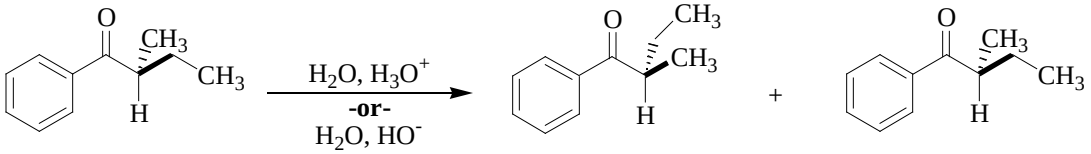
Problem Set #9

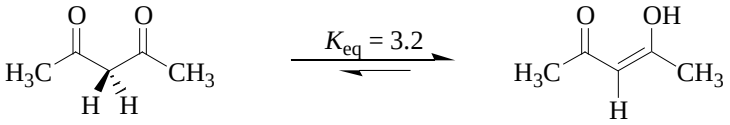
Chemistry 3231
October 30, 2001

1. (Re-submitted from PS #7): Account mechanistically for the fact that (*S*)-ketone **1** is racemized in the presence of acid or base. Write two mechanisms: one for the racemization in acid, one for the racemization in base.



(*S*)-**1** (*R*)-**1** (*S*)-**1**

2. Explain why acetylacetone (**2**), unlike simple ketones and aldehydes, exists mainly in its enol form at equilibrium.



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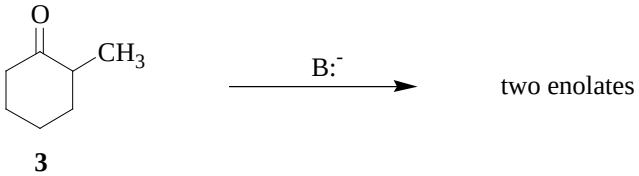
3. When treated with base, ketones **3** and **4** can, in principle, each generate two different enolates. Propose structures for the enolates.



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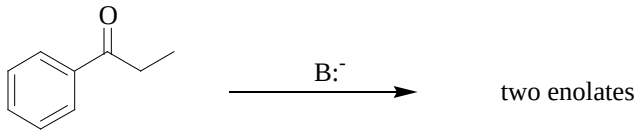

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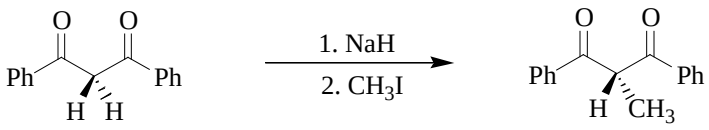
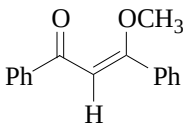
4. Write a mechanism for the alkylation of β-diketone **5** to give α-methylated product **6**.



5 **6**

5. In the above reaction, a small amount of vinyl ether **7** is isolated as well. Account for thie formation of this product.



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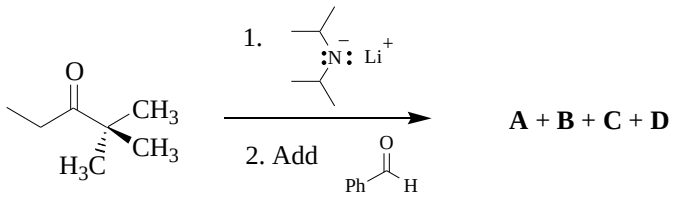
6. Enolate formation from *tert*-butyl ethyl ketone **8**, followed by addition of benzaldehyde provides a mixture of four stereoisomeric aldol products (**A**-**D**). The ^{1}H and ^{13}C NMR spectra of **A** and **B** are identical. The ^{1}H and ^{13}C NMR spectra of **C** and **D** are identical. The spectra of **A** and **C**, while similar, are not exactly the same. Propose structures for **A**, **B**, **C**, and **D**.



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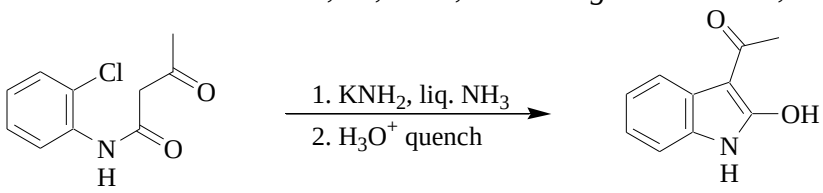
7. Provide a mechanism for the conversion of 2-chloroaniline derivative **9** to **10**. (Refs.: Bunnett, et al. *J. Am Chem. Soc.* **1961**, *83*, 1691, and *J. Org. Chem.* **1963**, *28*, 1.)



9 **10**