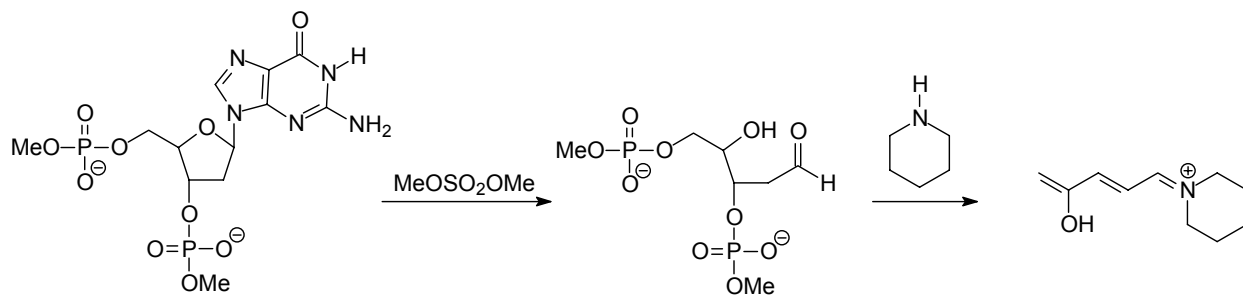


Organic Cumulative Examination. May, 2005

1. For the determination of the structure of glucose, Fischer first needed to determine the structure of arabinose, which he knew was the precursor of both glucose and mannose. Describe how he determined the structure of arabinose given the four possible structures.

2A. The 2'-deoxyguanosine-3',5'-diphosphate shown below will react with dimethyl sulfate to give the abasic sugar derivative shown in the first reaction below. Provide a mechanism for the reaction showing all intermediates formed and showing electron flow with arrows.



2B. The abasic sugar derivative reacts with hot piperidine to cleave the phosphate esters (second reaction). This reaction is the DNA cleaving reaction that follows DNA damage by a variety of agents. Draw a mechanism for the reaction showing all intermediates formed in the reaction and showing electron flow with arrows.

3. Catalytic reactions typically demonstrate "saturation kinetics".

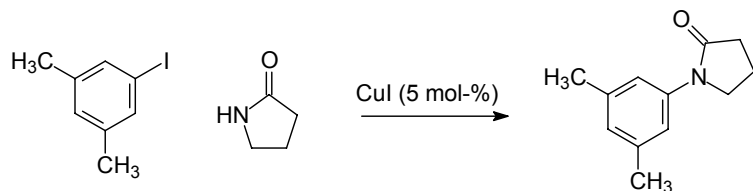
A. Derive a rate law that would be found for conversion of reactant **A** to give product **P** (no other reactants or products of interest) in a process that is catalyzed by catalyst **C** and displays saturation kinetics.

3B. Describe a set of kinetic studies that would demonstrate that the above system reacted with saturation kinetics.

3C. Provide a graphical illustration of what the kinetic data would look like for the above system for a series of studies with varying concentration of catalyst **C**. The kinetic values can be given in a qualitative manner, but your graph should have appropriate axes.

3D. What kinetic parameters would be obtained from the kinetic data you plotted in part 3C?

4. Amidation of aryl iodides is an area of contemporary interest. The reaction shown below was recently studied (JACS, 2005, 127, 4120).



**A.** Provide a mechanism for the above reaction showing all intermediates formed in the reaction and show electron flow with arrows.

**B.** In a series of kinetic studies where the concentrations of the species shown above were held at constant concentration, 1,2-bis(methylamino)cyclohexane was demonstrated to have a catalytic effect on the reaction. Provide a mechanism for catalysis by the diamine.