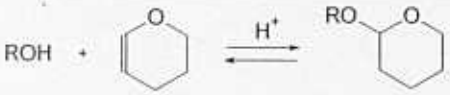
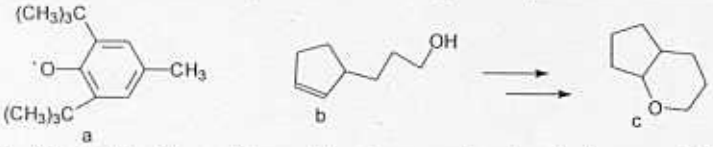
Problem Set 4 Chem 232

1. The protection of alcohols as ethers is often accomplished by generating oxane derivatives as shown below. Propose a mechanism for this reaction.

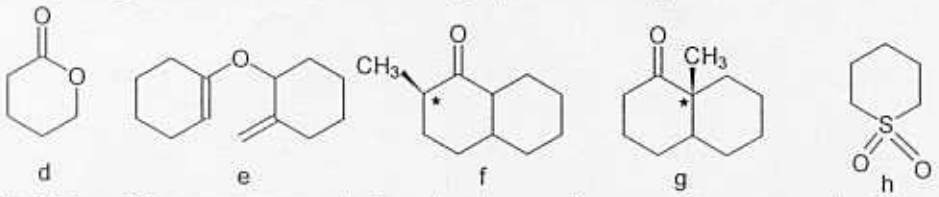


2. BHT (see text book or slides) is a common food additive. It works by removing free radicals and gets converted into the very stable radical a in the process. Discuss why a is exceptionally stable!



3. Alcohol b is transformed to ether c when treated sequentially with mercury(II)acetate, then sodium borohydride. This process is called alkoxymercuration. Propose a mechanism!

4. Propose a mechanism and show the product(s) for the reaction of the ester d below with two moles of methylmagnesium bromide, followed by aqueous workup.

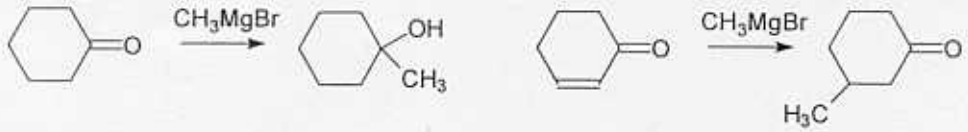


5. Claisen-like rearrangements do not only occur in aromatic compounds. Show a mechanism for the rearrangement of ether e, which results in the formation of a ketone.

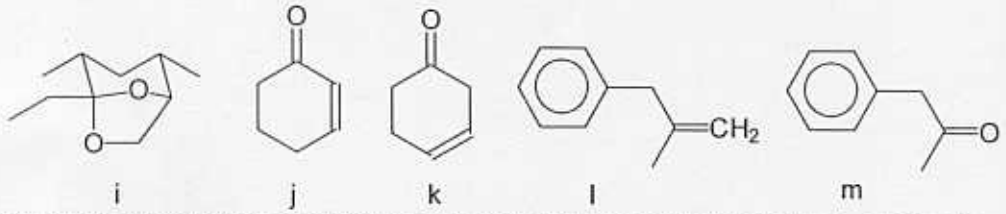
6. Both enantionmers of ketone f racemize readily while those of ketone g do not. Explain!

7. The common solvent sulfolane h can be manufactured from 1,5-dichloropentane. Propose a method for this!

8. Cyclohexanone and cyclohexenone react with methylmagnesium bromide to generate very different products after aqueous workup, as shown below. Suggest a reasonable mechanism for each reaction!



9. Multistriatin i is hydrolyzed to a compound, $C_{10}H_{18}O_3$ when treated with dilute aqueous acid. Suggest a structure for this compound! (Hint: this compound is an acetal!)



10. The two cyclohexenones j and k are easily interconverted under base-catalyzed or acid-catalyzed conditions. Suggest plausible mechanisms for both the base-catalyzed or acid-catalyzed cases.

