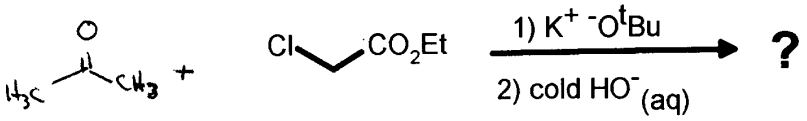
UNIVERSITY OF WINDSOR

School of Physical Sciences-Chemistry and Biochemistry

Chemistry 59-331/333 — Feb. 12, 1999

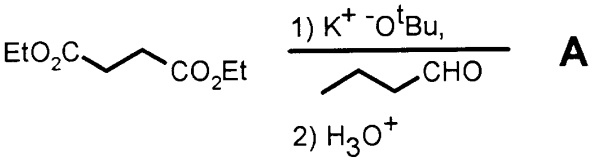
First Test-Makeup — Time 50 min

1. Give the complete mechanism of the Darzens' condensation between ethyl chloroacetate and acetone, and it's subsequent decomposition in cold aqueous base. Please show which steps are reversible or irreversible, and any small molecules which are evolved during the reaction. (**10 marks**)

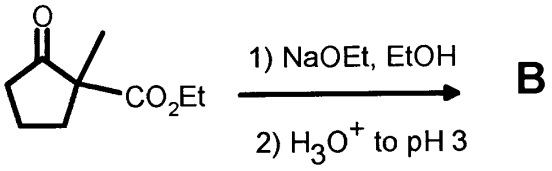


2. Indicate the structure of the expected major product(s) from each of the following reactions. Include stereochemistry where it is relevant. Mechanisms are not necessary, but showing your work is likely to be a help. (**5 for each letter, 40 marks total**)

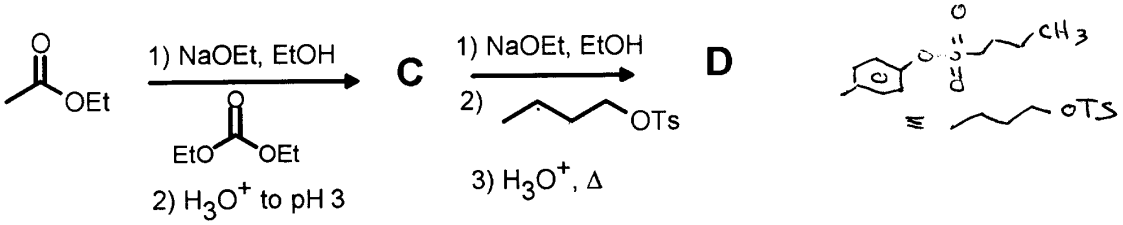
a.



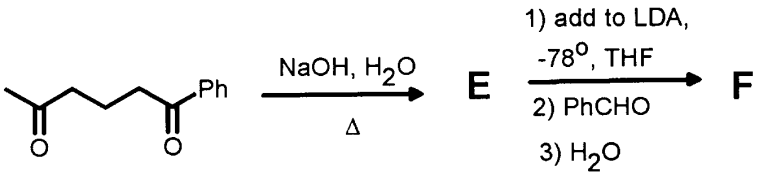
b.



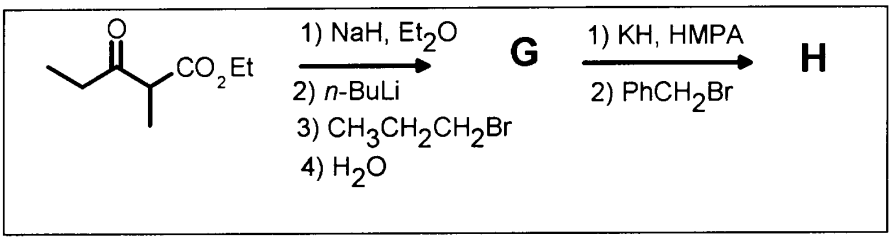
c.



d.

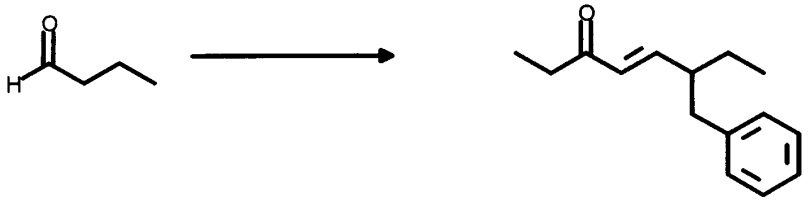


e.

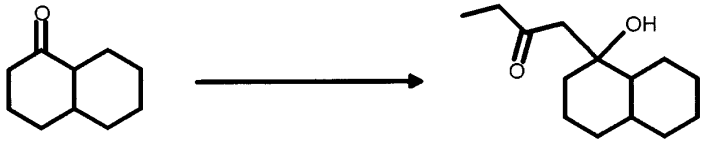


3. Show by equation how you would prepare the products illustrated from the given starting material. You many use any other reagent which you deem fit. Show all reagents, conditions, and *intermediates which could be isolated.* Mechanisms are not necessary, but may be a help. Note: Assume simple ketone alkylations are prone to polyalkylation unless told otherwise. (**10 marks each, 30 marks total**)

a.

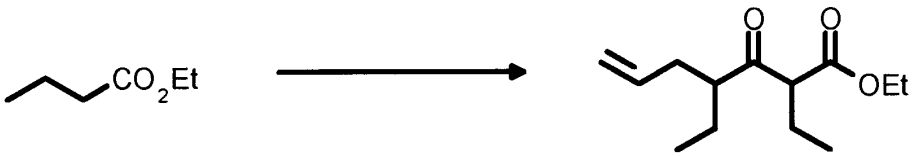


b.



neglect stereochemistry

c.



Bonus: One of the traditional methods for the synthesis of the pyridine ring system is the *Hantzsch* synthesis. A modified version of this used a β-diketone and ammonium acetate. Keeping in mind that ammonium acetate is essentially just (NH_3 + acetic acid), propose a reasonable mechanism for the following: