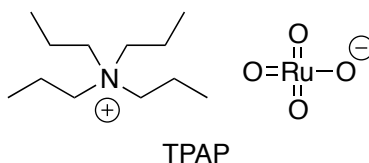


CHEM 330

Topics Discussed on Nov. 23

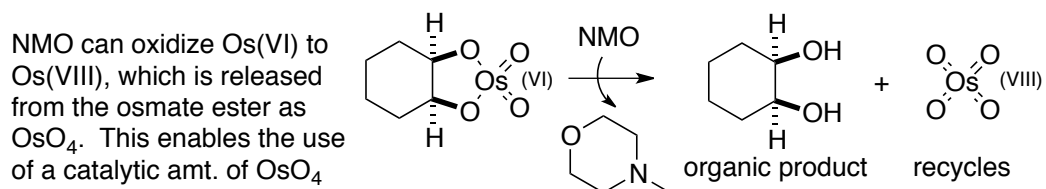
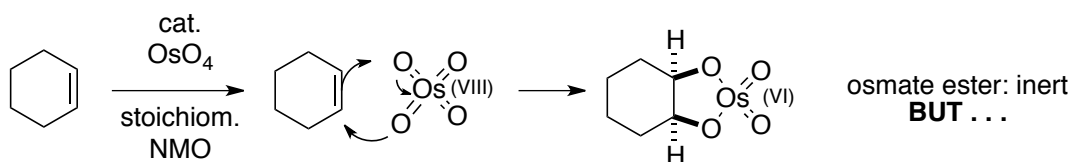
State-of-the-art in perruthenate oxidation of alcohols to carbonyls: use of catalytic tetrapropylammonium perruthenate ("TPAP") in the presence of NMO (Ley oxidation):



High cost and toxicity of OsO_4

Ability of NMO to oxidize low-valent forms of Os to OsO_4

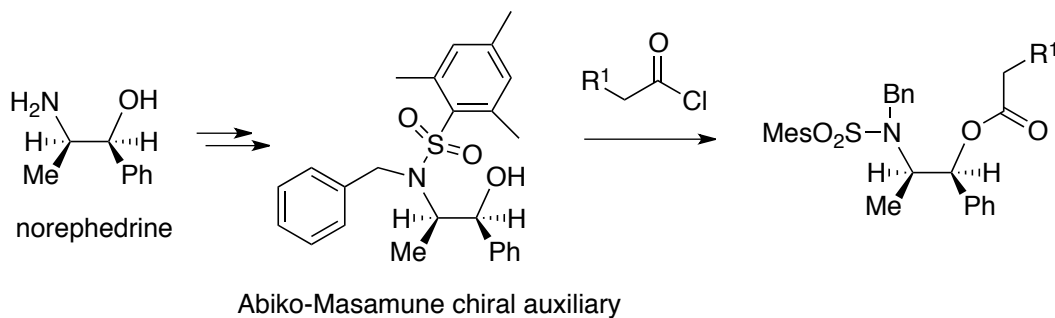
Use of NMO in catalytic osmylation reactions: the Upjohn catalytic osmylation reaction

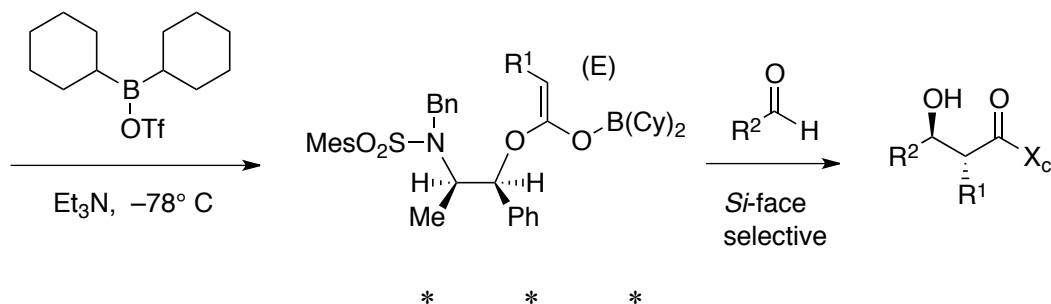


Limitation of Evans technology: the method can only afford *syn* aldol products

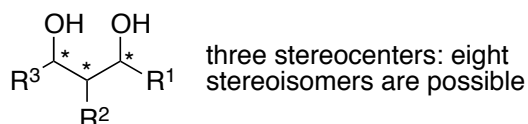
The question of enantioselective creation of *anti*-aldol motifs

The Abiko-Masamune *anti*-aldol technology (1997):

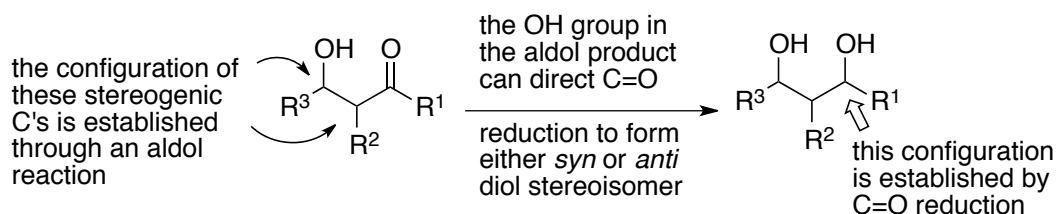




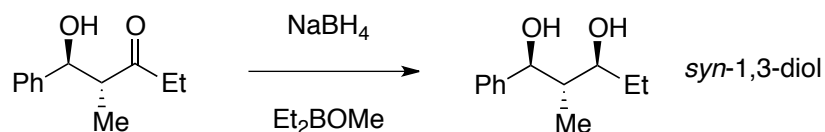
The assembly of 1,3-di-OH systems of the type:



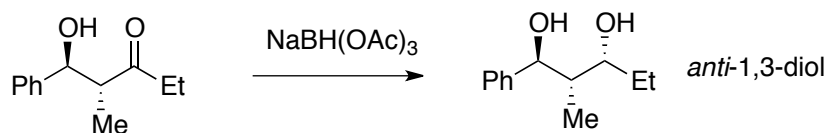
Preparation of 1,3-diol systems of the above type by reduction of an aldol product:



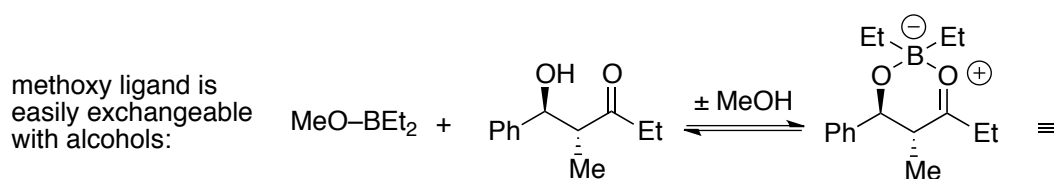
Stereoselective reduction of a β -hydroxyketone to the *syn*-1,3-diol with sodium borohydride, Na^+BH_4^- , in the presence of diethylboron methoxide, Et_2BOMe (Prasad reduction), e.g.:

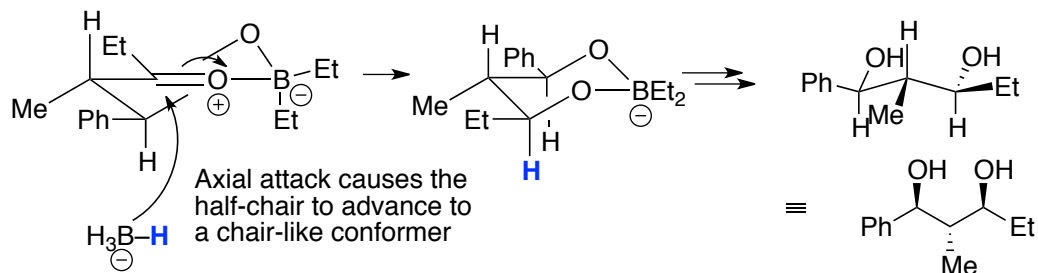


Stereoselective reduction of a β -hydroxyketone to the *anti*-1,3-diol with sodium triacetoxyborohydride, $\text{Na}^+\text{BH}(\text{OAc})_3^-$ (Evans reduction), e.g.:

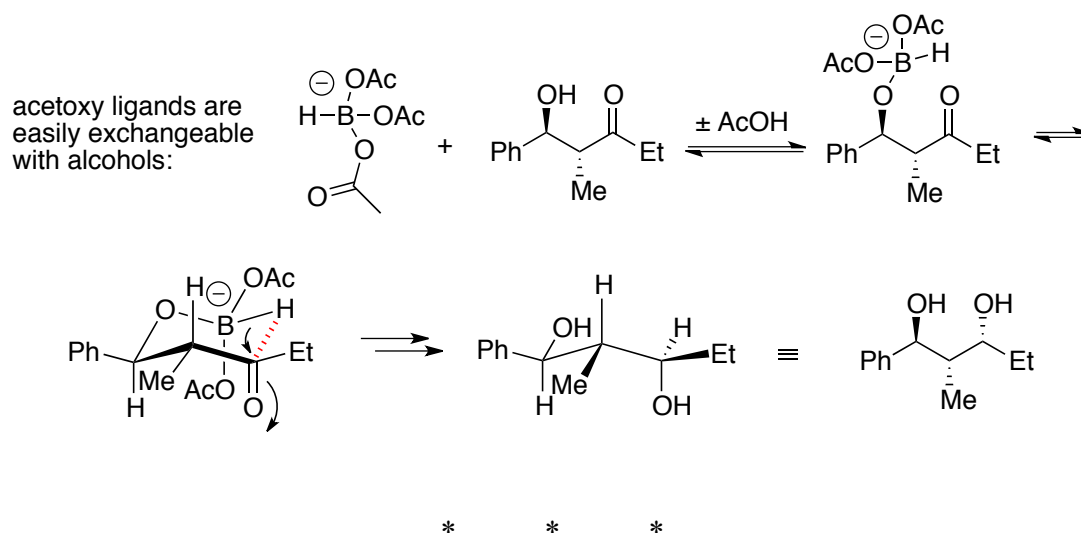


Presumed mechanism of the Prasad reduction:





Presumed mechanism of the Evans reduction:



Ionic reactions: processes that involve ionic intermediates (e.g., carbanions / enolates)

Radical reactions: processes that involve radical intermediates

Pericyclic reactions: a family of reactions that: (i) proceed only through the interaction of π systems, (ii) may be described by a "circular" movement of electrons, and (iii) occur in a concerted manner, i.e., do not proceed through reaction intermediates.

Cycloaddition reactions: pericyclic processes that lead to formation of new rings through the interaction of independent π systems

Cycloaddition reactions encountered thus far: the addition of O_3 and OsO_4 to olefins:

