17.5
Reactions of Aldehydes and Ketones:
A Review and a Preview

Reactions of Aldehydes and Ketones

Already covered in earlier chapters:

reduction of C=O to CH_2

Clemmensen reduction

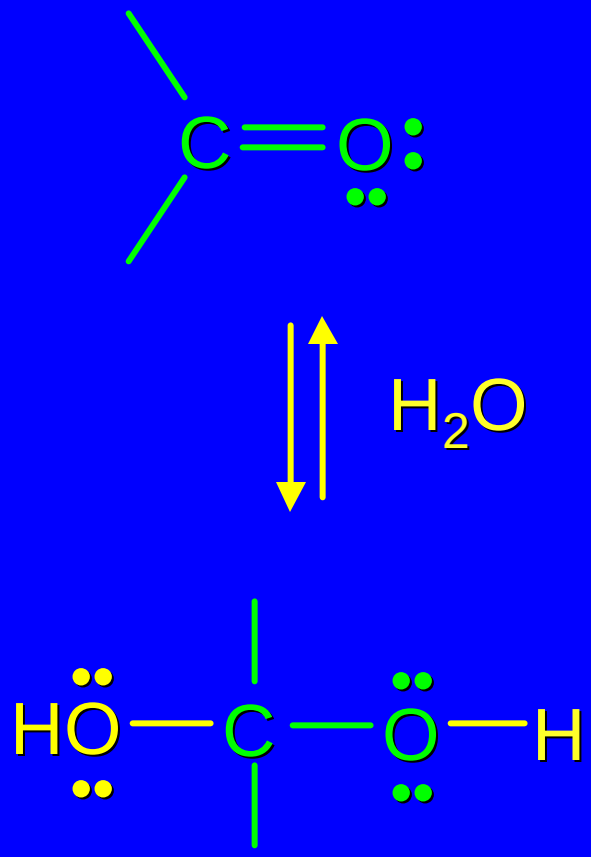
Wolff-Kishner reduction

reduction of C=O to CHOH

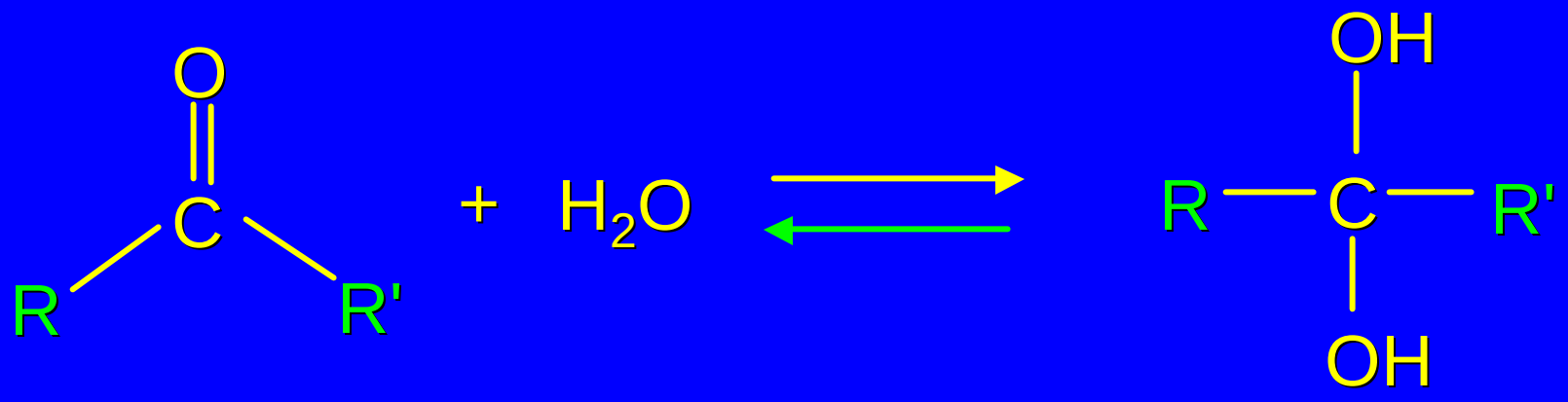
addition of Grignard and organolithium reagents

