

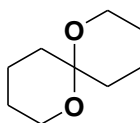


CHEM 8410_6410_4410 – Organic Synthesis

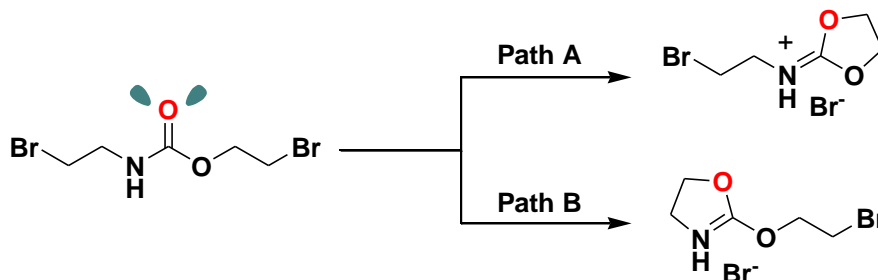
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Problem Set 2: This problem set is now available at (www.blackboard.utoledo.edu). It will be due in class 21 days (02/21/17) from today (01/31/17). Grades will be administered as follows: 10 (exceptional effort), 8 (complete), 5 (incomplete or inadequate effort), 2 (poor effort), 0 (nonexistent) per question (3 questions total). **No late problem sets will be accepted.**

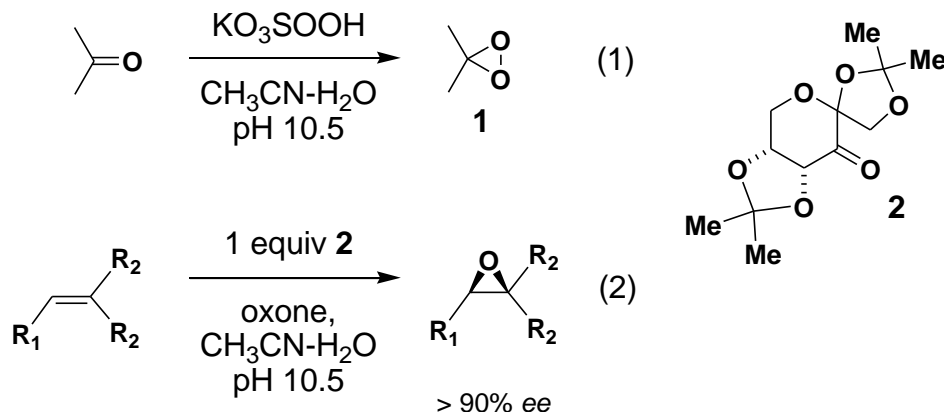
1. **Problem:** Predict the most stable conformation of the indicated dioxospiran. Use MO's to tailor your answer.



2. **Problem:** The molecule illustrated below can react through either **Path A** or **Path B** to form the bromine salts as illustrated. In both instances the carbonyl oxygen functions as the nucleophile in an intramolecular alkylation. What is the **preferred** path for the transformation in question?



3. **Problem:** The useful epoxidation reagent dimethyldioxirane (**1**) may be prepared from “oxone” (KO₃SOOH) and acetone (eq. 1). In an extension of this epoxidation concept, Shi has described a family of chiral fructose-derived ketones such as **2** that, in the presence of “oxone”, mediate the asymmetric epoxidation of di- and tri-substituted olefins with excellent enantioselectivities (>90% ee) (*JACS* **1997**, *119*, 11224).





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Part A. Provide a mechanism for the epoxidation of ethylene with dimethyldioxirane (**1**). Use three-dimensional representations, where relevant, to illustrate the *relative* stereochemical aspects of the oxygen transfer step. Clearly identify the frontier orbitals involved in the epoxidation.

Part B. Now superimpose chiral ketone **2** on to your mechanism proposed above and rationalize the sense of asymmetric induction of the epoxidation of trisubstituted olefins (eq. 2). Use three-dimensional representations, where relevant, to illustrate the *absolute* stereochemical aspects of the oxygen transfer step.

1.