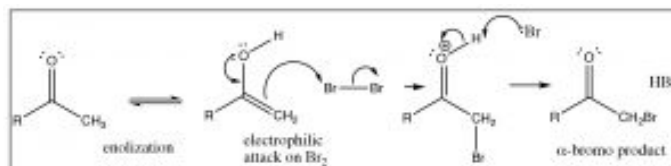
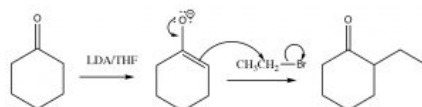


9.1: Reactions of Enols and Enolates

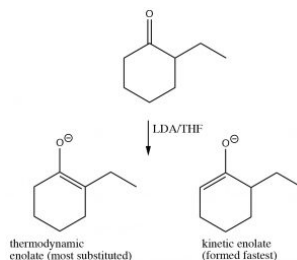
The keto and enol forms of carbonyl compounds can undergo completely different reactions. The carbonyl (keto) form undergoes nucleophilic attack at the carbonyl carbon and the enol/enolate form undergoes electrophilic attack, usually at the alpha carbon (although the O is also reactive). For example, aldehydes and ketones can be halogenated at the alpha carbon just by treatment with a solution of the halogen, either with acid or base catalysis. The first step is enolization, which produces the very electron-rich alkene that attacks the bromine (just like the first step of addition to a normal alkene). This intermediate then loses a proton to give to the halogenated compound and HBr.



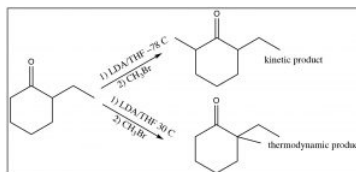
The reaction can also be done in a base via the enolate, but in this case the reaction is difficult to stop after one halogen has added and, typically, all alpha positions will end up brominated. Such a reaction is analogous to the first step of addition of halogens to an alkene, but the second step involves the regeneration of the carbonyl. Just as reversible nucleophilic addition to the carbonyl typically produces the sp² hybridized product, these enol/enolate forms also end up as substitutions rather than additions.



A reaction of an alpha carbon that has no analogy in alkene chemistry involves their acting as a nucleophile in an S_N2 reaction. The reaction occurs via the enolate anion, which then attacks any appropriate alkyl halide via an S_N2 reaction.



If the ketone undergoing such a reaction has the possibility of forming two different enolates, and therefore producing two different alpha alkylation products, the enolate that has the most substituted double bond is the most stable and is thermodynamically favored. Typically, the enolate formed from the least-hindered carbon is formed fastest (it has the lowest activation energy). It is therefore possible to control the product of such a reaction by carefully controlling the reaction conditions. At very low temperatures, the kinetic product is formed, while at higher temperatures thermodynamic product is formed.



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