

20.18

Preparation of Nitriles

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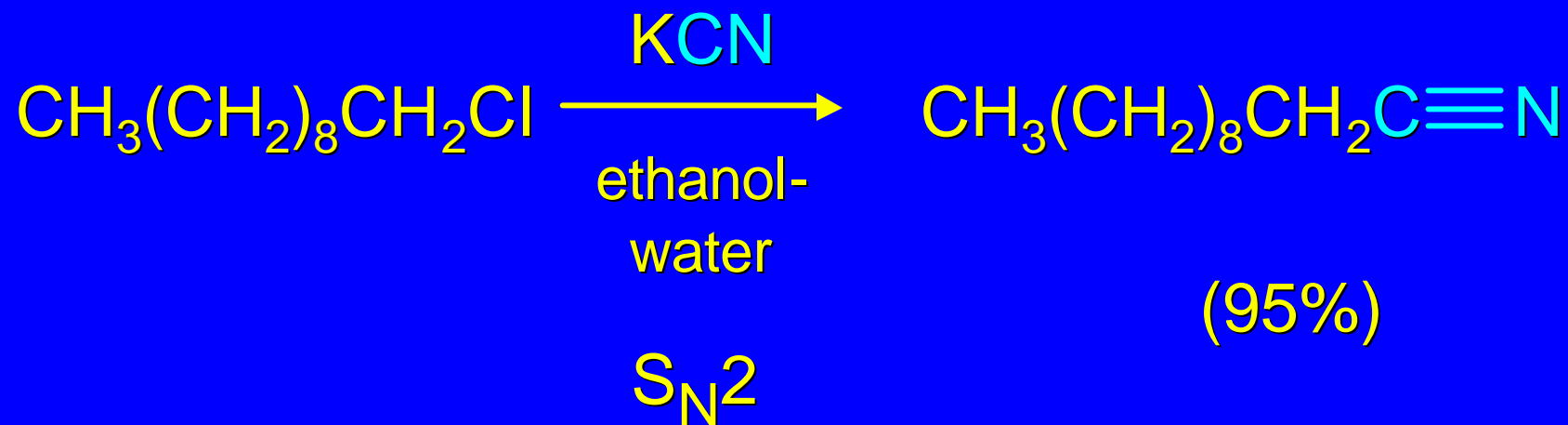
Nitriles are prepared by:

nucleophilic substitution by cyanide on
alkyl halides (Sections 8.1 and 8.13)

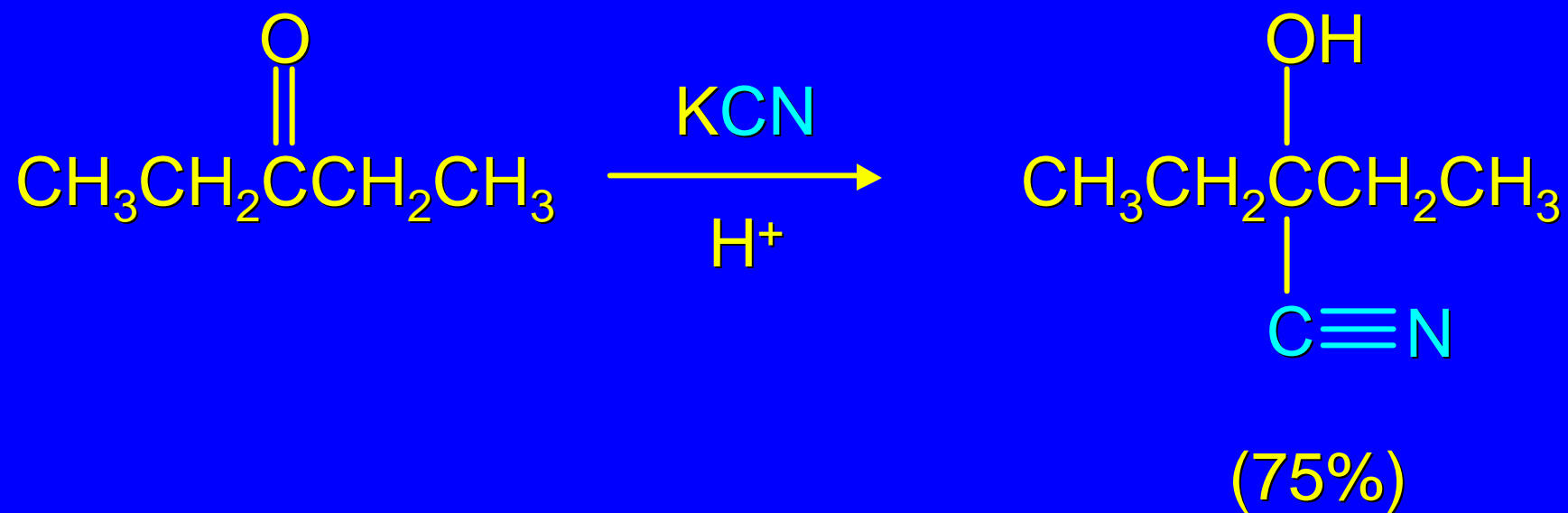
cyanohydrin formation (Section 17.7)

dehydration of amides

Example



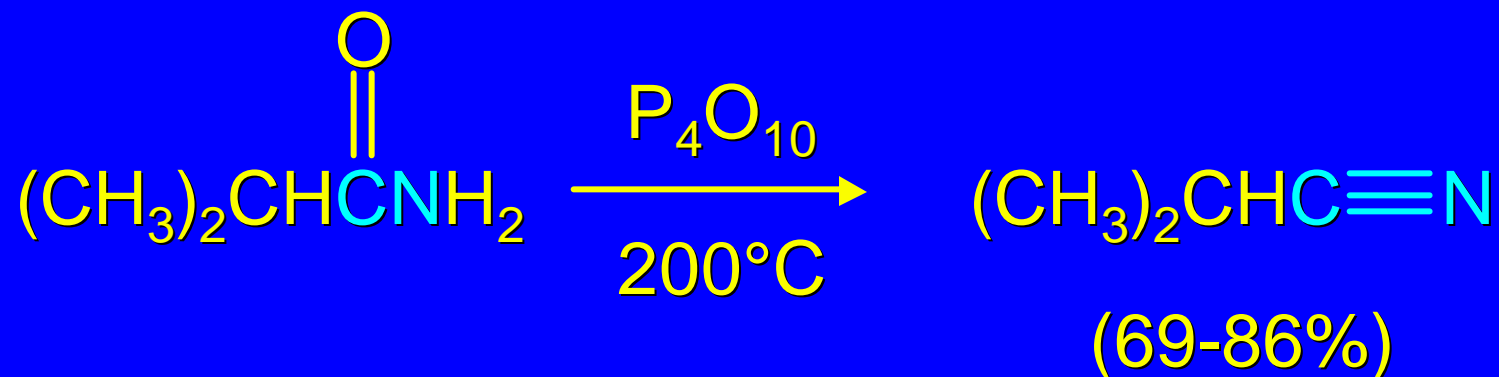
Example



Preparation of Nitriles

By dehydration of amides

uses the reagent P_4O_{10} (often written as P_2O_5)



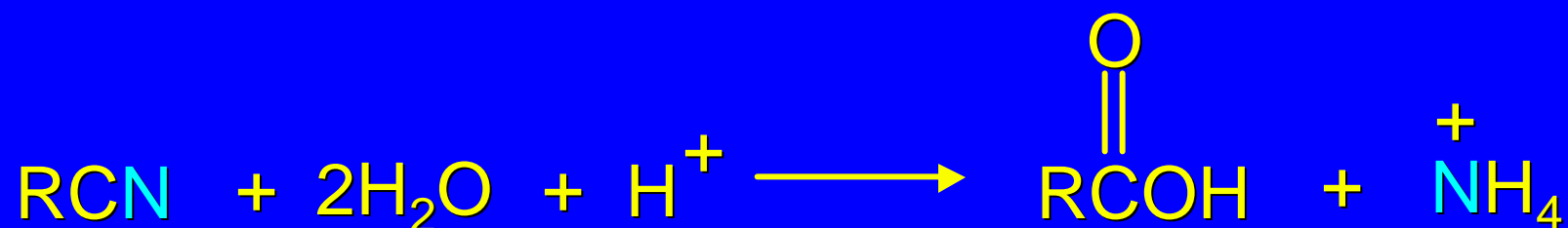
20.19

Hydrolysis of Nitriles

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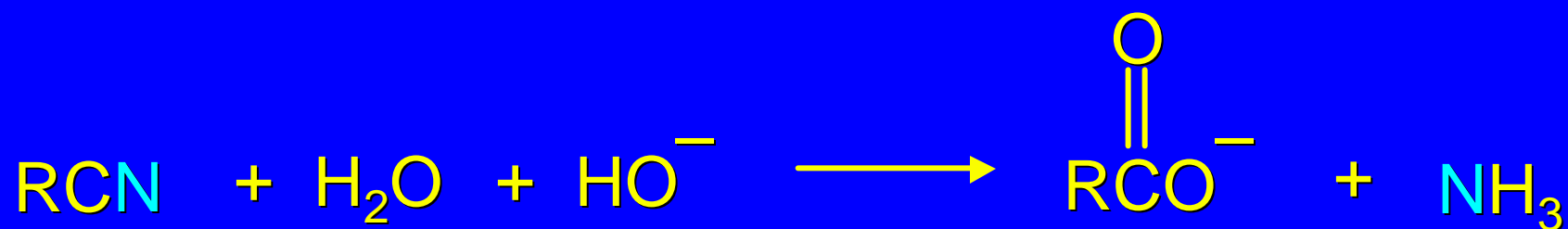
Hydrolysis of nitriles resembles the hydrolysis of amides. The reaction is irreversible.

Ammonia is produced and is protonated to ammonium ion in acid solution.

