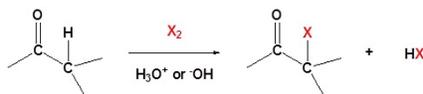


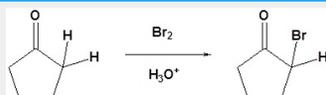
21.8: Halogenation at the α Carbon

A carbonyl containing compound with α hydrogens can undergo a substitution reaction with halogens. This reaction comes about because of the tendency of carbonyl compounds to form enolates in basic condition and enols in acidic condition. In these cases even weak bases, such as the hydroxide anion, is sufficient enough to cause the reaction to occur because it is not necessary for a complete conversion to the enolate. For this reaction Cl_2 , Br_2 or I_2 can be used as the halogens.

General reaction



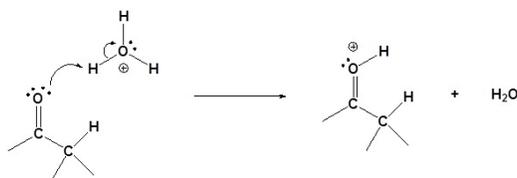
Example



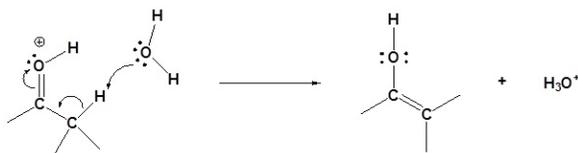
Acid Catalyzed Mechanism

Under acidic conditions the reaction occurs through the formation of an enol which then reacts with the halogen.

1) Protonation of the carbonyl



2) Enol formation



3) $\text{S}_{\text{N}}2$ attack



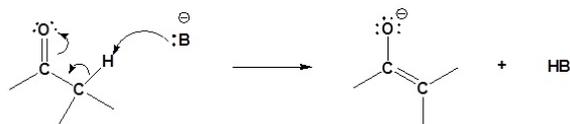
4) Deprotonation



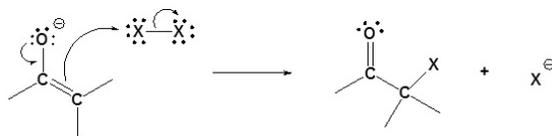
Base Catalyzed Mechanism

Under basic conditions the enolate forms and then reacts with the halogen. Note! This is base promoted and not base catalyzed because an entire equivalent of base is required.

1) Enolate formation

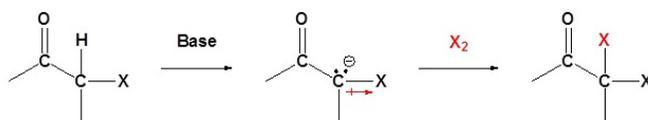


2) S_N2 attack



Overreaction during base promoted α halogenation

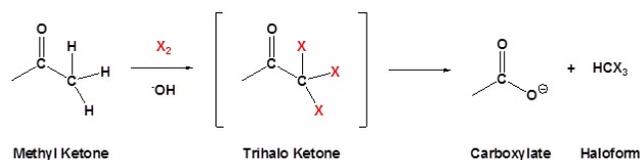
The fact that an electronegative halogen is placed on an α carbon means that the product of a base promoted α halogenation is actually more reactive than the starting material. The electron withdrawing effect of the halogen makes the α carbon even more acidic and therefore promotes further reaction. Because of this multiple halogenations can occur. This effect is exploited in the haloform reaction discussed later. If a monohalo product is required then acidic conditions are usually used.



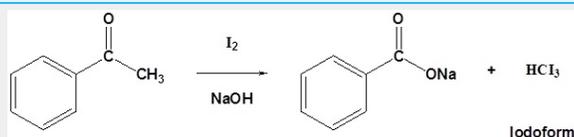
The Haloform Reaction

Methyl ketones typically undergo halogenation three times to give a trihalo ketone due to the increased reactivity of the halogenated product as discussed above. This trihalomethyl group is an effective leaving group due to the three electron withdrawing halogens and can be cleaved by a hydroxide anion to effect the haloform reaction. The product of this reaction is a carboxylate and a haloform molecule (CHCl₃, CHBr₃, CHI₃). Overall the haloform reaction represents an effective method for the conversion of methyl ketones to carboxylic acids. Typically, this reaction is performed using iodine because the subsequent iodoform (CHI₃) is a bright yellow solid which is easily filtered off.

General reaction

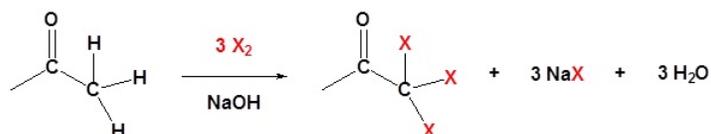


Example: The Haloform Reaction

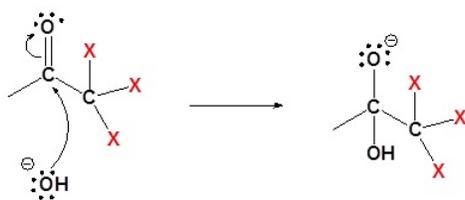


Mechanism

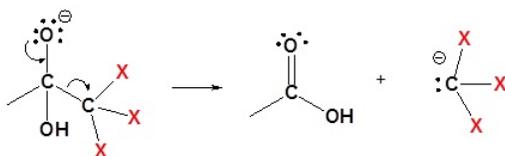
1) Formation of the trihalo species



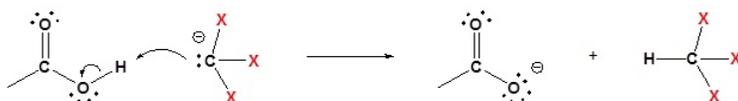
2) Nucleophilic attack on the carbonyl carbon



3) Removal of the leaving group

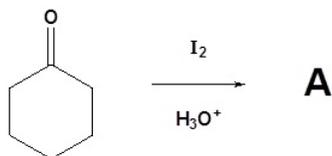


4) Deprotonation



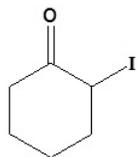
Problems

1) Please draw the products of the following reactions



Answers

1)



A

Contributors

- Prof. Steven Farmer (Sonoma State University)

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