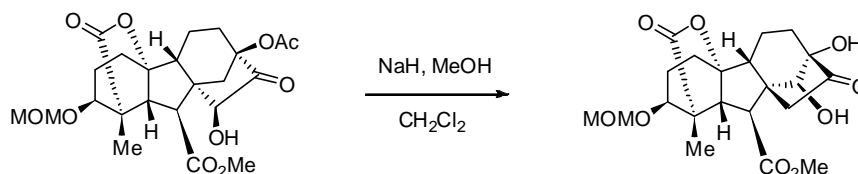


VanNieuwenhze Group Problem Set – 12/1/09

“Rearrangements”

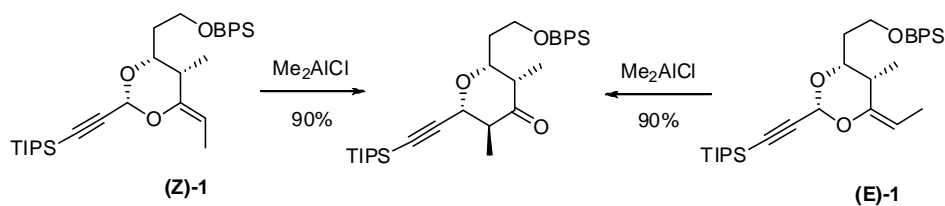
1. a) Propose a mechanism for the following transformation, which is an example of a name reaction.



b) Would you expect the reaction to be reversible or irreversible?

c) No specific yield is given for this transformation. Assuming that $\Delta G^\circ_{\text{rxn}} = -5.73 \text{ kcal/mol}$, estimate the “yield” for this reaction.

2. a) The following transformation was studied en route to phorboxazole A. Provide a mechanism for the conversion of the *Z* isomer below to the pyran derivative. Your mechanism should account for the observed stereochemical outcome. What is the name reaction?

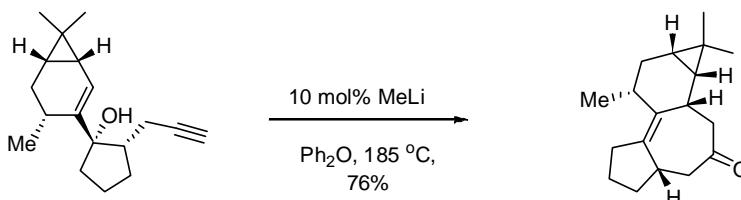


b) Provide an explanation (i.e. T.S. analysis) for the fact that the *E* isomer gives the same product.

c) Is this a thermodynamically or kinetically controlled reaction?

d) Assuming that the remaining yield for conversion of (*E*)-1 is the undesired product, estimate the energetic value of the overall destabilizing interactions leading to this product in relation to those for the T.S. in part a) above, i.e. $\Delta\Delta G^\ddagger$. Does its magnitude make sense?

3. Propose a mechanism for the following reaction that accounts for the observed stereochemical outcome.



4. Propose a mechanism for the following reaction. Hint: NaNO_2 converts to an intermediate with oxidizing potential.