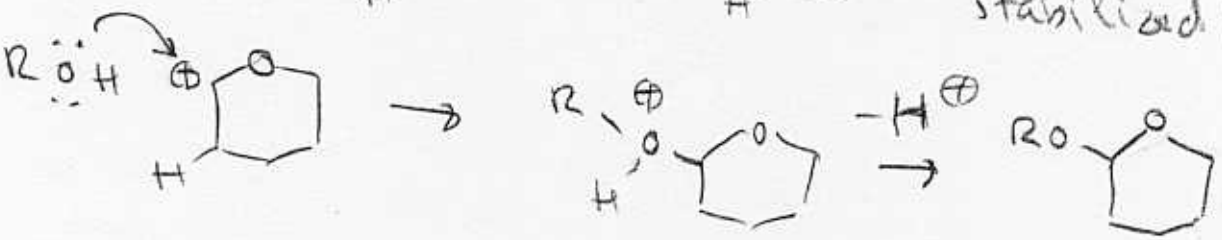
11. Suggest a method to convert compound l to m, then suggest a method to convert m back to l!

12. Show structures for the reaction products of cyclohexanone with a) cyclohexylamine, b) methylmagnesium iodide (followed by aqueous workup), c) phenylhydrazine, d) $NaBH_4$ (followed by aqueous workup), e) $KMnO_4/NaOH/H_2O$.

Prob 4 Chem 232 Key

1)

resonance stabilized!



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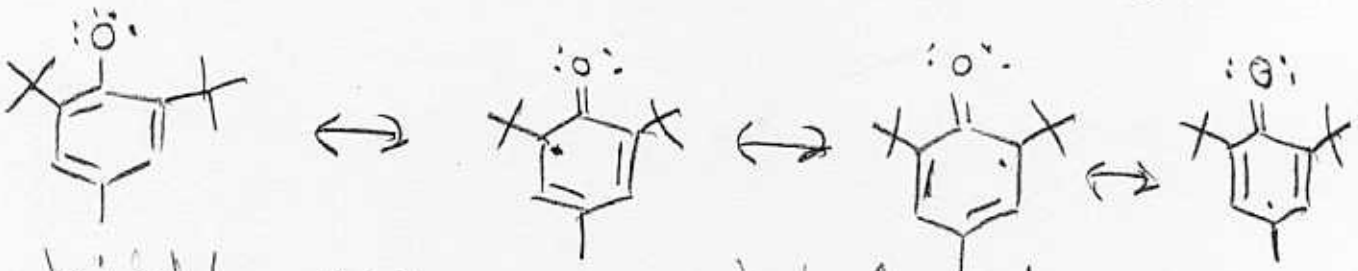
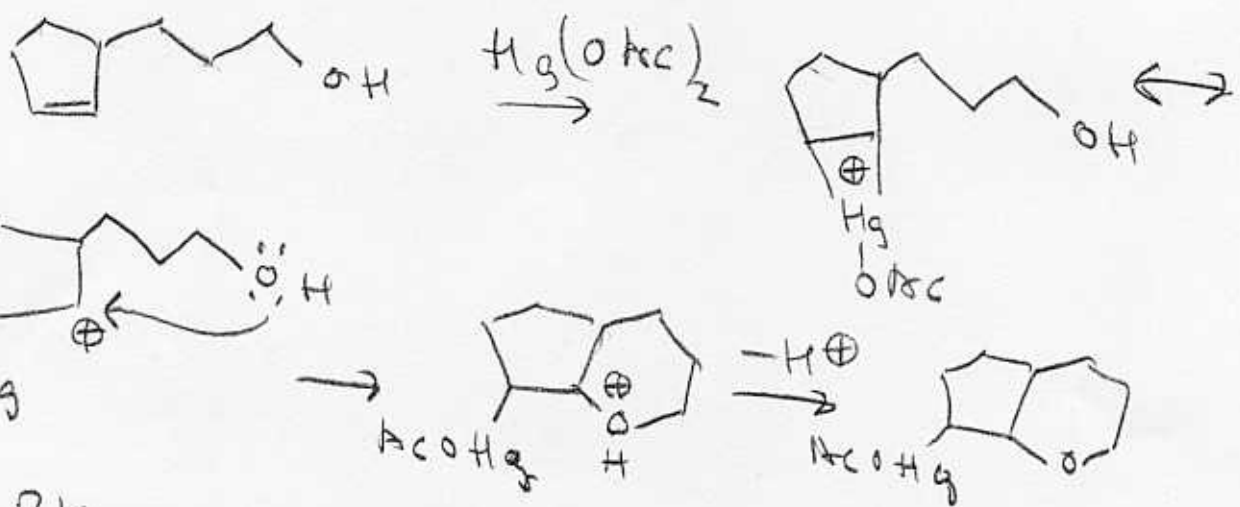
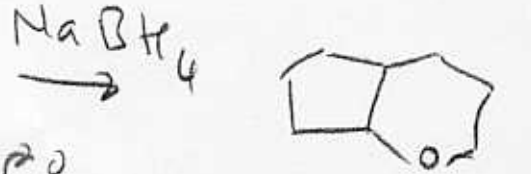