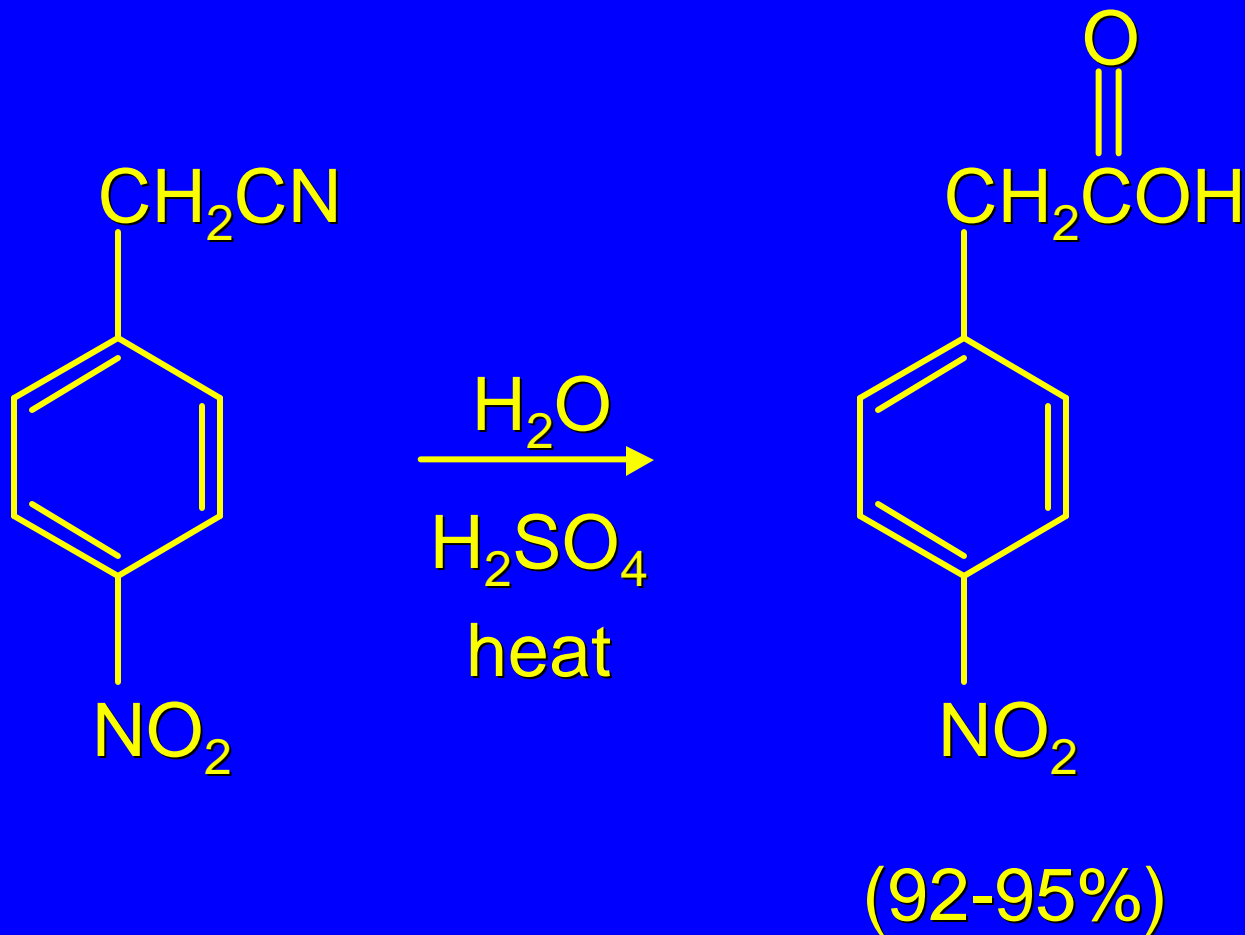


Hydrolysis of Nitriles

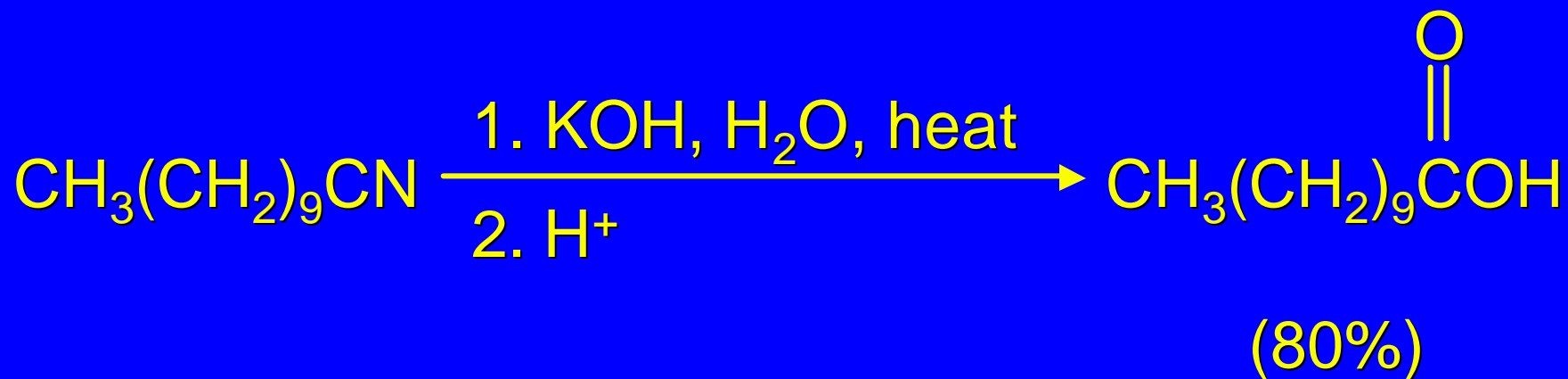
In basic solution the carboxylic acid product is deprotonated to give a carboxylate ion.



