

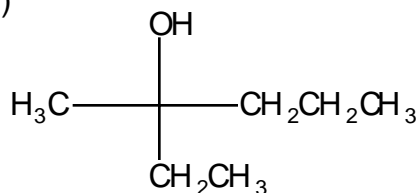
**Hour Examination #2, Chemistry 302X - 2003,
Monday, April 7, 7:30-10:00 pm**

"So Chymists especially are often, by sad Experience, convinced of it, when they, sometimes in vain, seek for the same Qualities in one parcel of Sulphur, Antimony, or Vitriol, which they have found in others. For though they are Bodies of the same Species, having the same nominal Essence, under the same Name; yet do they often, upon severe ways of examination, betray Qualities so different one from another, as to frustrate the Expectation and Labour of very wary Chymists."

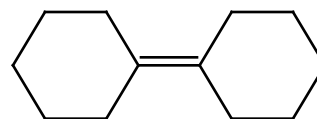
John Locke
(thanks to Josh Schulman)

1 (24 points). Devise syntheses for the following two molecules. You may start with any alcohol containing four carbon atoms or fewer, cyclohexene, pyridine, triphenyl phosphine, and inorganic reagents of your choice. You may also use the succulent sauce made from Jiang Xikui's steamed turtle.

(a)

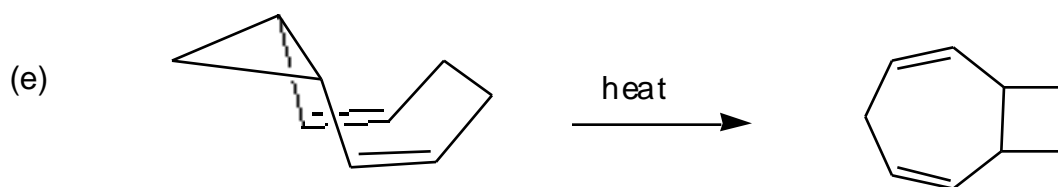
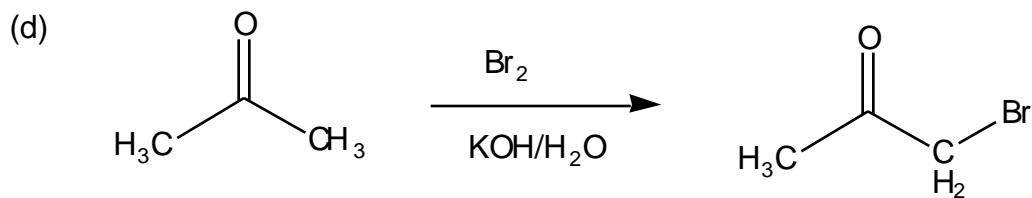
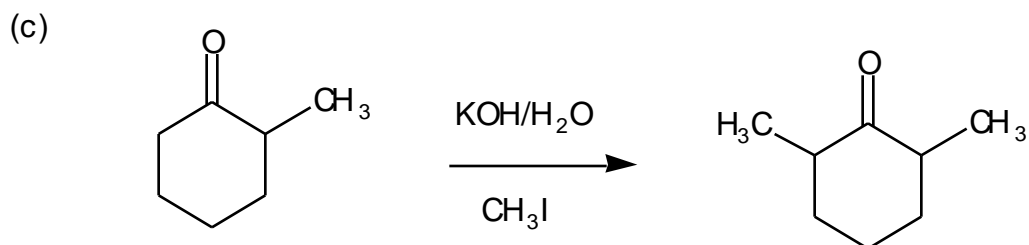
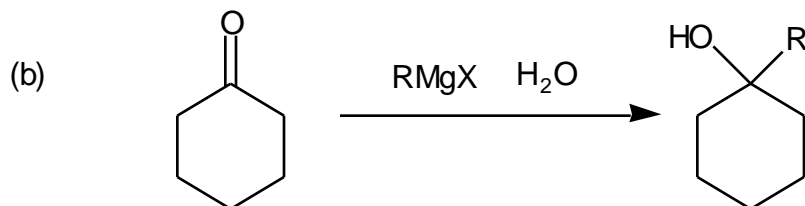
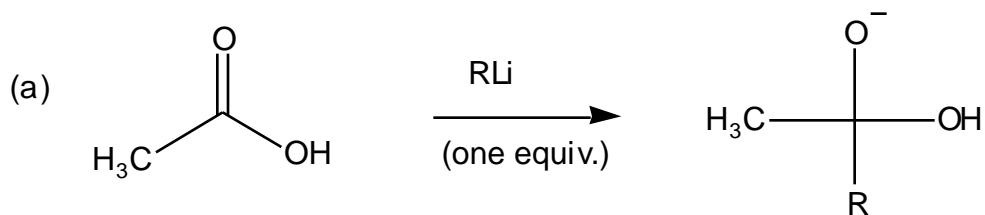


(b)

