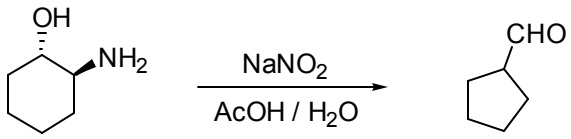
Paul Bracher
Chem 30 – Section 4

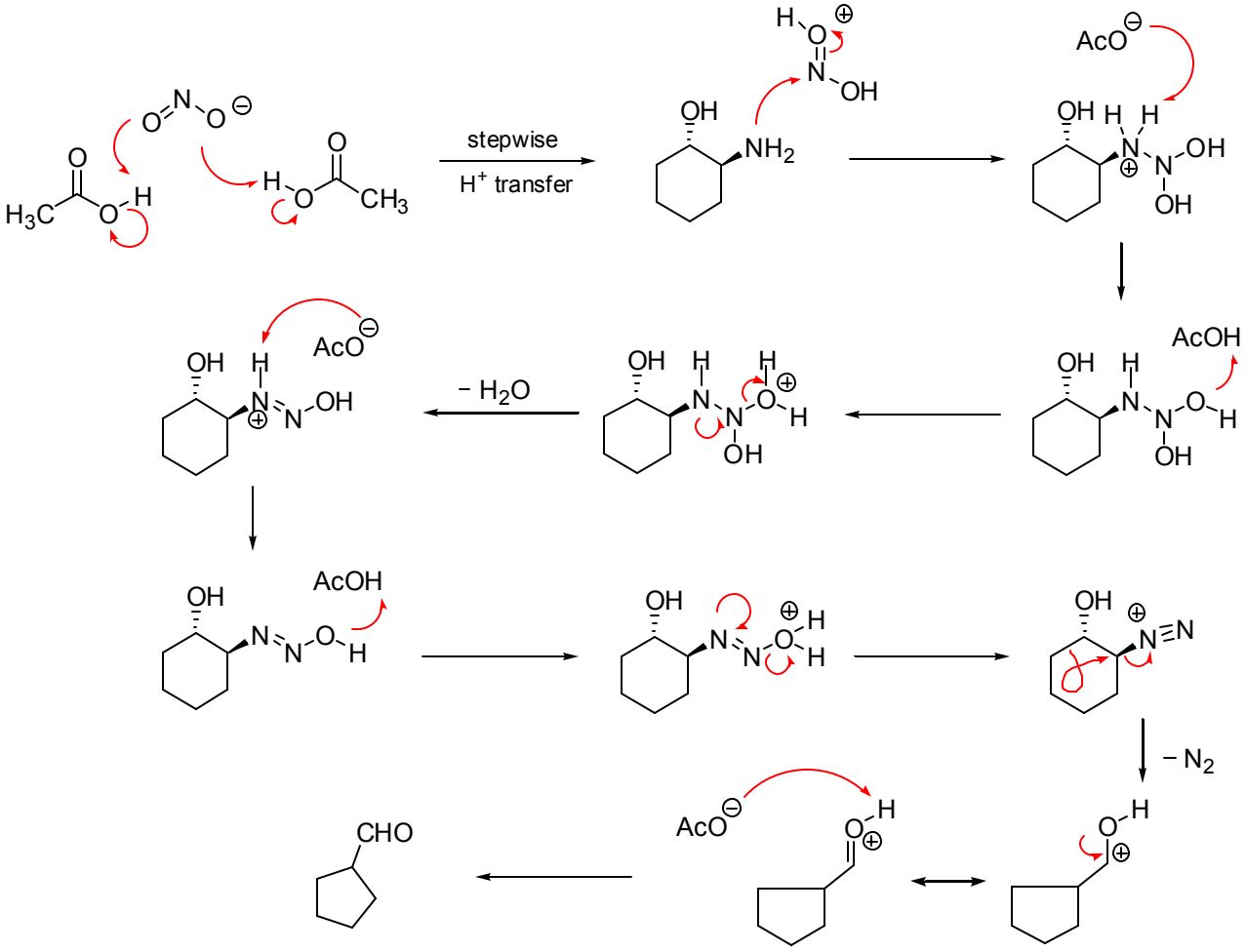
Section Solution Set

Carbonyl Chemistry I: Electronic Structure and Additions

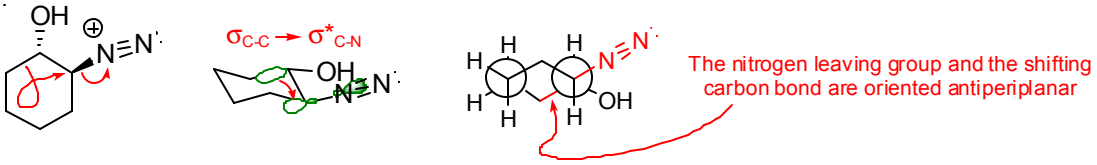
Problem 1 (from Fall 2003 Chem 30 Exam III Review Session). The amine below undergoes the following reaction when treated with sodium nitrite in the presence of acid.



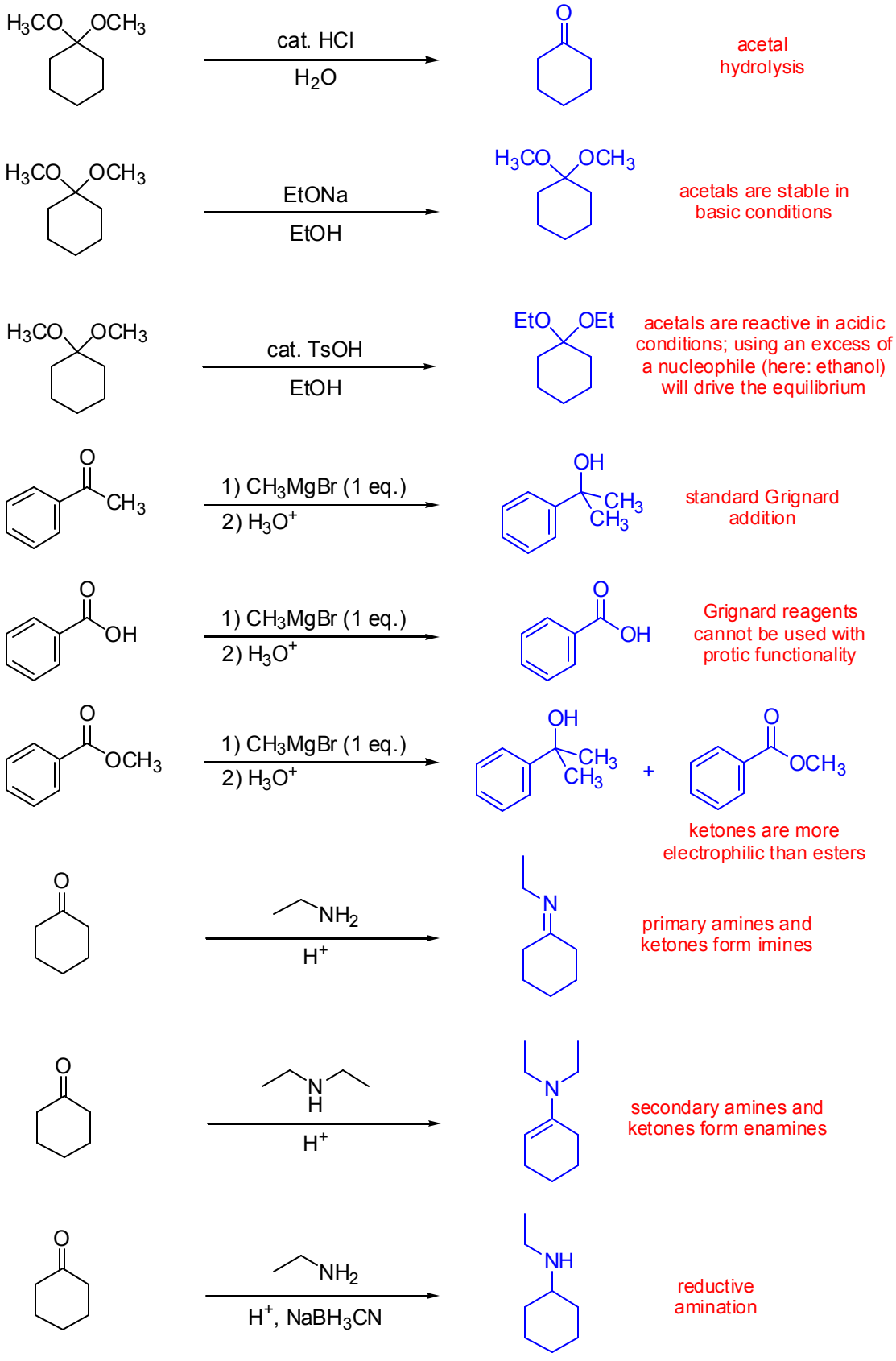
a) Provide an arrow formalism mechanism for this transformation



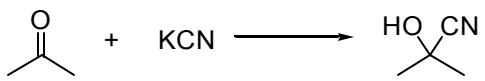
b) Draw a Newman projection showing the orbitals that interact in the step where the nitrogen atom attached to the ring is lost.



