

CHEM 8322/4322

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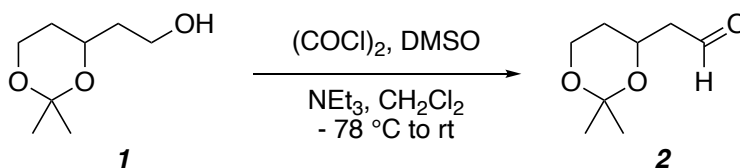
Problem Set #3

T. R. Hoye

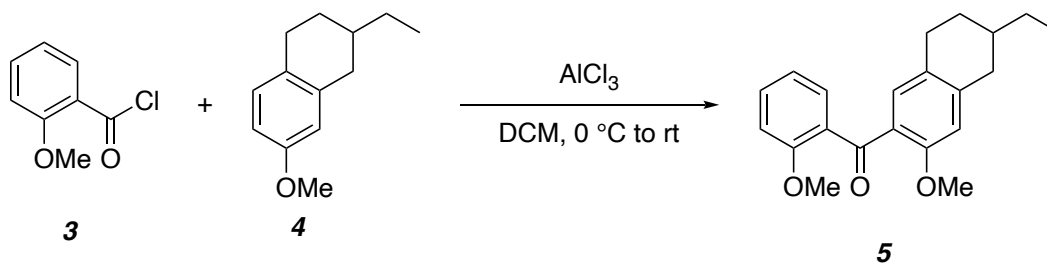
Due in class, Monday September 25, 2023

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**.

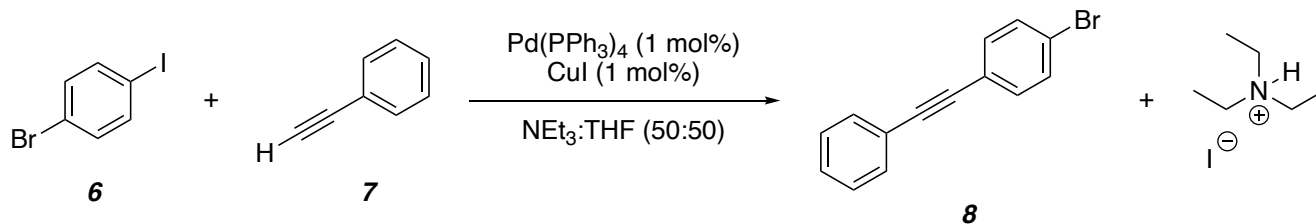
(a) The Swern oxidation of alcohol **1** to aldehyde **2**.



(b) The Friedel-Crafts acylation of the acid chloride **3** and the tetralin derivative **4** to form the ketone **5** as the major product.

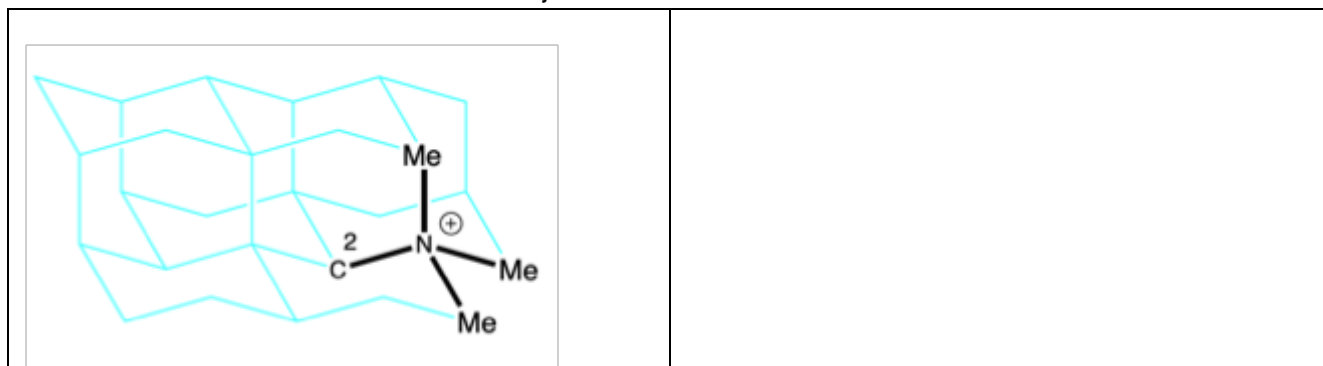
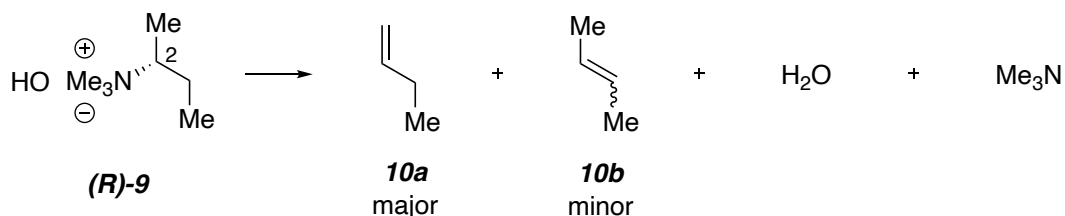


(c) The Sonogashira cross-coupling reaction between the iodobenzene **6** and phenylacetylene, **7**, to form the diphenylacetylene **8** and triethylammonium iodide.



Other Problems

1. The Hofmann elimination of quaternary ammonium hydroxide salts results in preferential formation of the less highly substituted (and thermodynamically less stable) alkene. That is to say, the product distribution is under kinetic rather than thermodynamic control. As you know, the preferred geometry for an E2 elimination involves an antiperiplanar relationship between the vicinal (or β) proton that is lost and the leaving group. On the partial diamond lattice below, provide a carefully drawn representation of the most stable conformation of the tetra-alkylammonium hydroxide (**(R)-9**) and use it to rationalize (with accompanying text you add within the blank box) why the pyrolysis of (**(R)-9**) yields mostly 1-butene with only a minor amount of the (more stable) 2-butenes.



2. An enantiopure sample of (*S,S*)-dibromodiphenylethane (**11**) exhibited an optical rotation of $[\alpha]^{23}_{\text{D}} +154.5^\circ$. Upon subjection of (*S,S*)-**11** to benzene and heat, the optical rotation (measured in a polarimeter, which uses plane polarized light) decreased over time, asymptotically approaching 0° . The formation of *meso*-**11** was not observed. Explain these observations.