17.6
Principles of Nucleophilic Addition to Carbonyl Groups: Hydration of Aldehydes and Ketones

Hydration of Aldehydes and Ketones



Substituent Effects on Hydration Equilibria



compared to H

electronic:	alkyl groups stabilize reactants
steric:	alkyl groups crowd product

Equilibrium Constants for Hydration

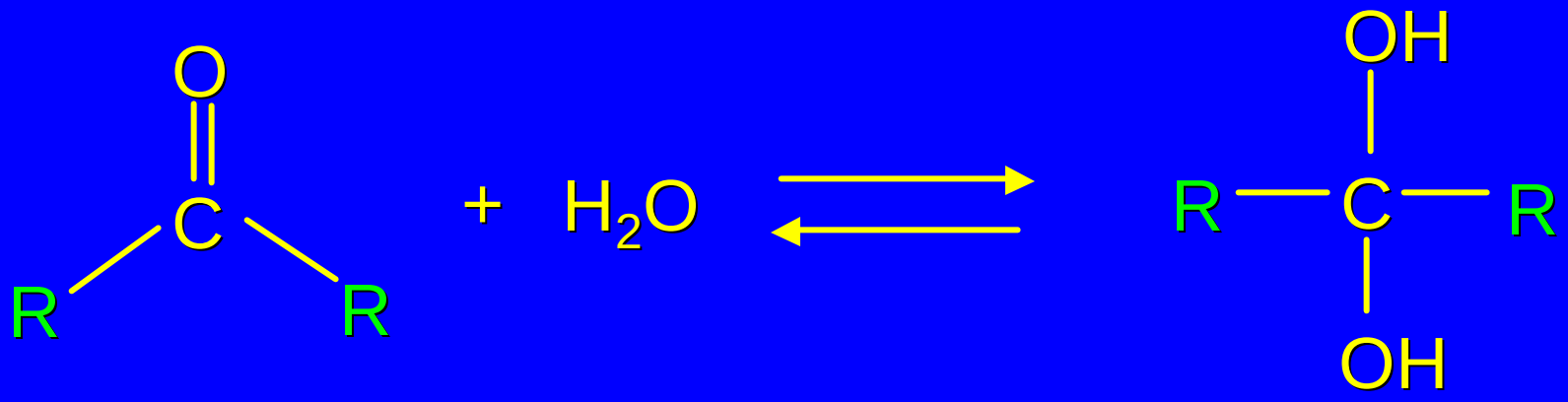
C=O	hydrate	*K*	%
$CH_2=O$	$CH_2(OH)_2$	41	99.96
$CH_3CH=O$	$CH_3CH(OH)_2$	0.018	50
$(CH_3)_3CCH=O$	$(CH_3)_3CCH(OH)_2$	0.0041	19
$(CH_3)_2C=O$	$(CH_3)_2C(OH)_2$	0.000025	0.14

When does equilibrium favor hydrate?

when carbonyl group is destabilized

- alkyl groups stabilize C=O
- electron-withdrawing groups destabilize C=O

Substituent Effects on Hydration Equilibria

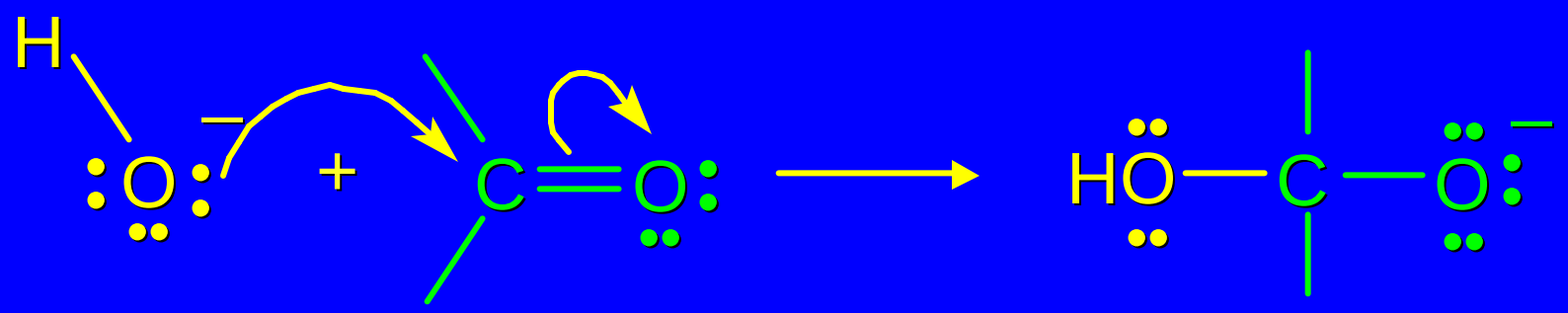


← $R = CH_3$: $K = 0.000025$

$R = CF_3$: $K = 22{,}000$ →

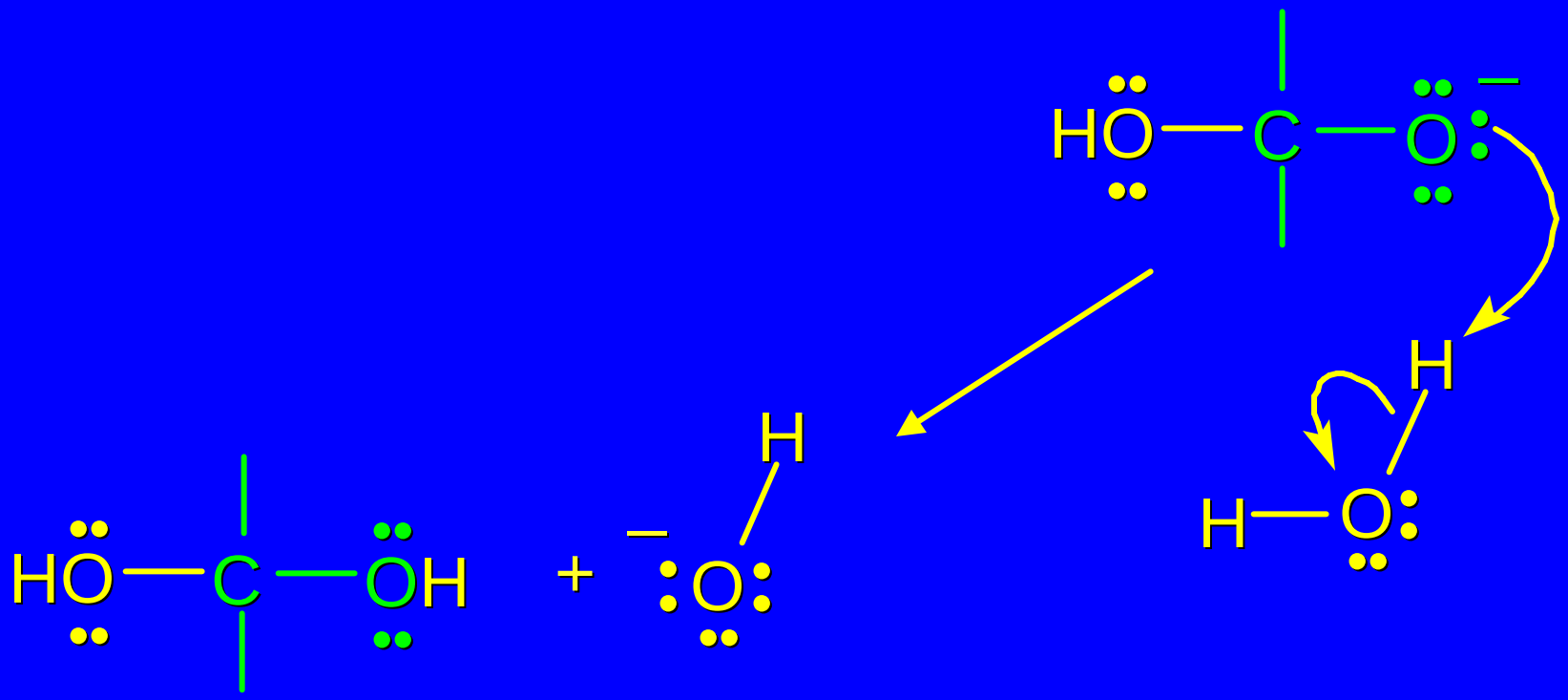
Mechanism of Hydration (base)

Step 1:



