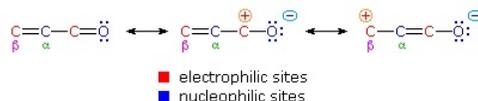


18.15: α,β -Unsaturated Carbonyl Compounds

Introduction

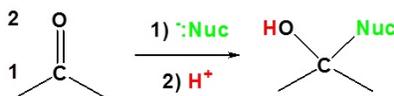
One of the largest and most diverse classes of reactions is composed of nucleophilic additions to a carbonyl group. Conjugation of a double bond to a carbonyl group transmits the electrophilic character of the carbonyl carbon to the beta-carbon of the double bond. These conjugated carbonyl are called enones or α, β unsaturated carbonyls. A resonance description of this transmission is shown below.



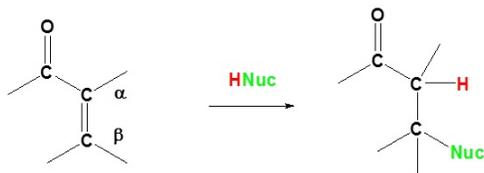
From this formula it should be clear that nucleophiles may attack either at the carbonyl carbon, as for any aldehyde, ketone or carboxylic acid derivative, or at the beta-carbon. These two modes of reaction are referred to as 1,2-addition and 1,4-addition respectively. A 1,4-addition is also called a conjugate addition.

Basic reaction of 1,2 addition

Here the nucleophile adds to the carbon which is in the one position. The hydrogen adds to the oxygen which is in the two position.



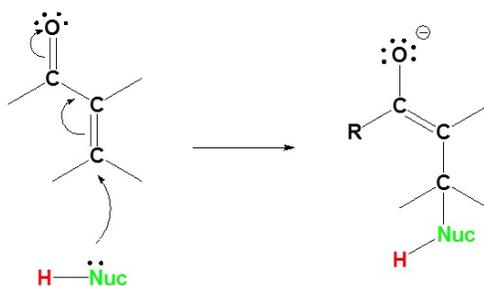
Basic reaction of 1,4 addition



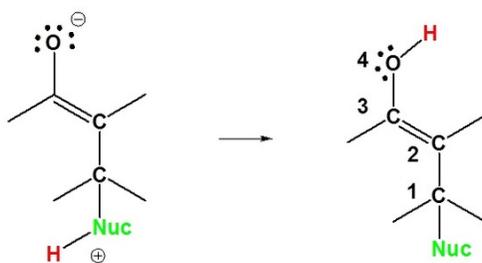
In 1,4 addition the Nucleophile is added to the carbon β to the carbonyl while the hydrogen is added to the carbon α to the carbonyl.

Mechanism for 1,4 addition

1) Nucleophilic attack on the carbon β to the carbonyl

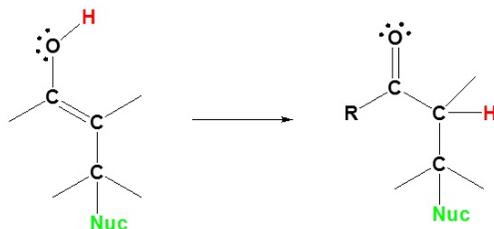


2) Proton Transfer

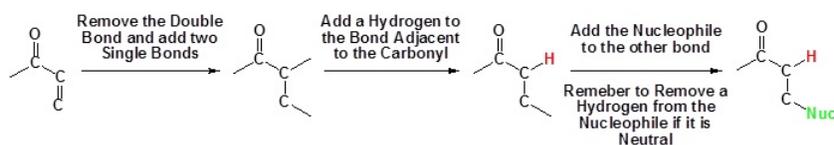


Here we can see why this addition is called 1,4. The nucleophile bonds to the carbon in the one position and the hydrogen adds to the oxygen in the four position.

3) Tautomerization



Going from reactant to products simplified



1,2 Vs. 1,4 addition

Whether 1,2 or 1,4-addition occurs depends on multiple variables but mostly it is determined by the nature of the nucleophile. During the addition of a nucleophile there is a competition between 1,2 and 1,4 addition products. If the nucleophile is a strong base, such as [Grignard reagents](#), both the 1,2 and 1,4 reactions are irreversible and therefore are under kinetic control. Since 1,2-additions to the carbonyl group are fast, we would expect to find a predominance of 1,2-products from these reactions.

If the nucleophile is a weak base, such as alcohols or amines, then the 1,2 addition is usually reversible. This means the competition between 1,2 and 1,4 addition is under thermodynamic control. In this case 1,4-addition dominates because the stable carbonyl group is retained.

Gilman Reagents

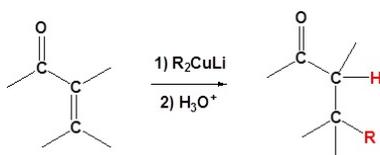
Another important reaction exhibited by organometallic reagents is metal exchange. Organolithium reagents react with cuprous iodide to give a lithium dimethylcopper reagent, which is referred to as a Gilman reagent. Gilman reagents are a source of carbanion like nucleophiles similar to Grignard and Organo lithium reagents. However, the reactivity of organocuprate reagents is slightly different and this difference will be exploited in different situations. In the case of α, β unsaturated carbonyls organocuprate reagents allow for an 1,4 addition of an alkyl group. As we will see later Grignard and Organolithium reagents add alkyl groups 1,2 to α, β unsaturated carbonyls

Organocuprate reagents are made from the reaction of organolithium reagents and CuI

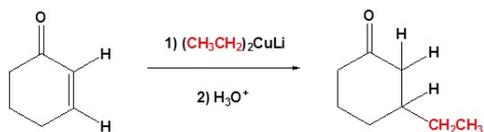


This acts as a source of R^- :



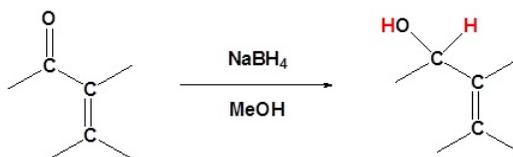
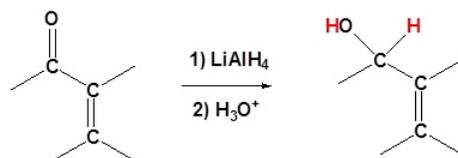


Example

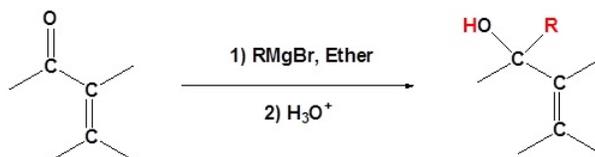


Nucleophiles which add 1,2 to α , β unsaturated carbonyls

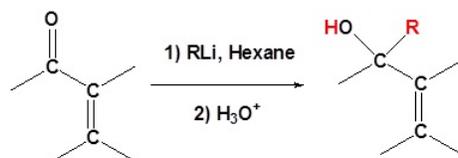
Metal Hydrides



Grignard Reagents



Organolithium Reagents



Contributors

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