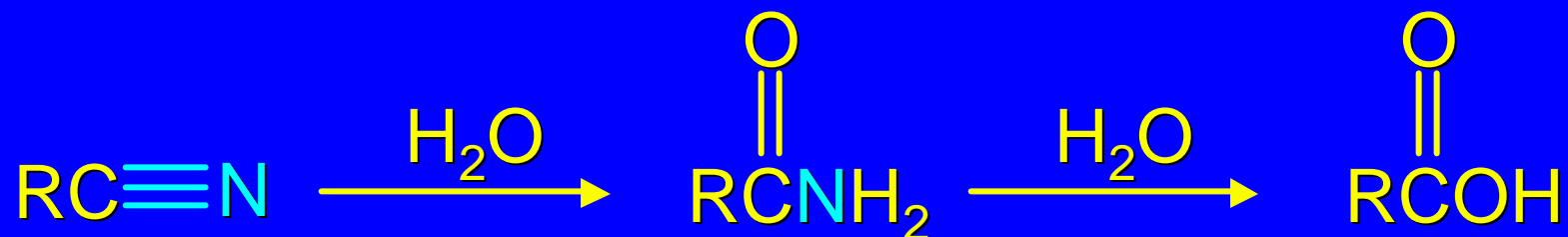
Example: Acid Hydrolysis



Example: Basic Hydrolysis



Mechanism of Hydrolysis of Nitriles

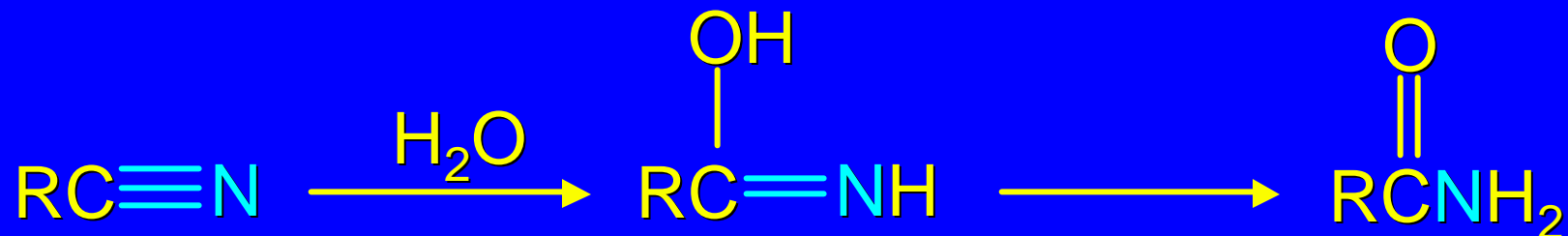


Hydrolysis of nitriles proceeds via the corresponding amide.

We already know the mechanism of amide hydrolysis.

Therefore, all we need to do is to see how amides are formed from nitriles under the conditions of hydrolysis.

Mechanism of Hydrolysis of Nitriles

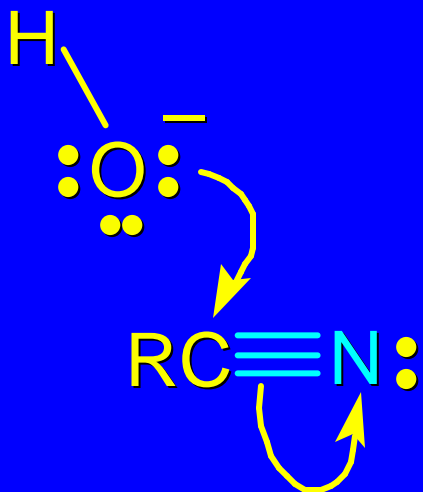


The mechanism of amide formation is analogous to that of conversion of alkynes to ketones.

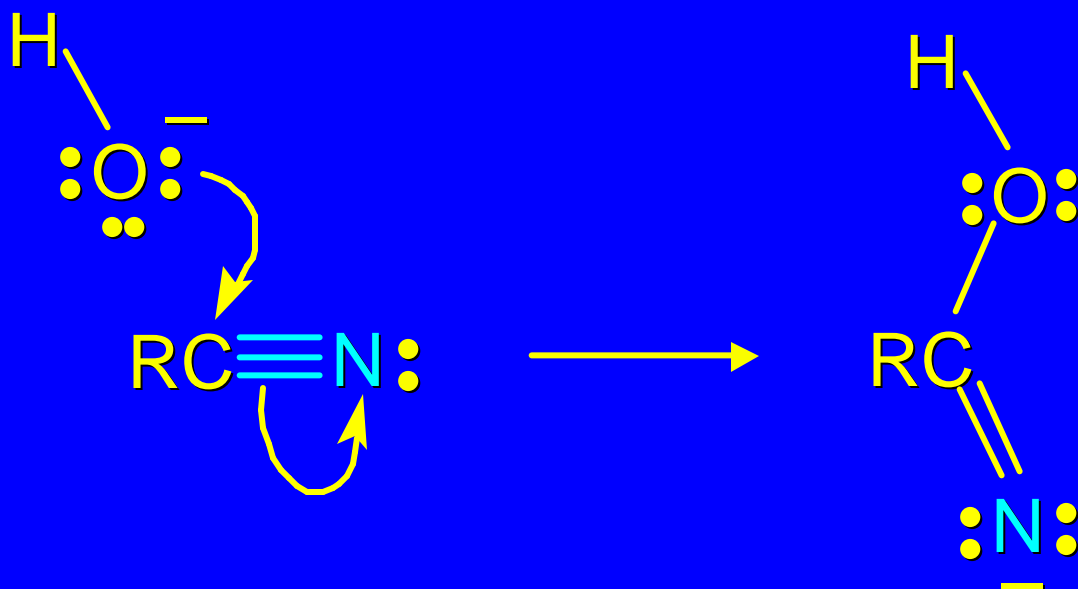
It begins with the addition of water across the carbon-nitrogen triple bond.

The product of this addition is the nitrogen analog of an enol. It is transformed to an amide under the reaction conditions.

