

CHEM 8321/4321

September 6, 2023

Problem Set #1

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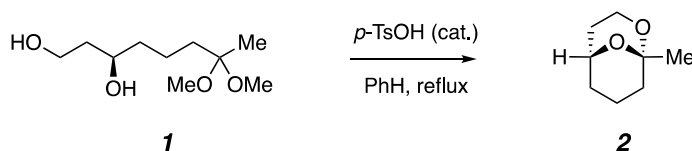
Due in class, Monday September 11, 2023

Detailed Mechanism Provide a detailed mechanism [i.e., explicitly show (using curly arrows) *EVERY* intermediate, formal charge (where relevant), equilibrium, and bond-making and -breaking step, including each proton transfer] to account for reactions a-c.

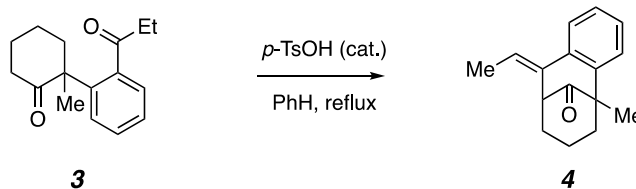
In most cases, mechanisms of reactions proceeding under acid (or cationic) conditions involve *only* neutral or positively charged intermediates,* and mechanisms of reactions proceeding under basic (or anionic) conditions involve *only* neutral or negatively charged intermediates.*

(* those species derived from the organic starting material. Of course, since charge is neither created nor destroyed, there is always a counterion of opposite charge present to balance the cationic or anionic nature of the charged intermediate.)

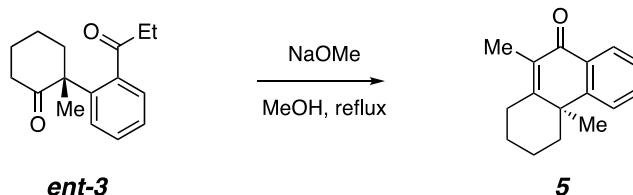
(a) the acid-catalyzed conversion of the acyclic ketal diol **1** to the cyclic ketal **2**.



(b) the acid-catalyzed cyclization of the diketone **3** to the enone **4** as the major product; this is an acid-catalyzed, intramolecular aldol condensation reaction. (hint: if you don't know or recall the "keto-enol tautomerization", look it up)



(c) the base-catalyzed cyclization of the enantiomer of ketone **3** (**ent-3**) to the conjugated enone **5** as the major product; this is a base-catalyzed, intramolecular aldol condensation reaction.



Other Problems

1. Draw the structure of MCPBA, DMP (two possibilities), MTPA, HMPA, DCC, DCM, DMA, NMP, THF, AIBN, TsOH, and PPTS. You will see the acronyms or abbreviations of many reagents, catalysts, and solvents throughout the semester. It is important that you know what each is (especially if you encounter it more than once!). If you are unfamiliar with *any* that you see, it is incumbent upon you to look it up. Google is a big help here. You can find many proper abbreviations here:

https://pubs.acs.org/userimages/ContentEditor/1218717864819/joceah_abbreviations.pdf

This link to the JOC Guide for Authors is also worth having on your computer:

https://publish.acs.org/publish/author_guidelines?coden=jocah

and

https://pubs.acs.org/doi/full/10.1021/acsguide.50308?_gl=1*1fi94ku*_ga*MTc4Mjg5NzI5Mi4xNjkyOTQyNDQ3*_ga_3YE6YD0SWD*MTY5Mzg0MTcxOC40OC4wLjE2OTM4NDE3MTguMC4wLjA.

2. Use Chem3D* to create a structure of each of a)-d); print out (or provide a screenshot) of each structure and turn in as your answer to this problem.

a) the most stable chair conformer of (1*R*,3*S*)-3-methylchlorocyclohexane.

b) the least stable chair conformer of (1*R*,3*S*)-3-methylchlorocyclohexane.

c) the anti-anti conformer of *n*-pentane

d) the syn-pentane conformer of *n*-pentane (https://en.wikipedia.org/wiki/Pentane_interference)

*directly available for use on a PC as a component of ChemOffice; Mac users need to use AppsToGo, a UMN website that allows you to access, e.g., applications that are only available on an alternative platform (OS). Instructions for accessing AppsToGo are available on the course website.