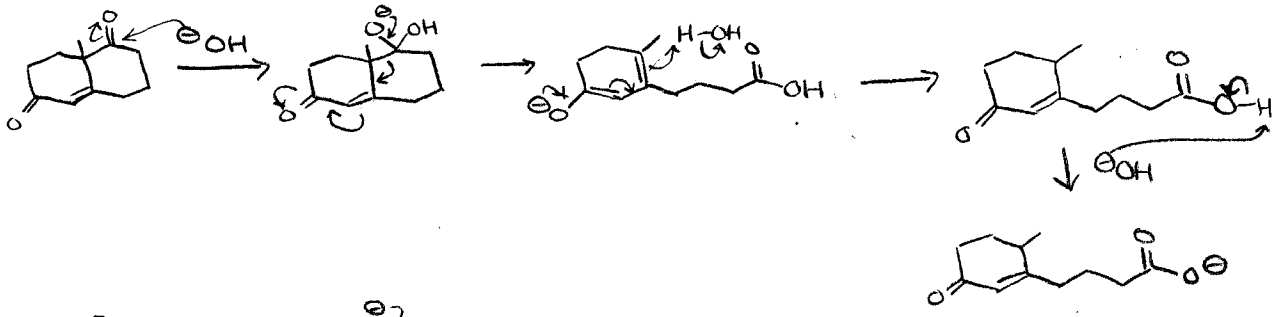
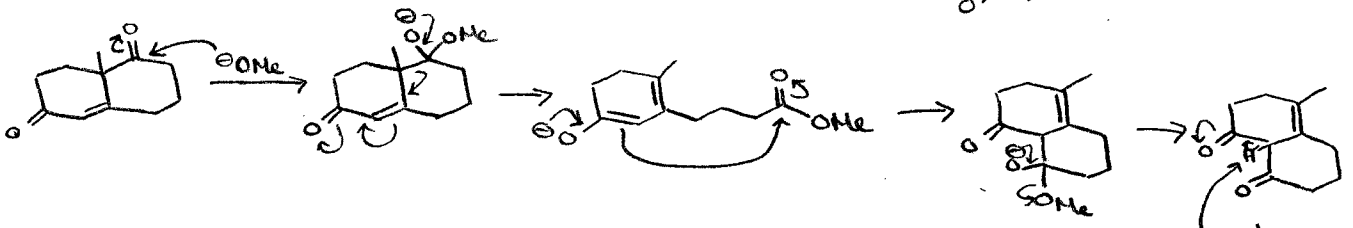
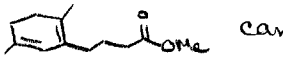
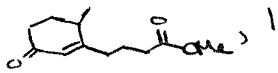
10a)

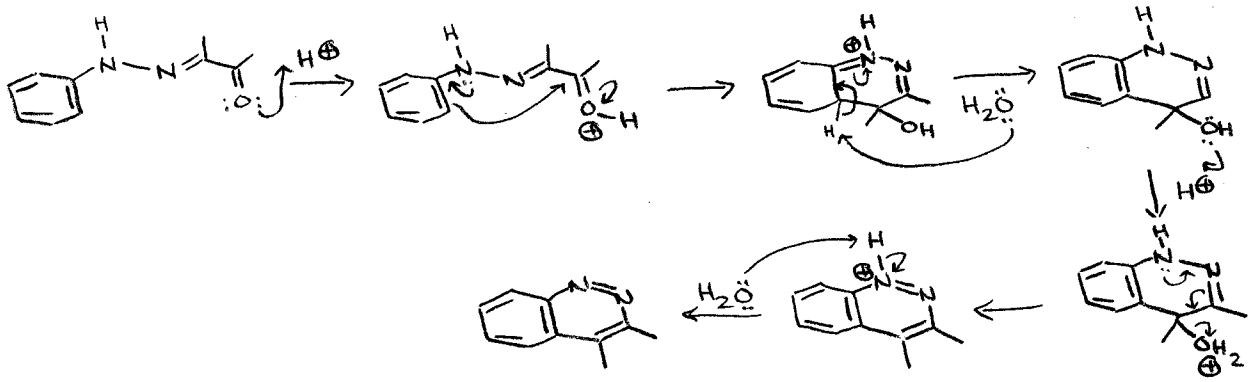


b)



c) in (a), the final deprotonation step is highly favorable since the carboxylate is resonance stablized. in (b), this deprotonation is not possible because an -OMe (instead of -OH) is attached. while  can collapse down to  , like (a), the claisen rxn can also occur since there is still $\ominus$OMe around. For (a), the claisen can not occur because the carboxylate is not an electrophile, unlike the ester.

11)



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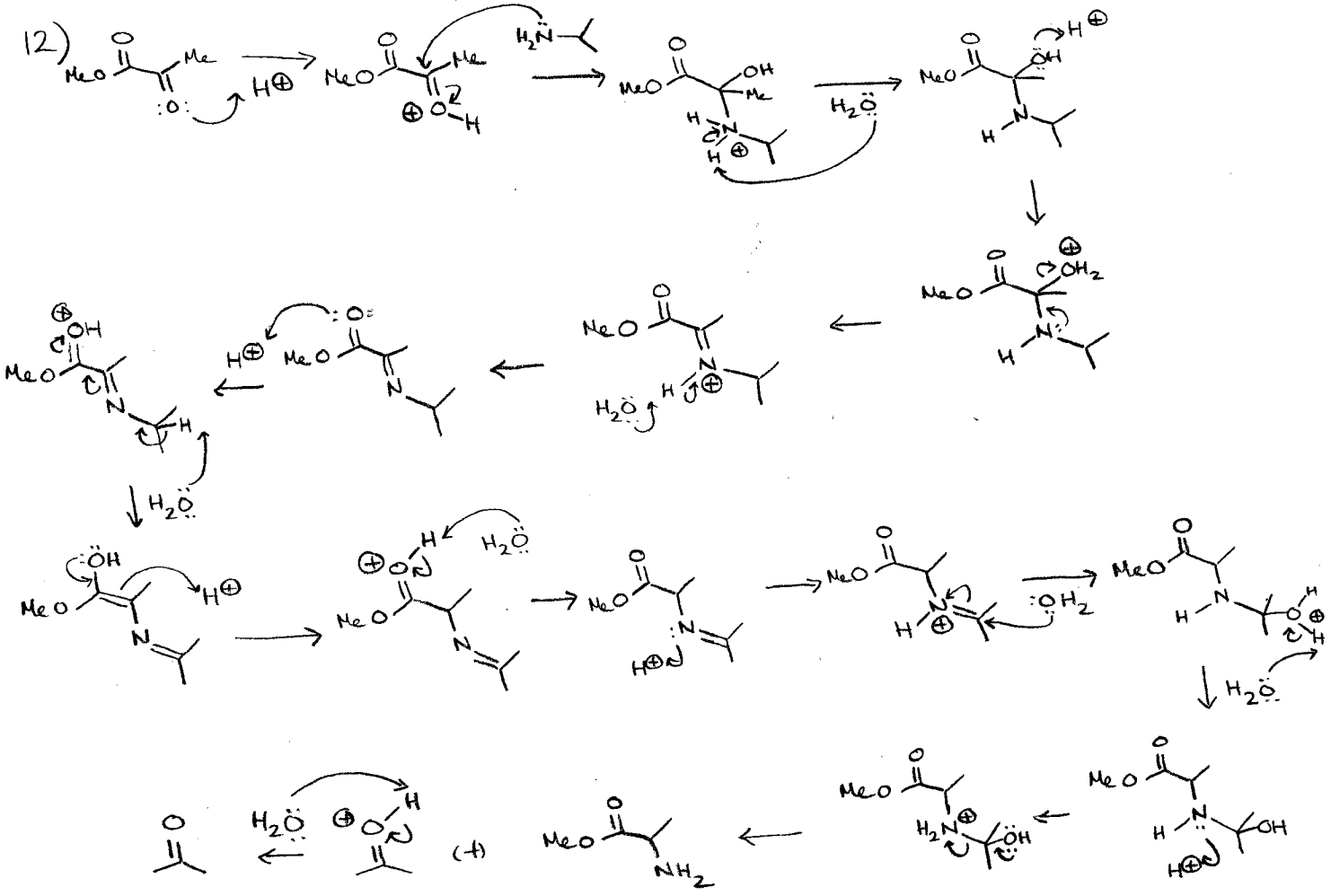
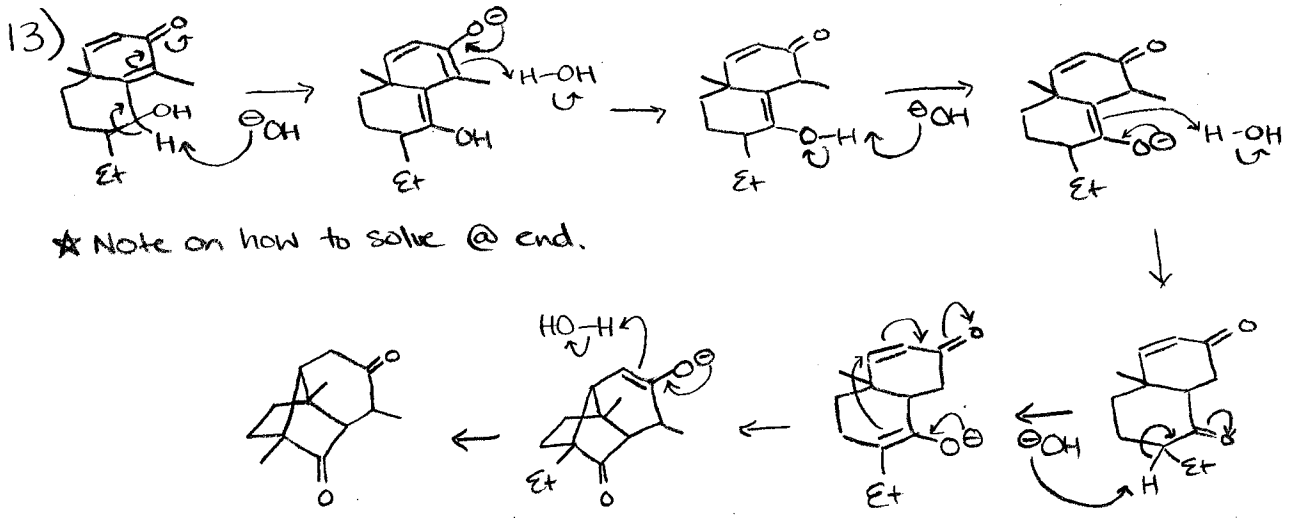
12)