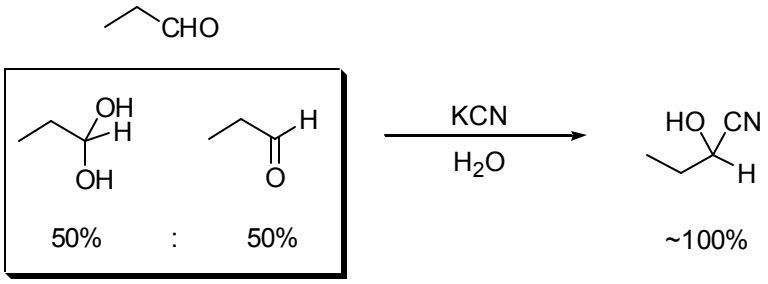
Problem 2. Predict the major product for each of the following reactions. Beware of non-reactions.



Problem 3 (based on a problem in *Organic Chemistry* by Maitland Jones). Cyanide ions readily add to carbonyl groups in water to form cyanohydrins:

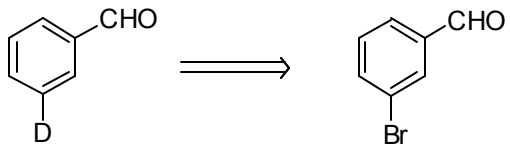


When dissolved in water, propionaldehyde exists roughly 50% in hydrated form. Despite this fact, when an aqueous solution of propionaldehyde is treated with potassium cyanide, the cyanohydrin forms in quantitative yield. Why isn't the maximum possible yield 50%?



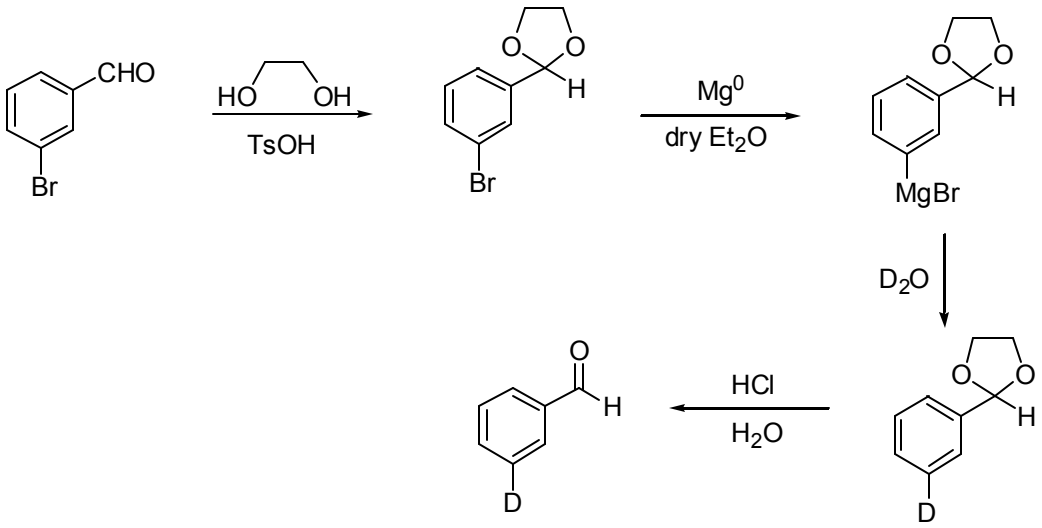
The hydration of aldehydes is reversible. While the hydrated propionaldehyde is unreactive, when it converts back to the carbonyl form, it is consumed by the cyanide and taken to the thermodynamically favored product. As we voyage into carbonyl chemistry, it is important to remember that many carbonyl additions are reversible reactions and a variety of factors can control the product mixture. These systems are dynamic!

Problem 4. Provide a concise synthetic route to compound **C** from starting material **B**.



C **B**

Solution



Note: It is preferable to combine the last two steps as D_2O/DCl or similar. In fact, the last three steps can be done "in the same pot" without having to isolate any of the intermediates shown. I just wanted to show the individual processes that take place along the way.

Take home lesson

- Understand the importance of protecting group strategy. If you hadn't protected the carbonyl group, the Grignard reagent would have added to the aldehyde and your precious compound would have polymerized.