highly resonance stabilized!

3)





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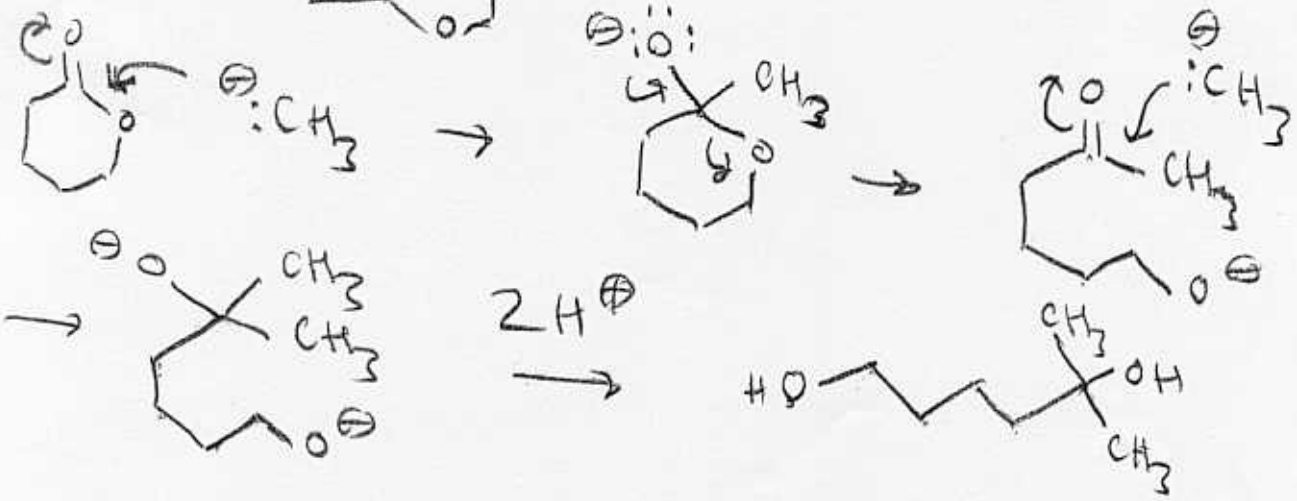

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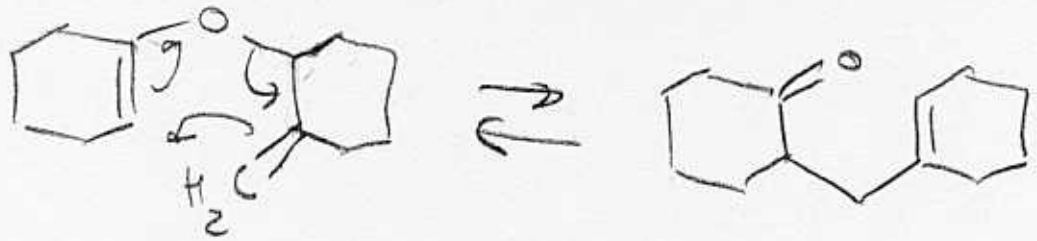

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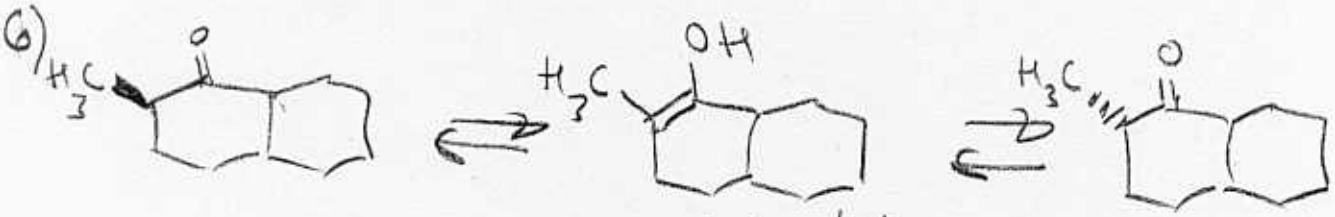
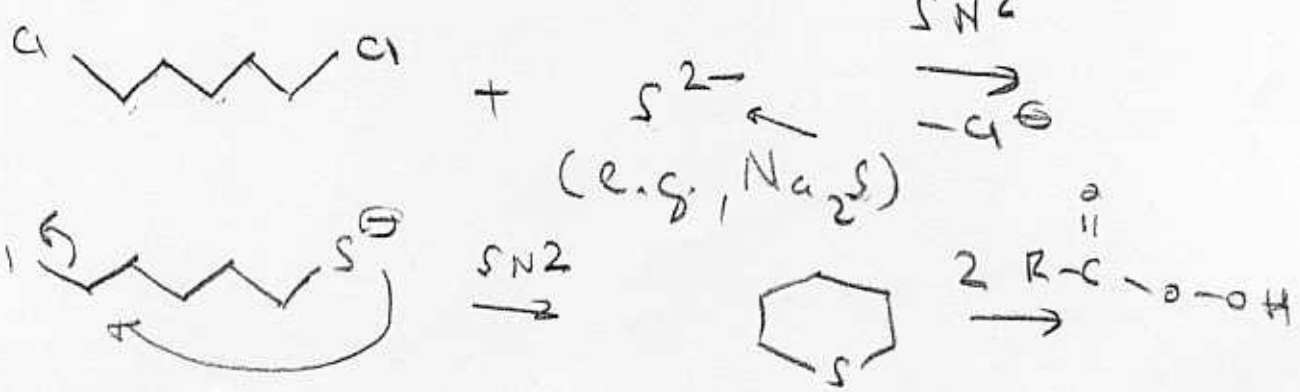


achiral!

not possible for a!

7)