13)



★ Note on how to solve @ end.

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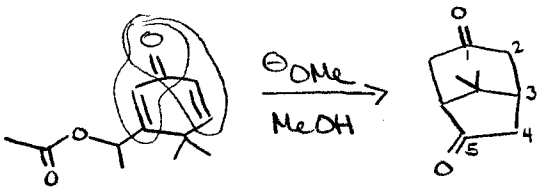
Problem Set 8 Solutions

Note on how to solve #8



Step #1 : look @ product to determine if possibly from aldol, claisen or michael.

→ Since dicarbonyl 1,5 related should be michael

→ michael works by putting an enol & an α,β-unsaturated carbonyl together (enol comes from carbonyl w/ an α-H)

Step #2 : look @ S.M. to try to get pieces for michael

→ contains α,β unsaturated carbonyl (circled above)

Step #3: correlate carbons in S.M. & products

→ C1-6 in S.M. probably same as C1-6 in product 'cus already in ring & C4 has 2 methyls attached in both.

∴ want to use α,β unsaturated carbonyl on right side of S.M

Step #4 : look for ways to connect. & disconnect

→ connect carbons 8 + 5 using michael

∴ C8 has the enolizable H for the enol component.

BUT need carbonyl (have ≠OR)

→ notice C9 & 10 not in product. disconnect by acyl transfer

Step #5 : can make carbonyl from enol

can make enol by deprotonation of H on C w/ ≠OR

this H is conjugated to π system of other carbonyl so acidic

→ after deprotonation can get 2 carbonyls from the 2 enols/enolates made.

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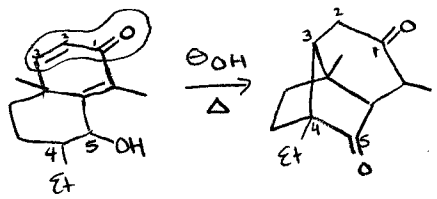
Note on how to solve #10



Step #1: from problem, know we want to do a michael

∴ need 

Step #2: find the 1,5 connection*

- in forward michael, C2 & 3 have dlb & bond btwn C3 & 4 made

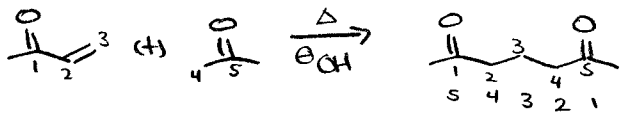
∴ want to use α,β unsat. carbonyl that is circled above

(can also arrive @ by correlating carbons btwn S.M & product)

Step #3: need to make carbonyl @ C5

Similar idea as step #5 from notes on how to solve #8

* michael #'ing of C.



~ can be #'ed left to right or right to left

~ in above, product has 2 -6-mem rings which are also present in S.M. ∴ should try not to break rings if possible (not always the case but work for this problem)