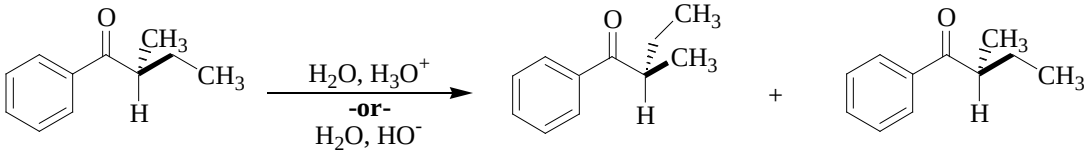
Problem Set #7

Chemistry 3231

October 16, 2001

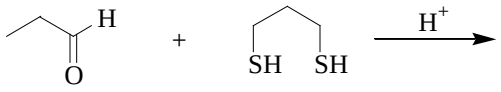
1. Account mechanistically for the fact that (*S*)-ketone **1** is racemized in the presence of acid or base. Write two mechanisms: one for the racemization in acid, one for the racemization in base.



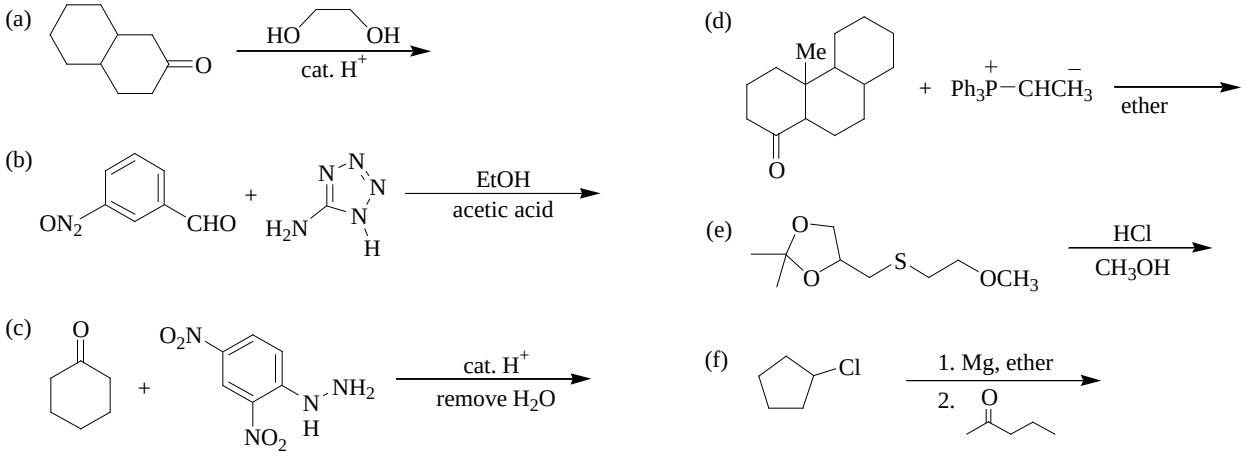
(*S*)-**1** (*R*)-**1** (*S*)-**1**

2. The equilibrium constant (K_{hydr}) for hydration of acetone (CH_3COCH_3) is 2 x 10^{-3}. This translates into a very small percent conversion to the corresponding hydrate. Would you expect the K_{hydr} for hexafluoroacetone (CF_3COCF_3) to be smaller or larger than that for acetone? Explain.

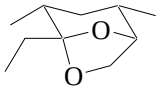
3. The following reaction is used to produce a thioacetal, the sulfur equivalent of an acetal. Draw the expected product and propose a mechanism for its formation.



4. Give the expected products from each of the following reactions:



5. Dutch elm disease is caused by a fungus transmitted to elm trees by the elm bark beetle. The female beetle, when she has located an attractive elm tree, releases several pheomones, including multistriatin, **2**. These pheromones attract male beetles which bring with them the deadly fungus.



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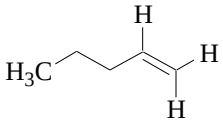
Treating **2** with dilute aqueous acid at room temperature leads to the formation of a product, $C_{10}H_{18}O_3$, which shows a strong IR peak near 1715 cm^{-1}. Propose a structure for this product.

6. What combinations of carbonyl compound and ylide could you use to prepare the alkenes **3** and **4** via a Wittig process?



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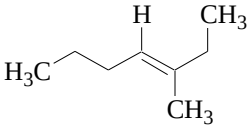

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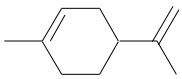
7. Limonene (**5**) is a natural product found in orange peels as its (*R*)-enantiomer. Take advantage of both the Diels-Alder and Wittig methodologies to propose an efficient synthesis of racemic limonene.



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