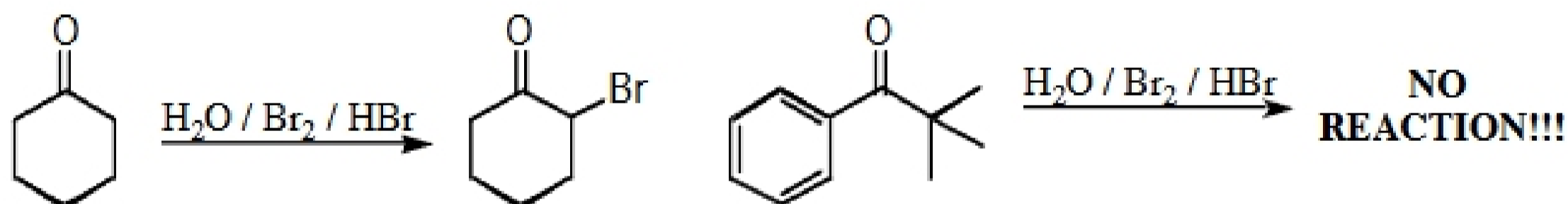
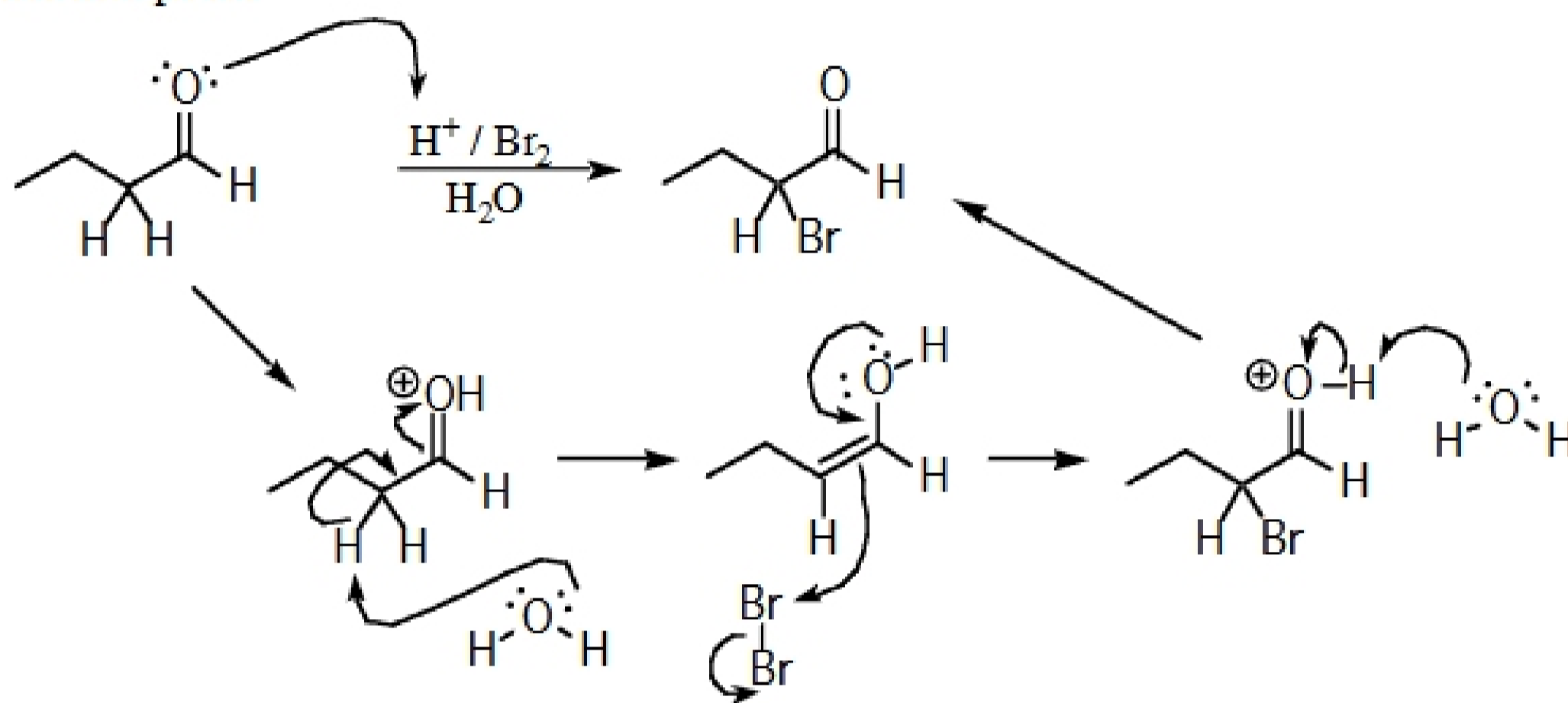


The addition of electrophiles to the *alpha* carbon via the acid or base-induced formation of enols (or enolates) forms the bulk of the material of this chapter. Let's begin with our first example.

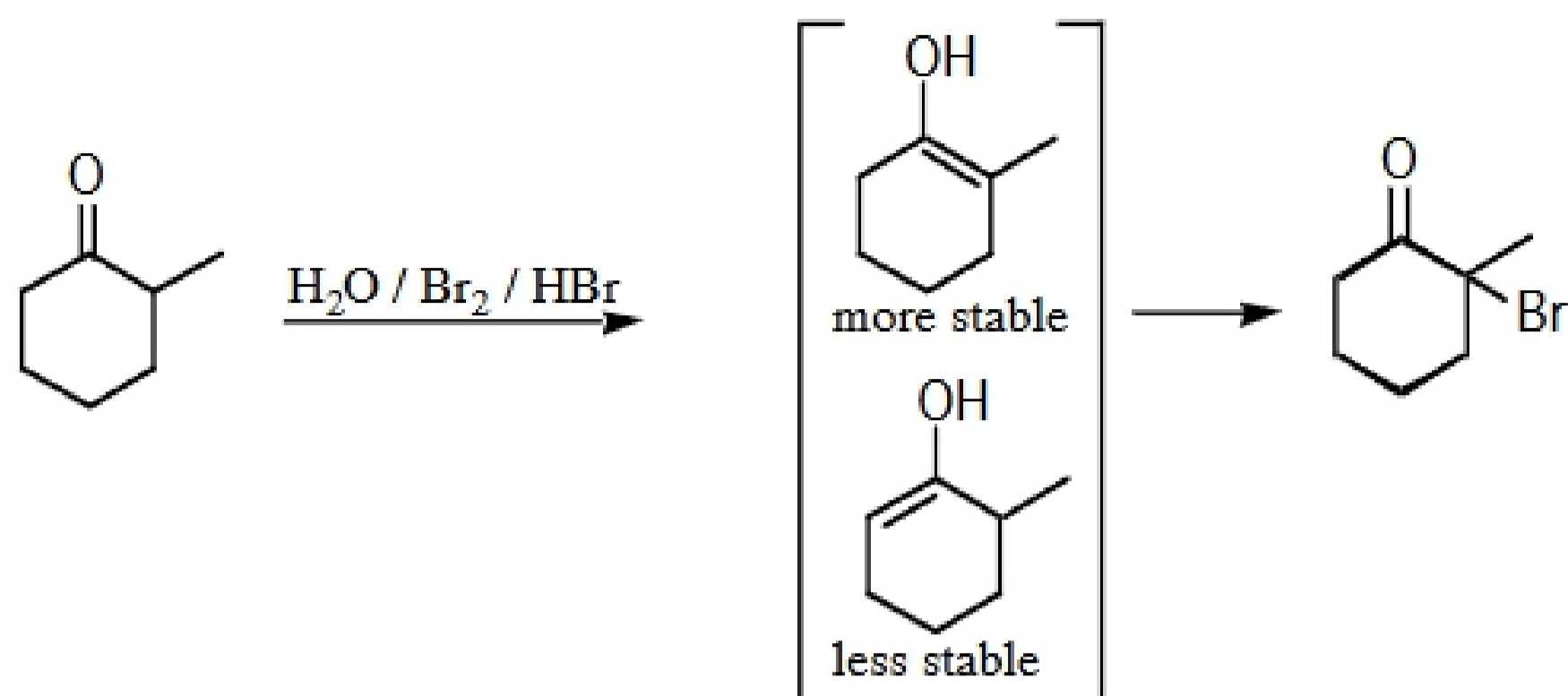
Reactions of Enols (i.e. Acidic conditions)

Acid-Catalyzed Halogenation of Aldehydes and Ketones

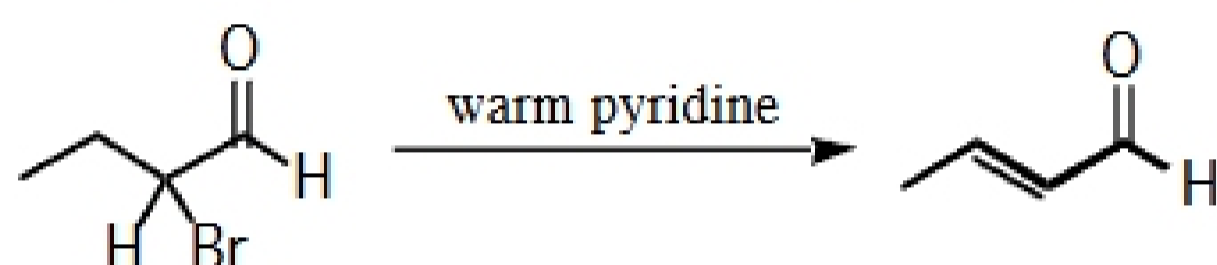
Our first example works under mild acidic conditions. Aldehydes can easily be mono-halogenated at the *alpha* position by simply mixing the aldehyde with a halogen (usually Br₂ or I₂) and a trace of acid. **IMPORTANT NOTE** - if there are no *alpha* hydrogens, this reaction will not take place!



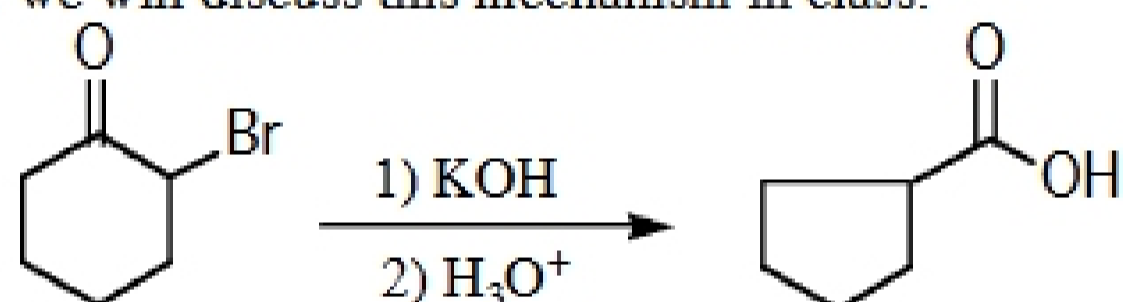
Because the various enols possible are under equilibrating conditions, usually the **MOST STABLE** enol is the one formed in the highest concentration - and thus the one which reacts with the halide. For example, methyl cyclohexanone can form two different enols - the more highly substituted one is the most stable, and thus predominates:



There are two major uses for these bromo-ketones and aldehydes. The first is elimination to form conjugated carbonyl compounds. This is a classic (and simple) method for preparing such compounds:

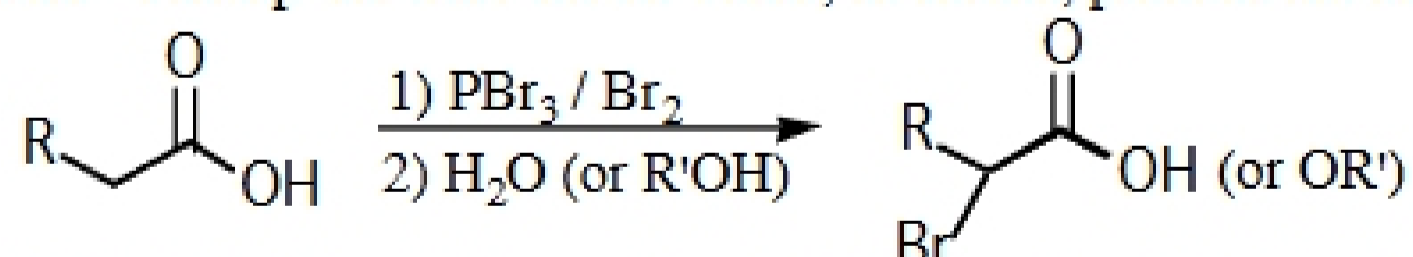


With cyclic ketones, these halogenated compounds can undergo what is called the Favorskii reaction. This is in essence a ring-contracting reaction, and usually proceeds in good yield. Time permitting, we will discuss this mechanism in class:



The Hell-Volhard-Zelinskii Reaction

As stated above, the acid-promoted *alpha* halogenation only works with aldehydes and ketones. What if you need to brominate a carboxylic acid? That's where the **HVZ** reaction comes in. The reaction basically takes a difficult-to-enolize carboxylic acid, and first turns it into a much more enolizable acid bromide. This reaction produces HBr, which then assists in the *alpha* bromination of this acid bromide. Aqueous workup returns the acid bromide to the carboxylic acid state. Workup with an alcohol would, of course, produce the ester.



Please remember that while this reaction can be used to *form* an ester, it cannot be used with an ester as starting material – you must start with the carboxylic acid!

