Exercise 105 - NAS

Question

Why do carboxylic acid derivatives undergo substitution reactions while aldehydes and ketones undergo addition?

Both mechanisms start with nucleophilic addition to the C=O to form a tetrahedral intermediate.



If X is an electronegative atom relative to C or H, then the CO pi bond can reform by kicking out X. This process is more favourable entropically than addition and the negative charge is stabilized to some degree by the electronegativity of X. If X is a C or H atom, the negative charge is not stabilized - R- and H- are terrible leaving groups so this process stops at the addition stage and nothing further happens.

Question Five

The following is a very useful reaction for the preparation of aldehydes. Classify the reaction mechanistically. What FGI does this now make available (Hint: what is the starting material for the prepn of alkyllithiums)?



Question Two

Acetic anhydride can be prepared by the addition of acetic acid to ketene. Propose a mechanism.

There are two possible mechanisms, one acid catalyzed and one not. Both are acceptable.





Question Three

Offer a mechanism for the following reaction.



This is simply TWO acyl substitutions followed by a nucleophilic addition to a ketone.