Synthesis of Ketones and Aldehydes

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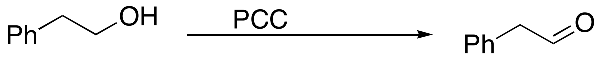

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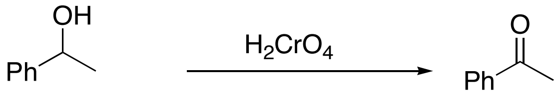

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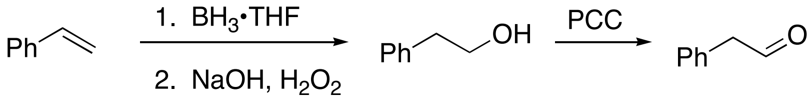

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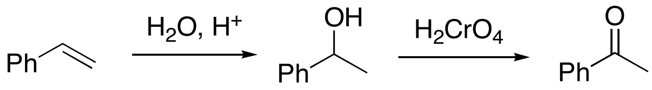

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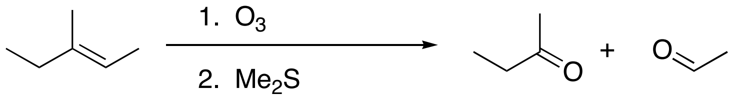

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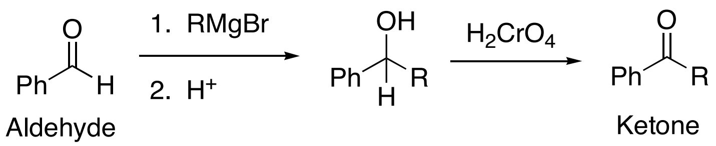

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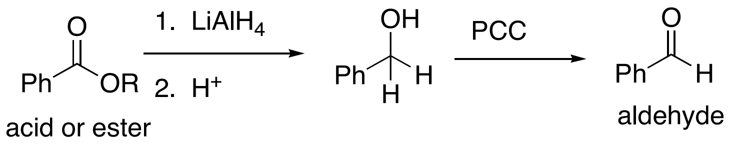

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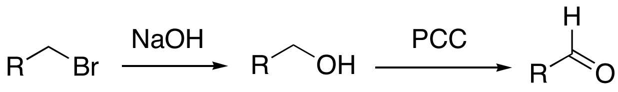

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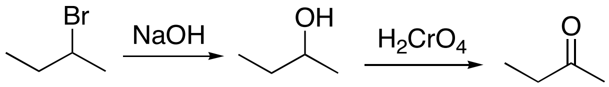

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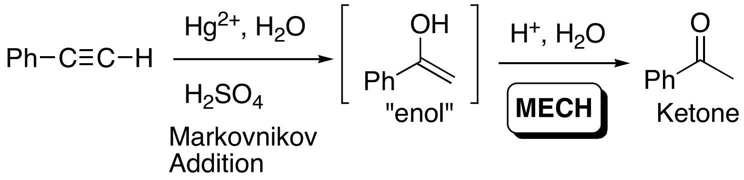

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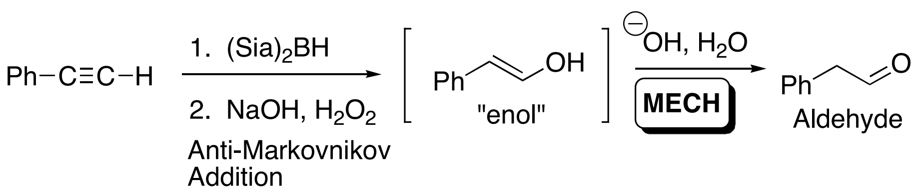

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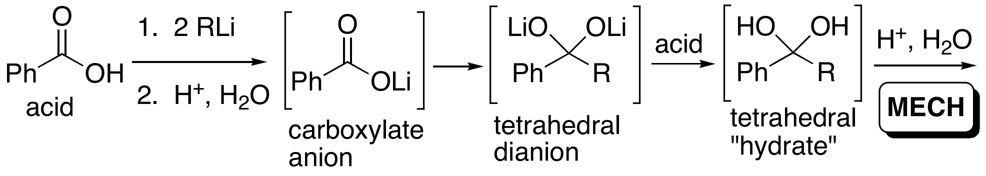
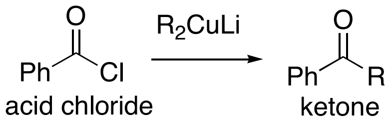
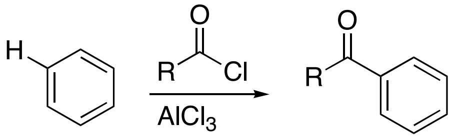
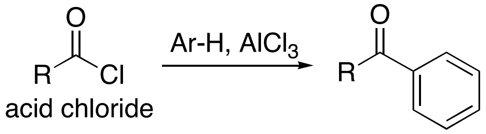
12  18.9

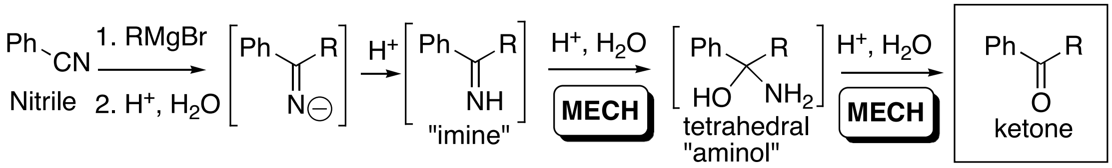
13  18.11

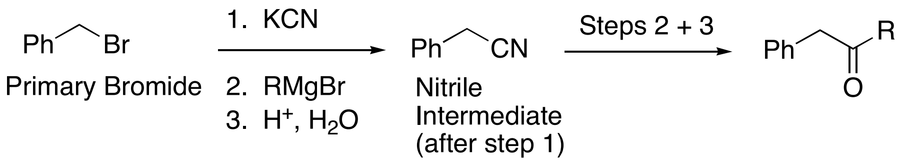
14  18.11

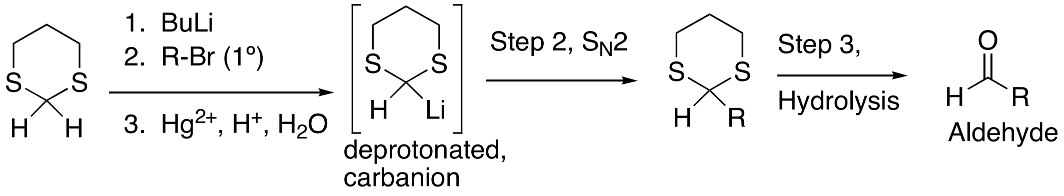
Aromatic ketone
(from the aryl group's perspective)

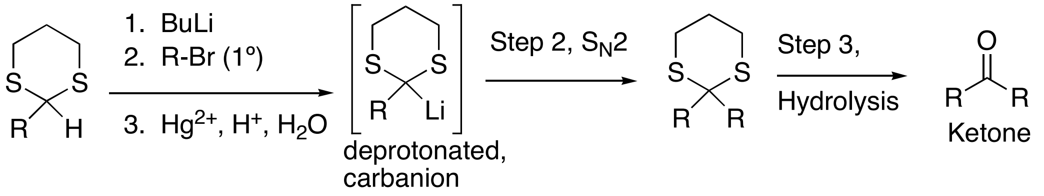


Aromatic ketone
(from the acyl group's perspective)

15  18.10

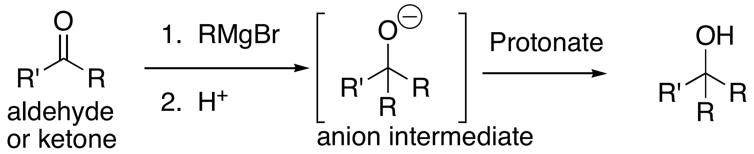
16  18.10

17  18.8

18  18.8

Reactions of Ketones and Aldehydes

19

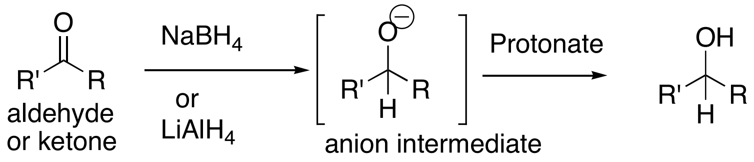


18.12, 10.9

Anionic

Mech: Addition-Protonation. Strong nucleophile, Strongly anionic. Irreversible.

20

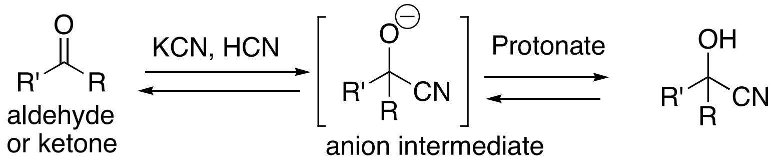


18.12, 10.11

Anionic

Mech: Addition-Protonation. Strong nucleophile, Strongly anionic. Irreversible.

21

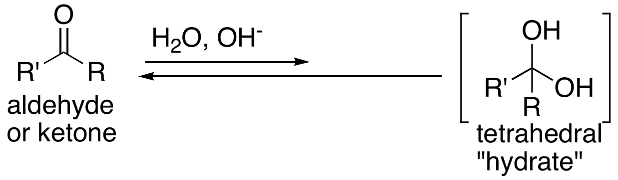


18.15

Anionic

Mech: Addition-Protonation. Medium nucleophile, Weakly anionic; literally buffered. Reversible.

22



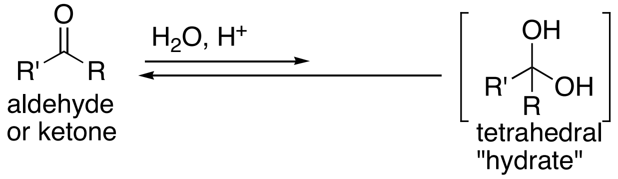
"Hydrates" are present only as transient equilibrium species. They never form to 100% and are never isolable. Always in equilbrium their aldehyde or ketone.

18.14

Anionic

Mech Forward: Addition-Protonation. Nucleophile, anionic mechanism. Reversible.
Mech Reverse: Deprotonation-Elimination. Anionic mechanism. Reversible.

23

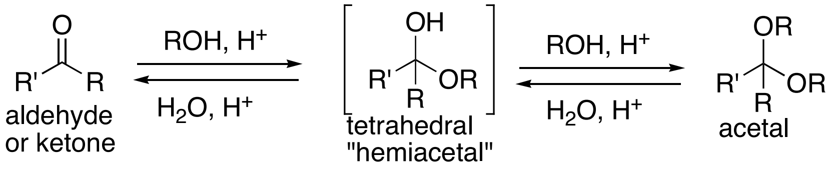


"Hydrates" are present only as transient equilibrium species. They never form to 100% and are never isolable. Always in equilbrium with their aldehyde or ketone.

18.14

Cationic

Mech Forward: Protonation-Addition-deprotonation. Weakly nucleophile, cationic mechanism. Reversible.
Mech Reverse: Protonation-Elimination-deprotonation. Cationic E1-type mechanism. Reversible.

24  18.18, 18.19

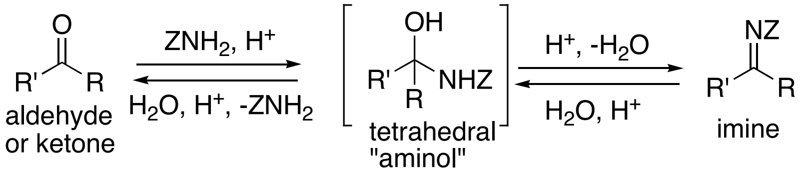
Cationic

Mech Forward: Protonation-Addition-deprotonation (hemiacetal) Protonation-elimination-addition-deprotonation (acetal). Weak nucleophile, cationic mechanism. Reversible.

Mech Reverse: Protonation-Elimination-Addition-deprotonation. (hemiacetal) protonation-elimination-deprotonation (aldehyde or ketone). Reversible.

Notes:

- Reactions are reversible
- The "hemiacetal" is an intermediate, and can never be isolated
- The acetal can be isolated.
- Equilibrium considerations (LeChatelier's principle) apply. When water is plentiful, things go to the left. When water is scarce or removed, and alcohol is abundant, things drive to the right.
- Use H_2O/H^+ to hydrolyze an acetal back to an aldehyde or ketone
- Use $MeOH/H^+$ to convert an aldehyde to an acetal
- Use $HOCH_2CH_2OH/H^+$ to convert a ketone to an acetal
- Aldehydes or ketones can be temporarily "protected" as their acetals, then later "deprotected" by hydrolysis

25  18.16, 18.17

Cationic

Mech Forward: Protonation-Addition-deprotonation (aminol) Protonation-elimination- deprotonation (imine). Mild nucleophile, cationic mechanism, buffered conditions. Reversible. Note: sometimes addition precedes protonation, or is concerted with protonation.

Mech Reverse: Protonation-Addition-deprotonation (aminol) Protonation-elimination- deprotonation (aldehyde or ketone). Reversible.

Notes:

- "Z" can be a carbon, nitrogen, oxygen, or hydrogen atom/group.
- The "aminol" can't be isolated, it's only present at equilibrium.
- Equilibrium factors apply. Water drives to the carbonyl side; removal of water drives to the imine side.

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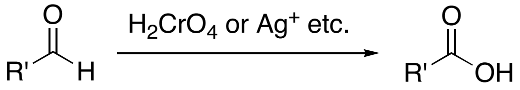
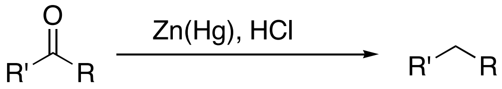


18.20

No Mech Responsibility

"Tollens test" is a common chemical test for aldehydes. Ag^+ undergoes redox reaction with aldeydes to produce shiny Ag metal, or a "silver mirror".

27



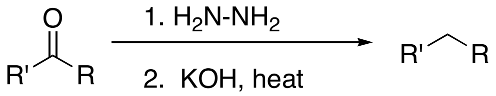
Acidic!
Works best for aromatic ketones.

18.21

Notes:

- Acidic conditions. Doesn't work well for molecules with acid-sensitive functionality.
- Works best for aromatic carbonyls. Saturated carbonyls are slower and less efficient.
- Acidic nature is complementary to the basic analog below.

28



Basic!

18.21

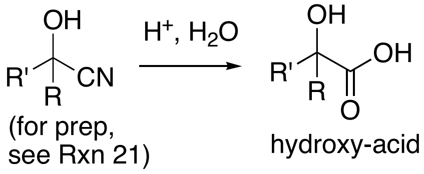
No Mech Responsibility

Notes:

- Basic conditions. Doesn't work well for molecules with base-sensitive functionality.

Basic nature is complementary to the acidic analog above.

29



18.15

No Mech Responsibility

Notes:

- Unique access to 2-hydroxyacids..

Used in combination with reaction 21, the formation of the hydroxy-nitrile.