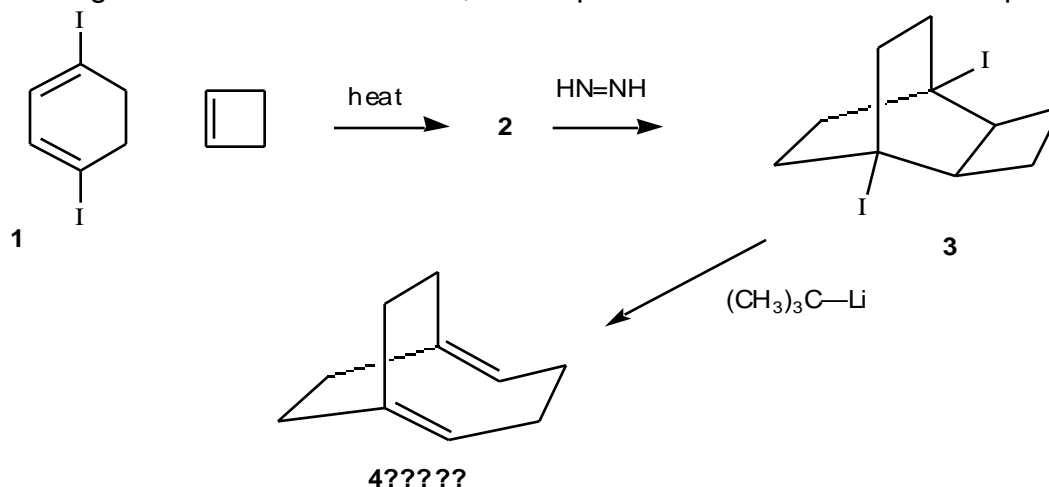


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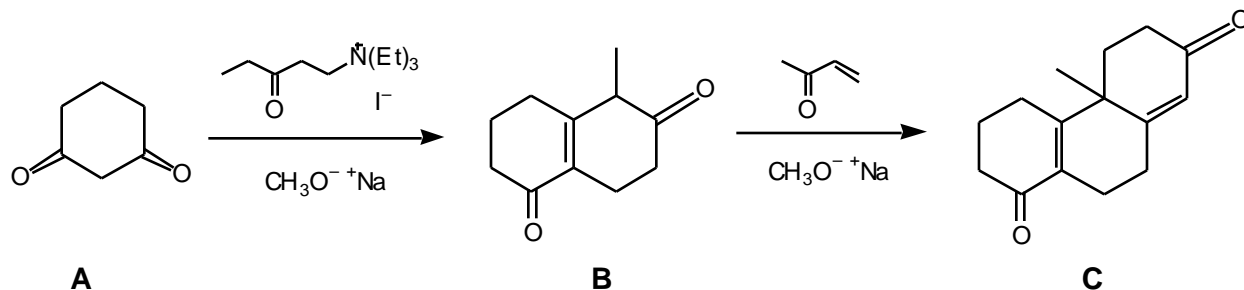
2 (20 points). In answering his orgo hour exam, Amos Alonzo Stagg suggested the following synthetic transformations. As is often the case for poor Amos Alonzo, there is an error in each answer. Your job is to point out the error in each part, and to suggest what product(s) will really be formed in parts a, b, c, and d



3 (20 points). When Wiseman and Vanderbilt heated compound **1** with cyclobutene, compound **2** was formed. Reduction with diimide (you remember: $\text{HN}=\text{NH}$) gives **3**. Wiseman and Vanderbilt hoped that treatment of **3** with *tert*-butyllithium would give **4**. No dice. They got a product of the correct formula, $\text{C}_{10}\text{H}_{14}$, but its ^1H NMR spectrum revealed four hydrogens between 4.5 and 5.0, not the two that **4** must have. You do not have to figure out how the *tert*-butyllithium reaction was supposed to work, but you do have to figure out the structure of **2**, and explain the formation of the real product.



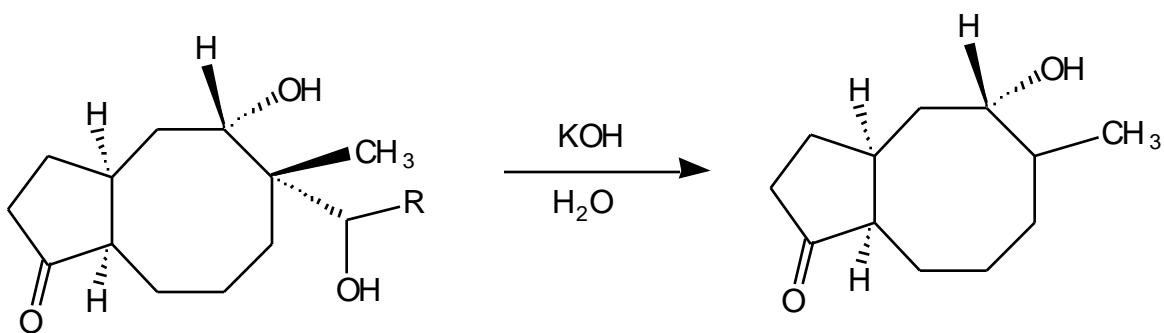
4 (24 points). The following transformations are part of Wild's synthesis of methyl 3-ketoetionate.



You are unlikely to get this problem right unless you work backward. If you do work backward, it should be quite easy. So:

- Analyze this problem starting with the transformation from **B** to **C**. Yes we want a written analysis. It need not be long, but it should be sufficient to guide you in seeing what happens. Subjective? Sure, but we can deal with the grading. That's why they pay us the big bucks.
- Next, sketch an arrow formalism for the reaction(s) involved. Be careful about detail.
- Repeat this process with the transformation from **A** to **B**. First provide an analysis.
- Sketch an arrow formalism for the reaction(s) involved in the transformation of **A** into **B**

5 (12 points). Here's a nice Fun in Base problem. Analyze! Use NO magic to give us a mechanism for this seemingly simple transformation.



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