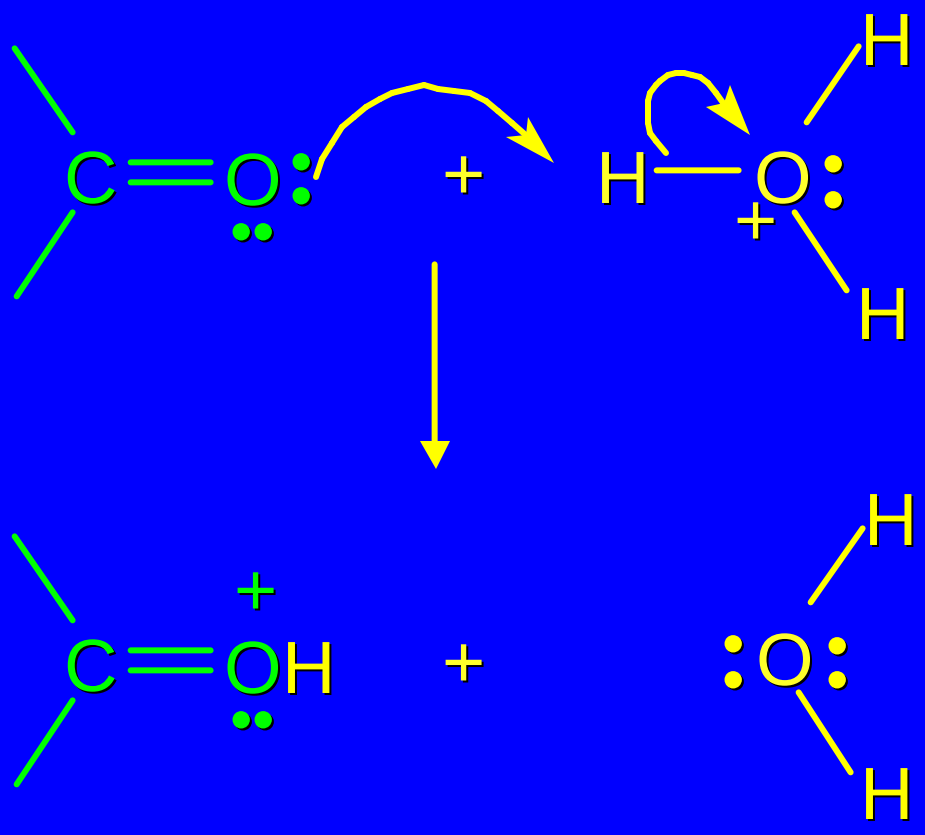
Mechanism of Hydration (base)

Step 2:



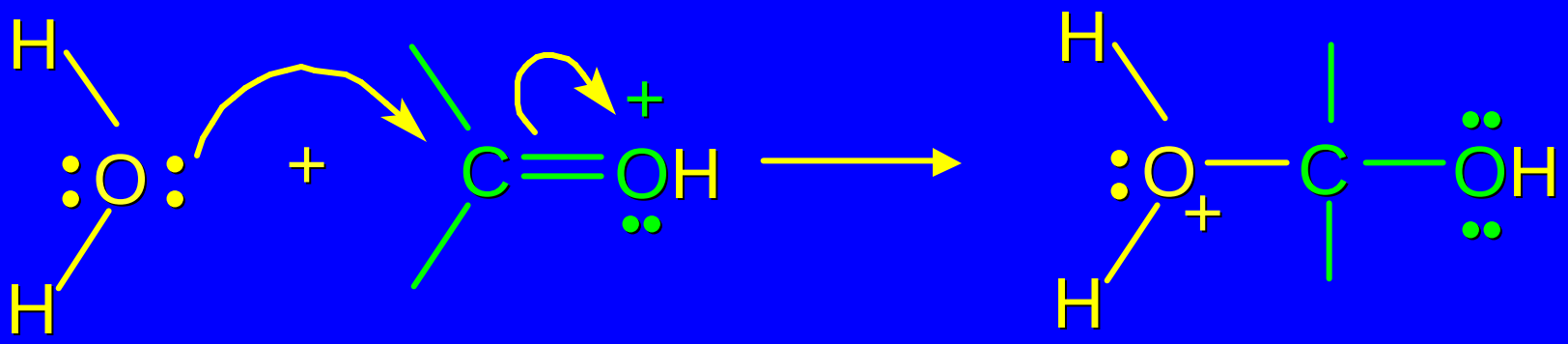
Mechanism of Hydration (acid)

Step 1:



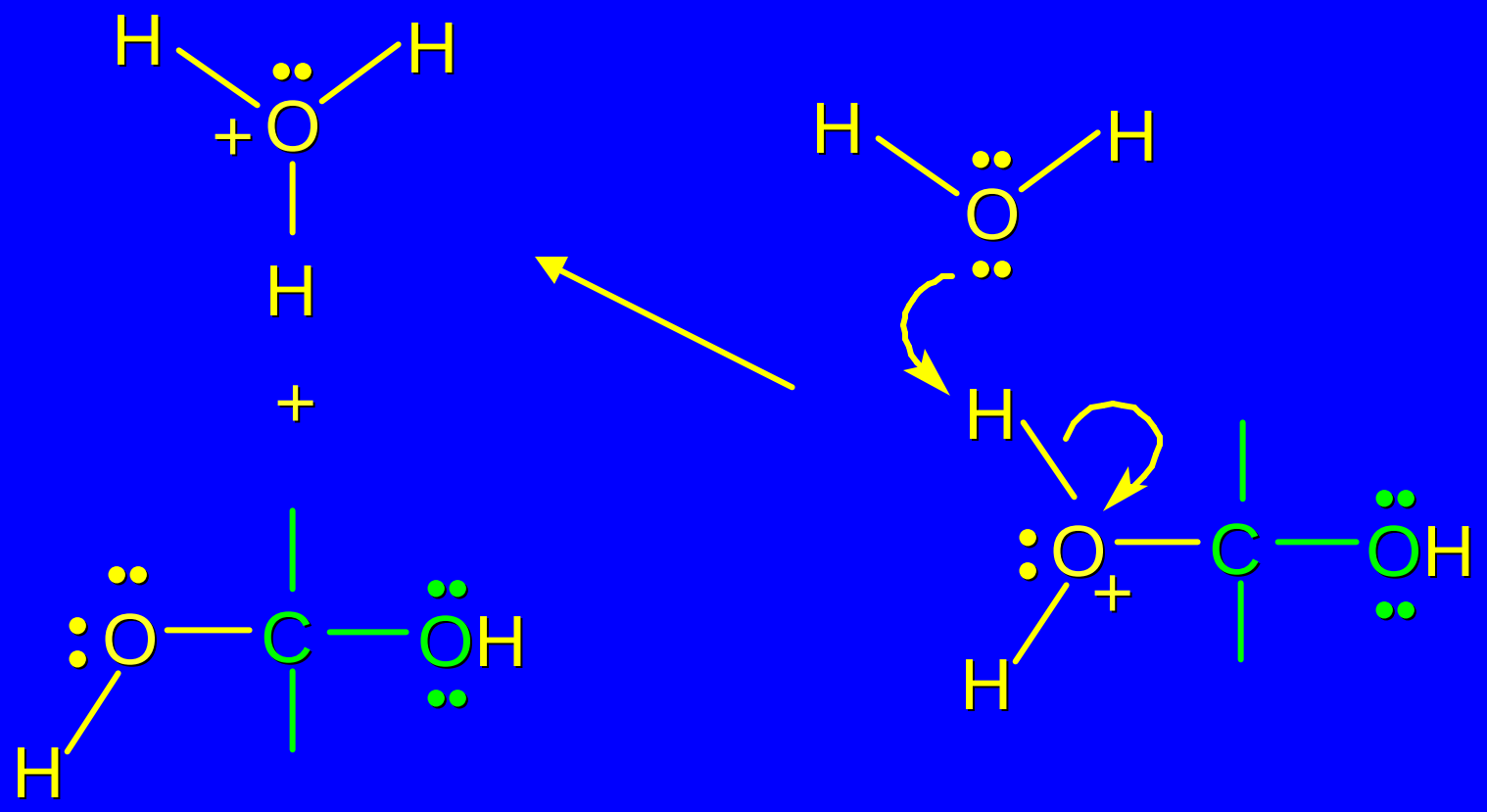
Mechanism of Hydration (acid)

Step 2:



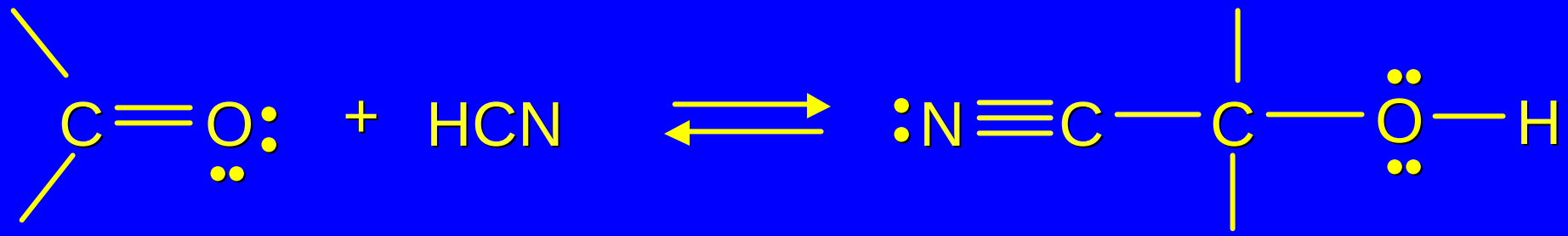
Mechanism of Hydration (acid)

Step 3:

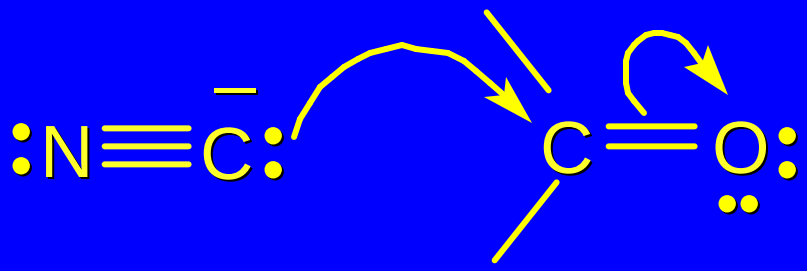


17.7
Cyanohydrin Formation

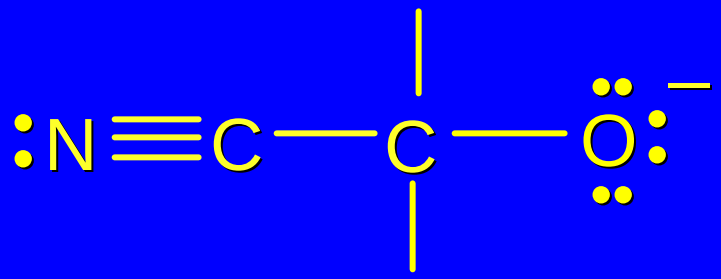
Cyanohydrin Formation



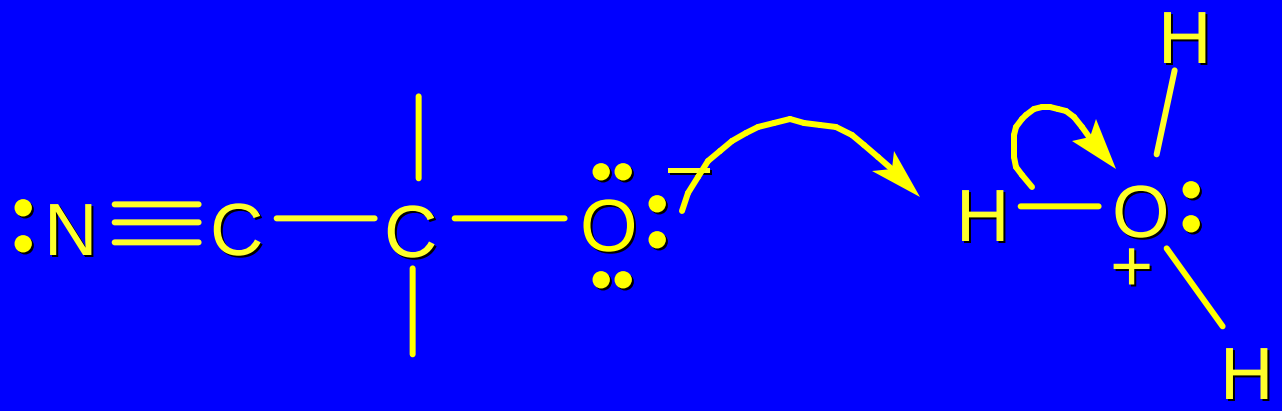
Cyanohydrin Formation



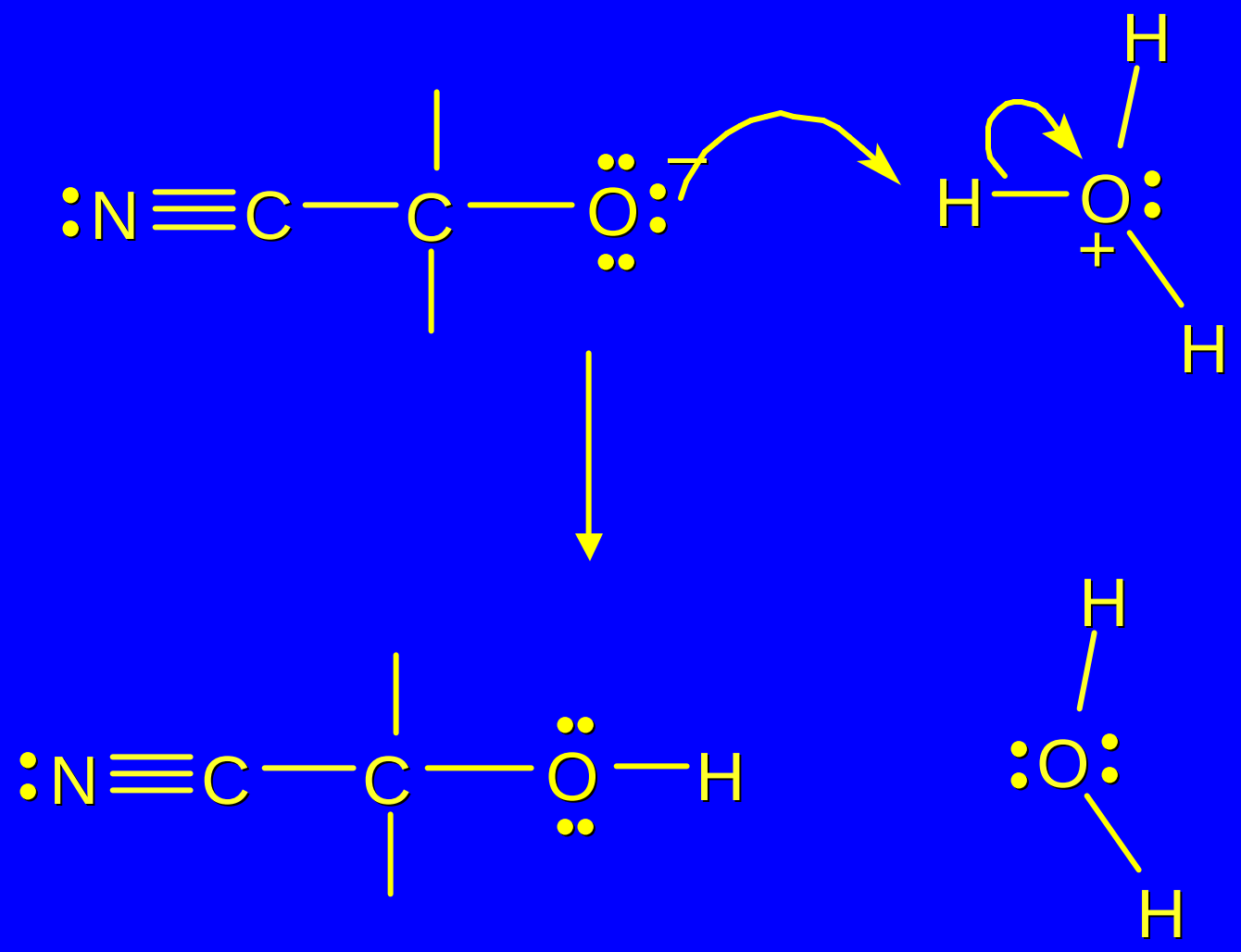
Cyanohydrin Formation



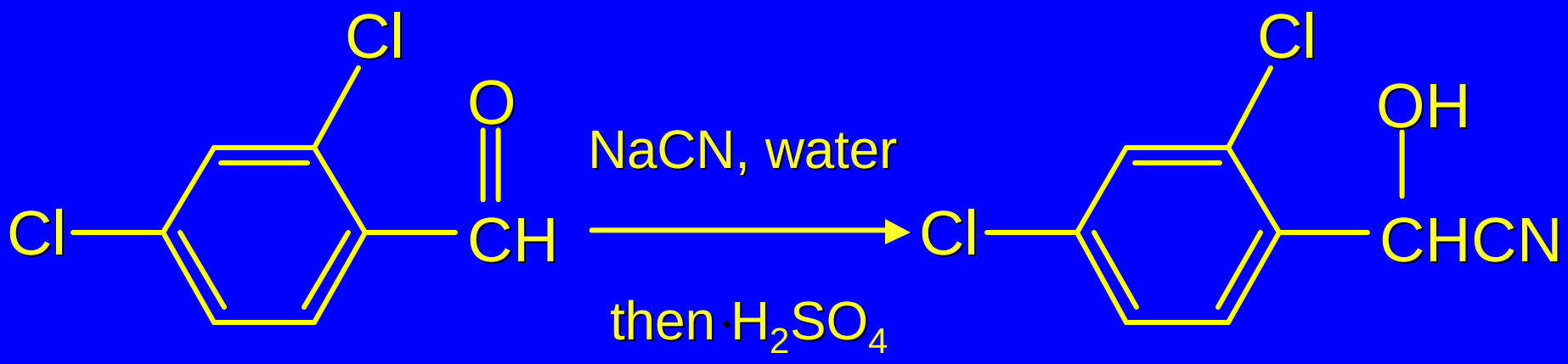
Cyanohydrin Formation



Cyanohydrin Formation

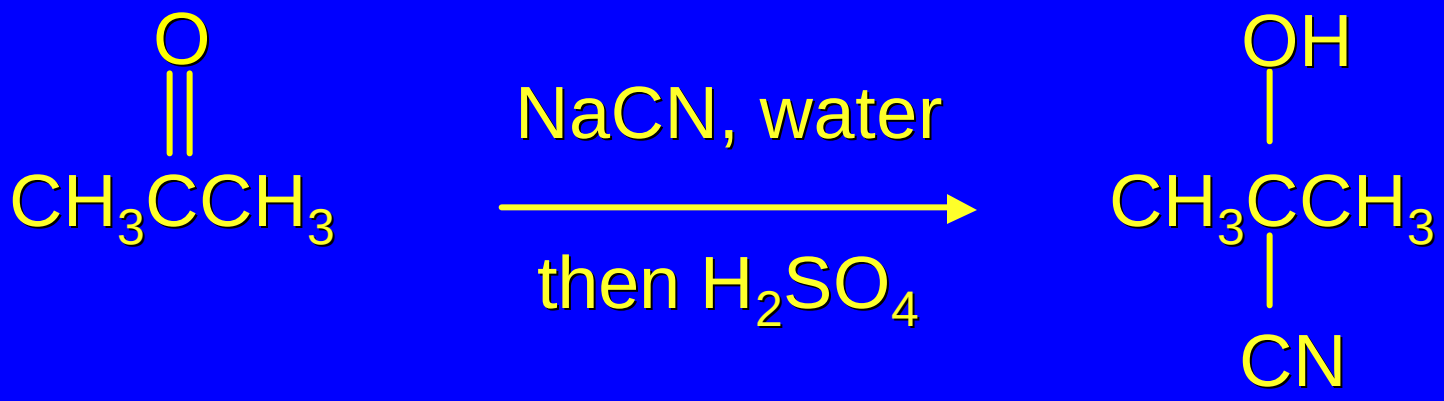


Example



2,4-Dichlorobenzaldehyde cyanohydrin (100%)

Example



(77-78%)

Acetone cyanohydrin is used in the synthesis of methacrylonitrile (see problem 17.6).