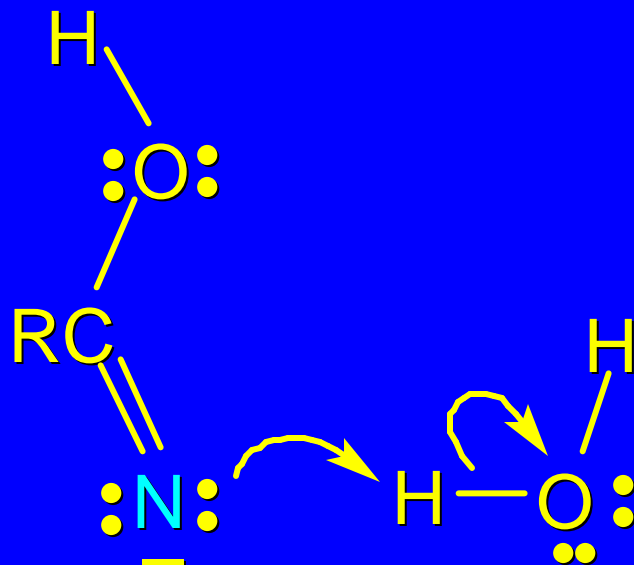
Step 1



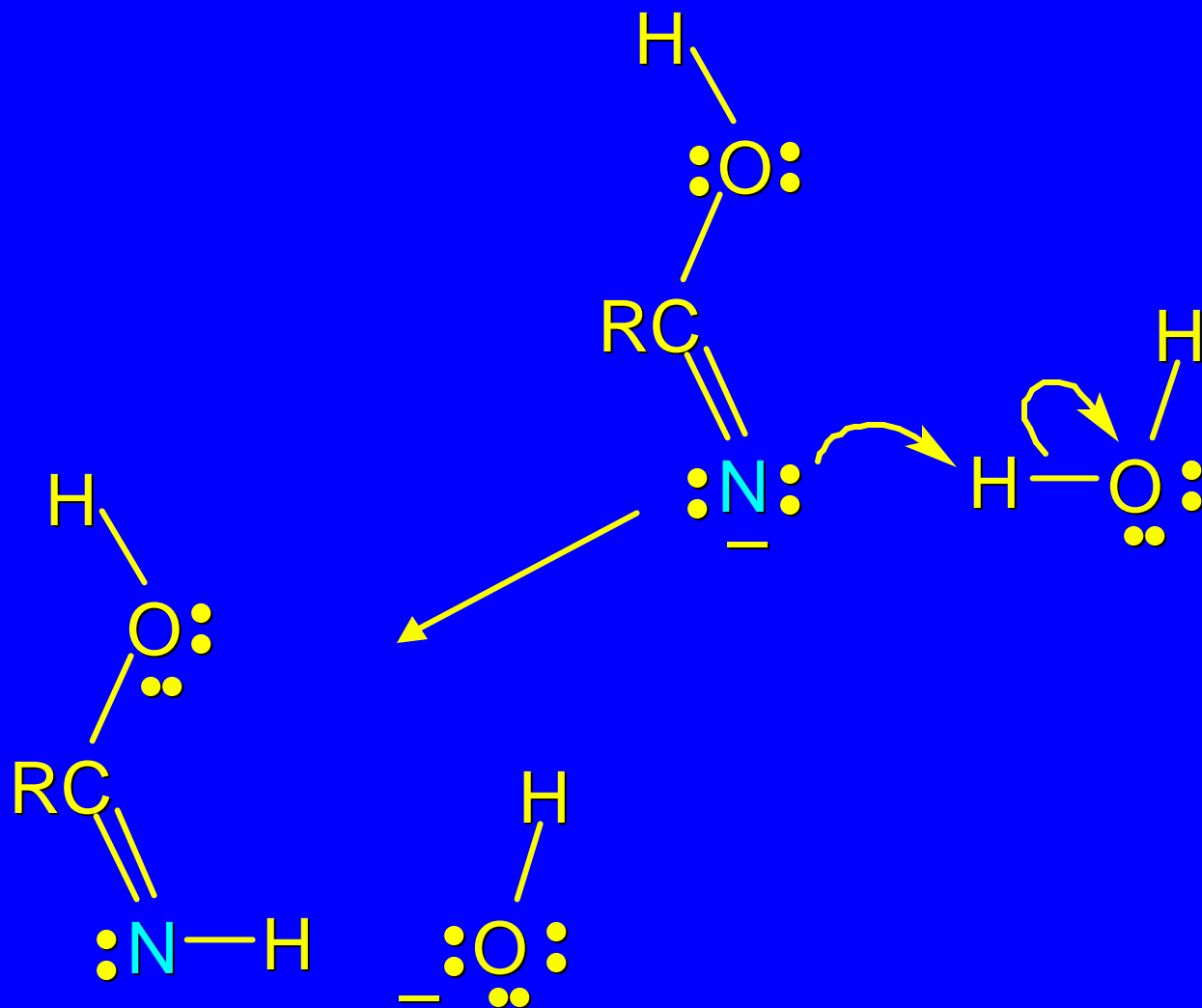
Step 1



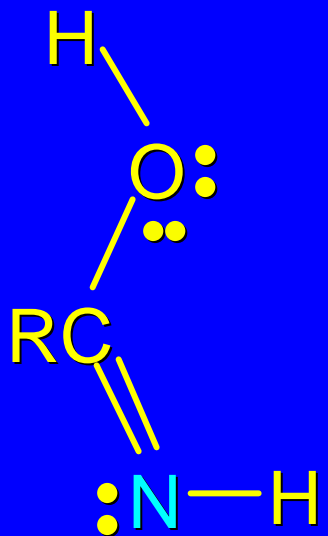
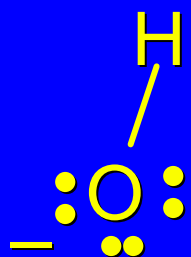
Step 2



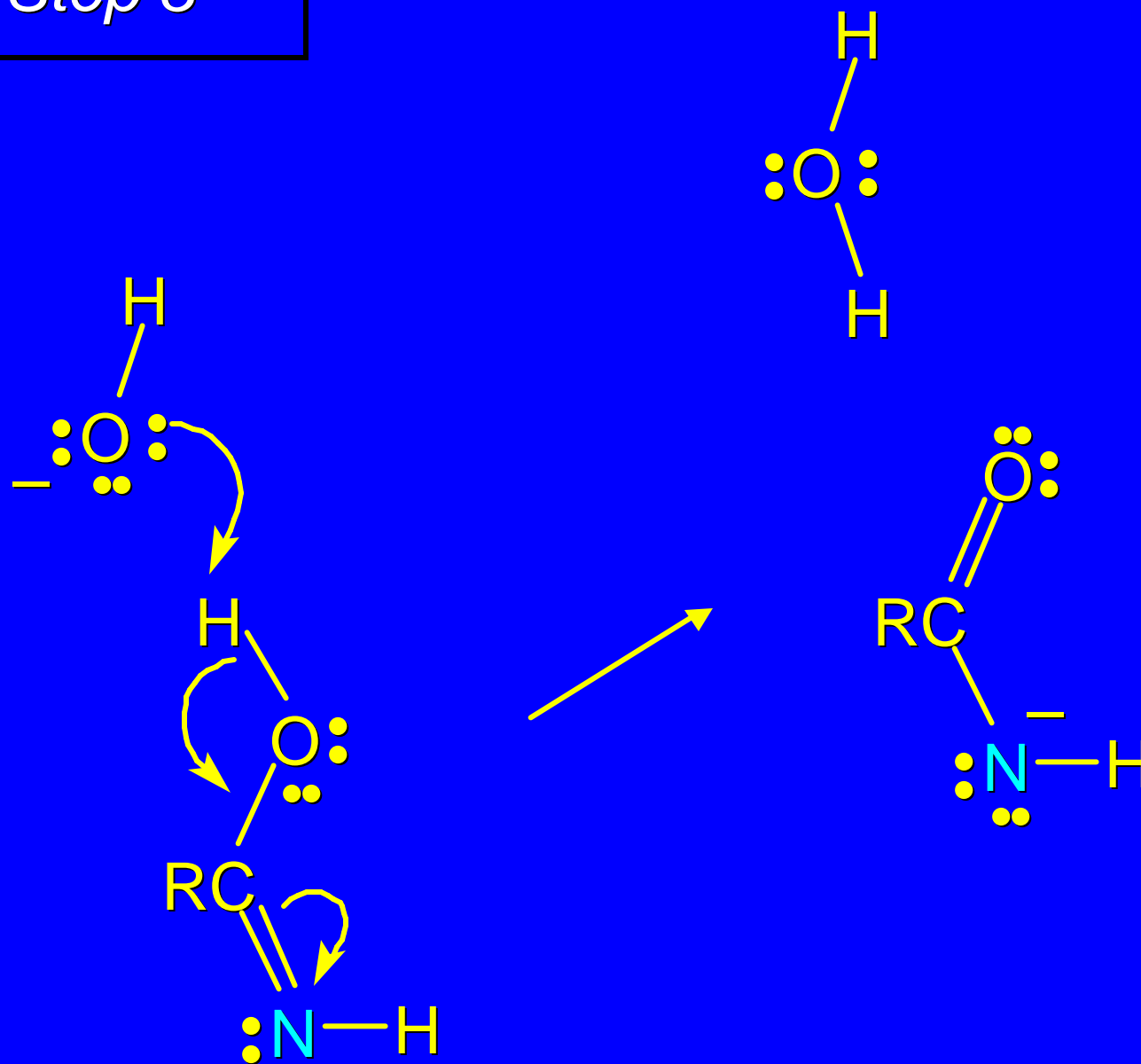
Step 2



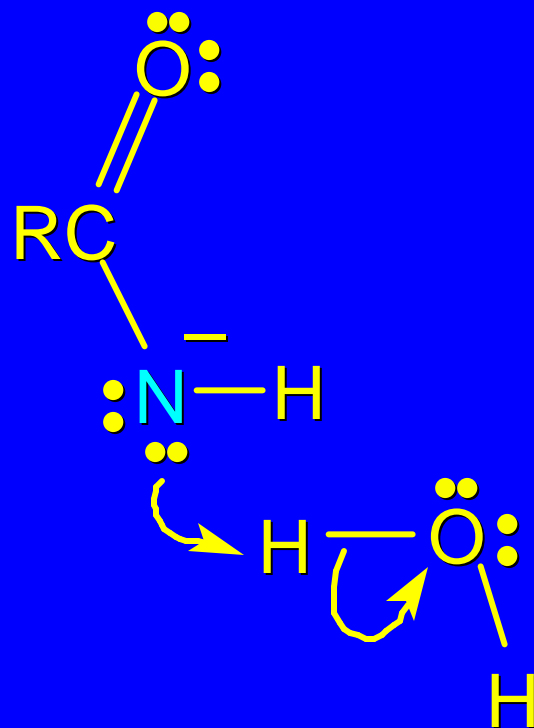
Step 3



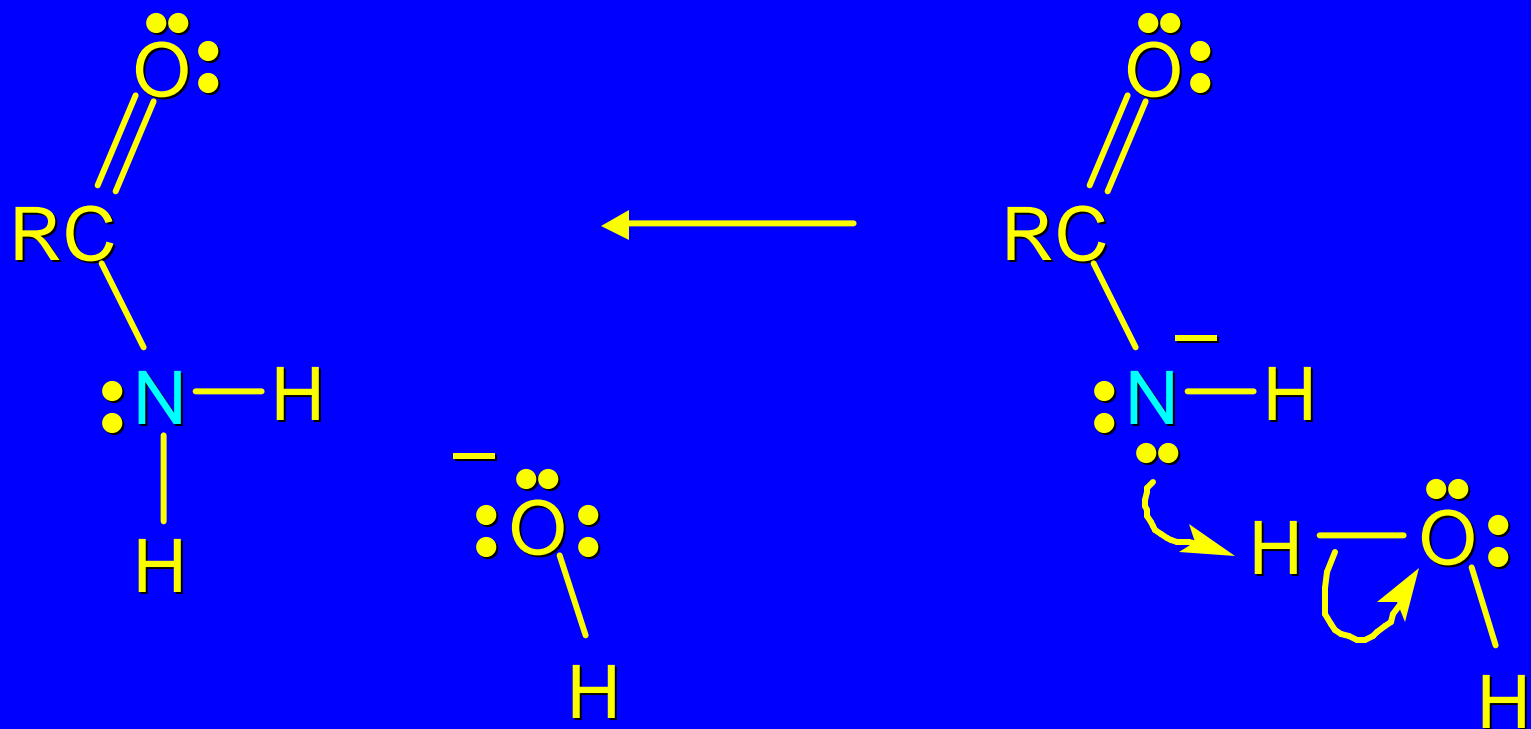
Step 3



Step 4



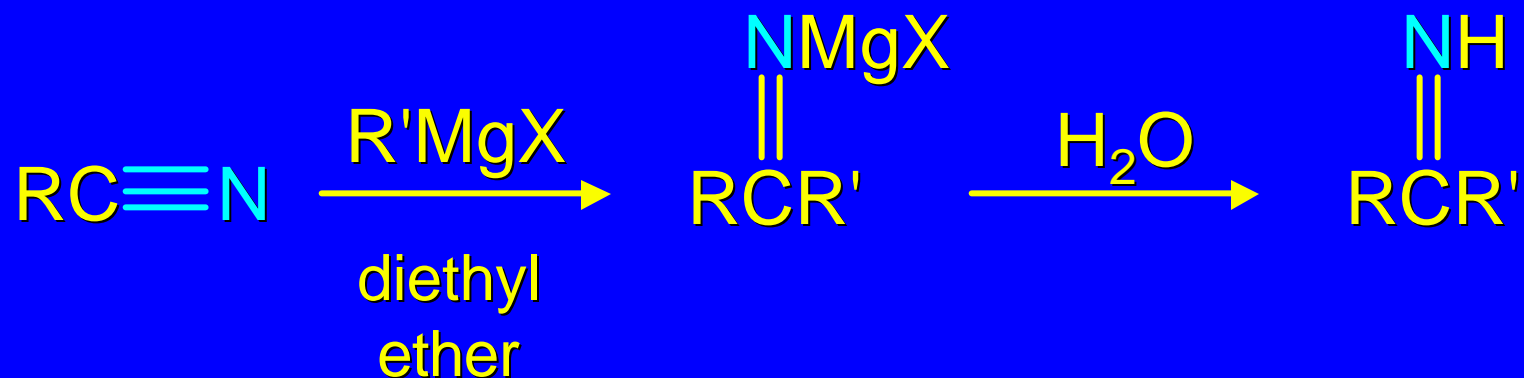
Step 4



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Addition of Grignard Reagents
to Nitriles

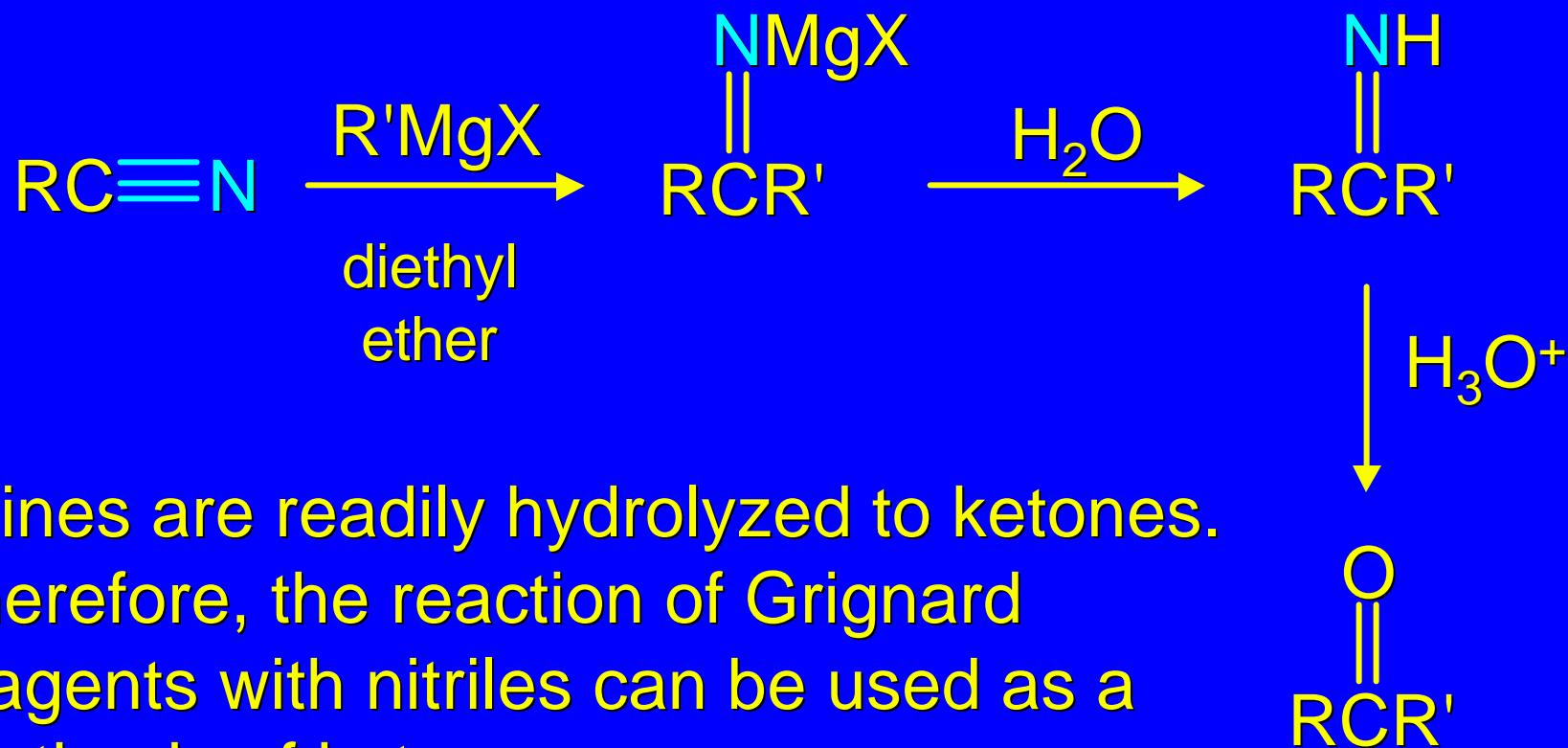
Addition of Grignard Reagents to Nitriles



Grignard reagents add to carbon-nitrogen triple bonds in the same way that they add to carbon-oxygen double bonds.

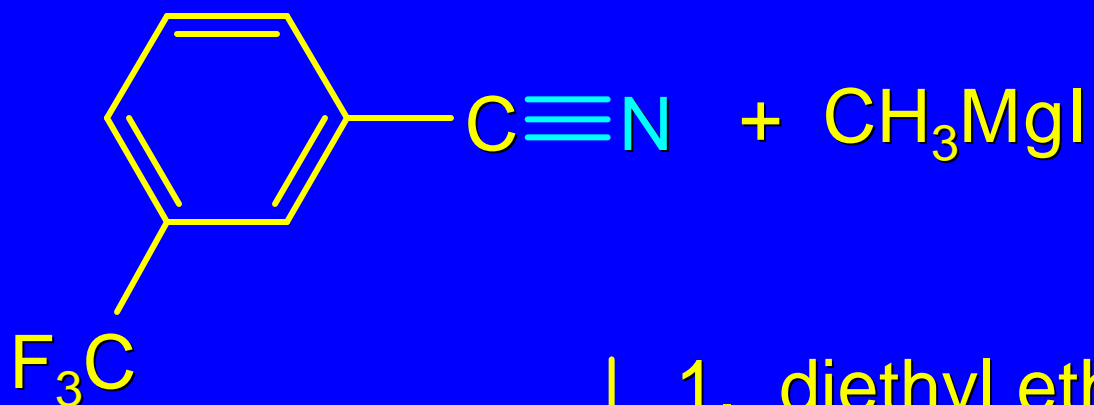
The product of the reaction is an imine.

Addition of Grignard Reagents to Nitriles



Imines are readily hydrolyzed to ketones. Therefore, the reaction of Grignard reagents with nitriles can be used as a synthesis of ketones.

Example



1. diethyl ether
2. H_3O^+ , heat