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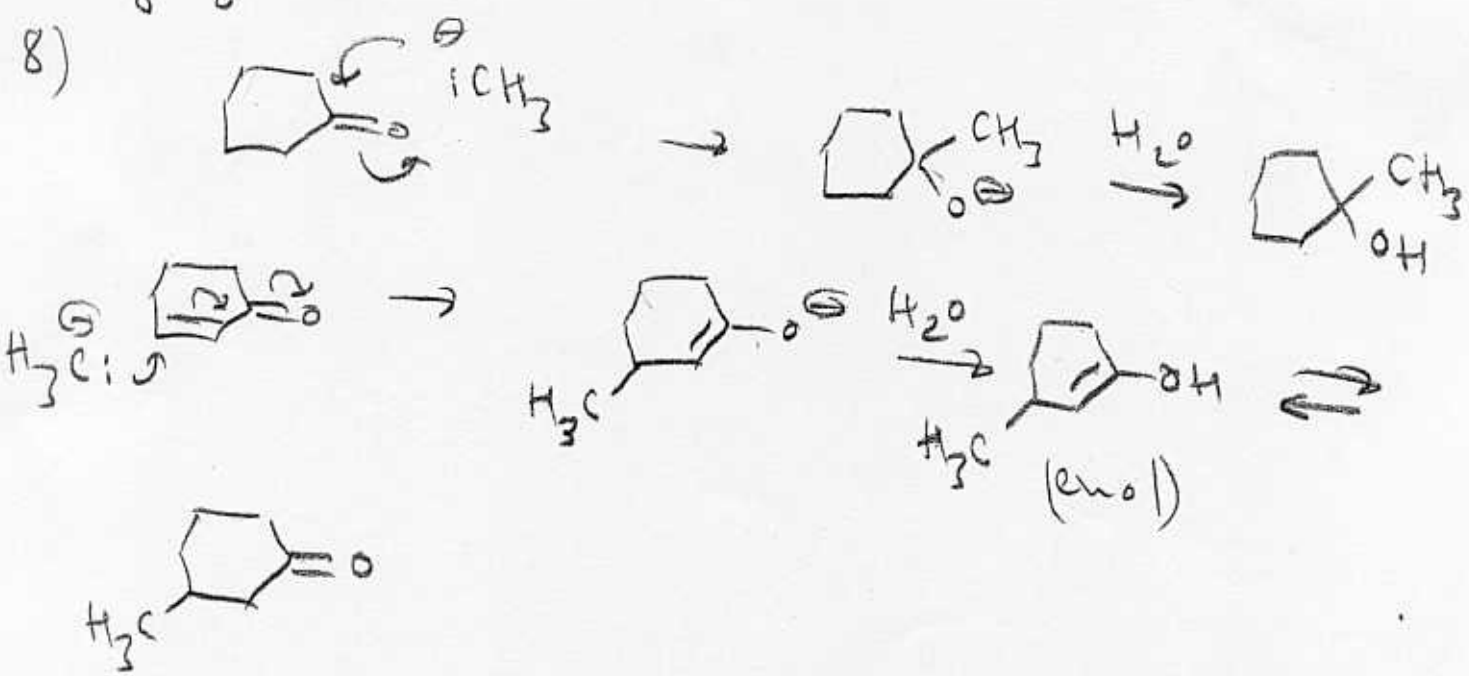

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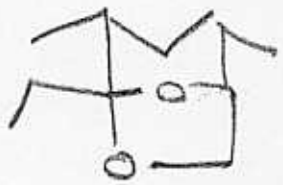
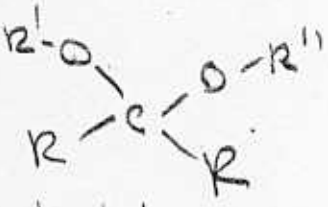
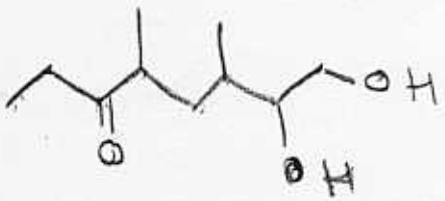


is of type 

This is an acetal!

↓ H_2O, $H_3O^{\oplus}$

same as 

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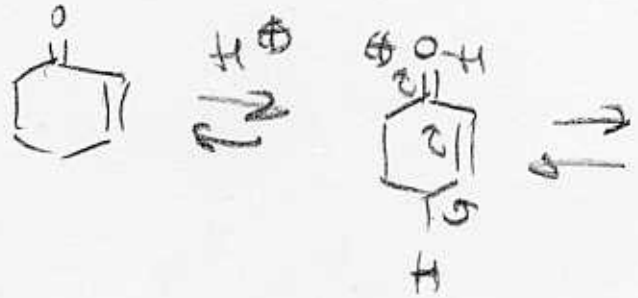
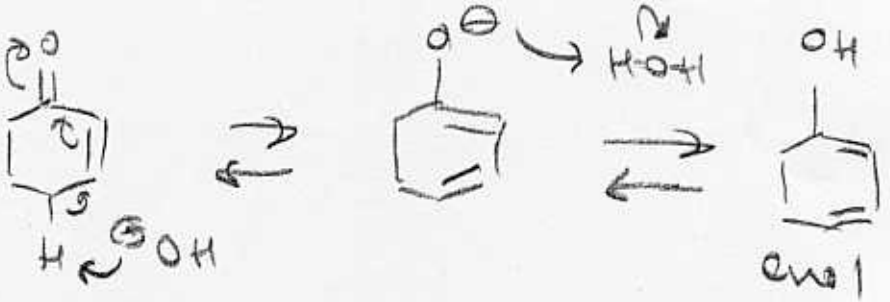
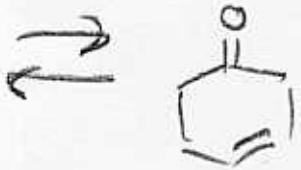


enol

basic:





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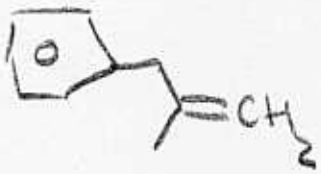
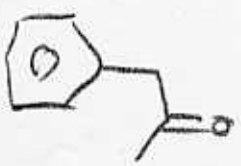
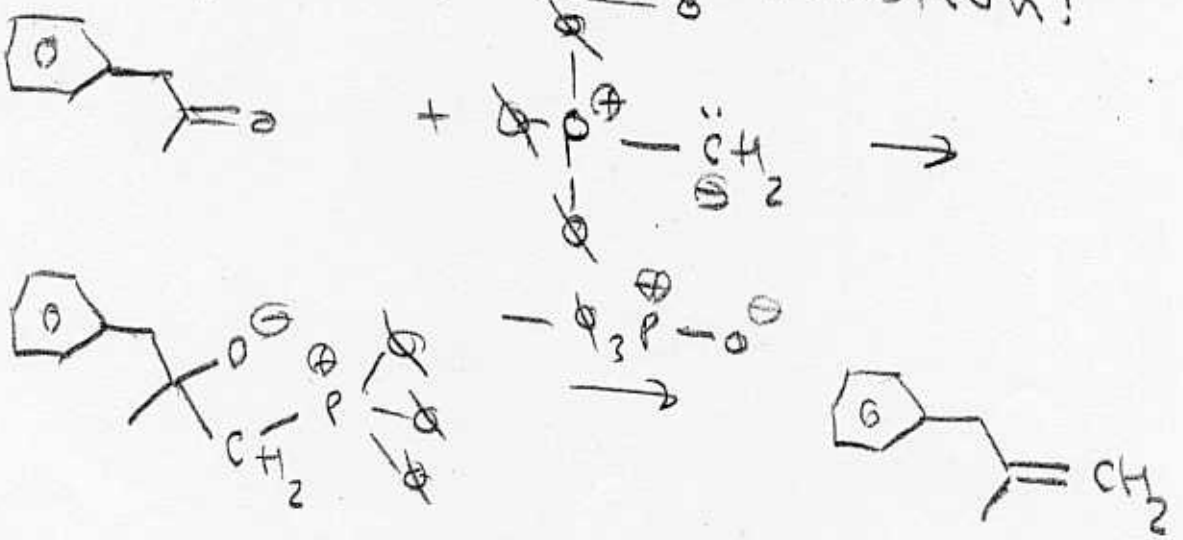


$KMnO_4$ →



$+ CO_2$

11) (cont'd.) by Wittig reaction:



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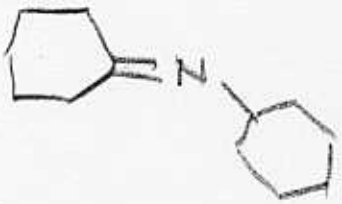

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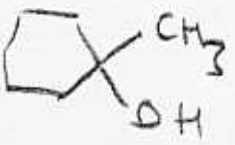
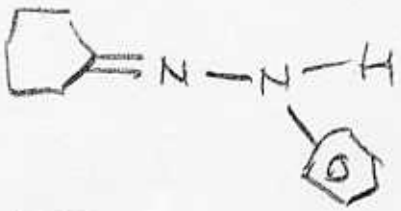


c)



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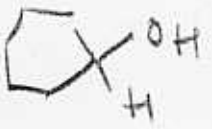

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