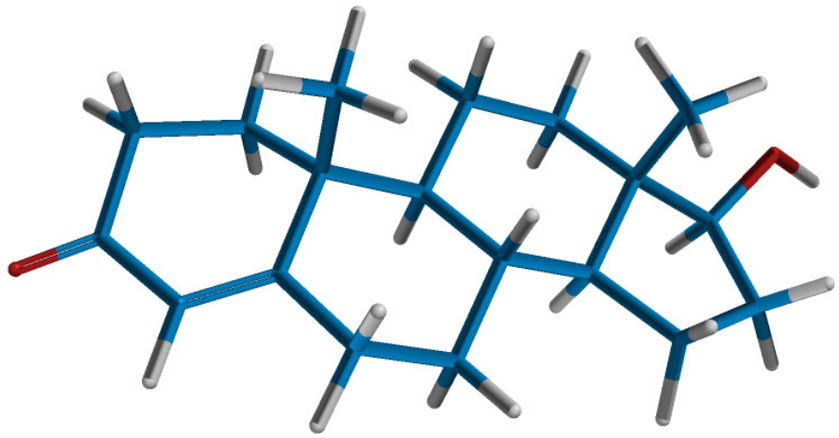
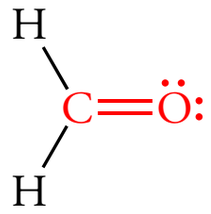
18 Aldehydes and Ketones

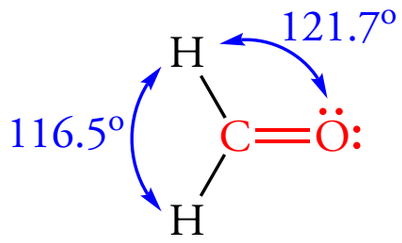


Testosterone

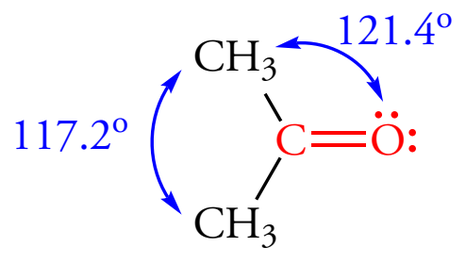
18.1 THE CARBONYL GROUP



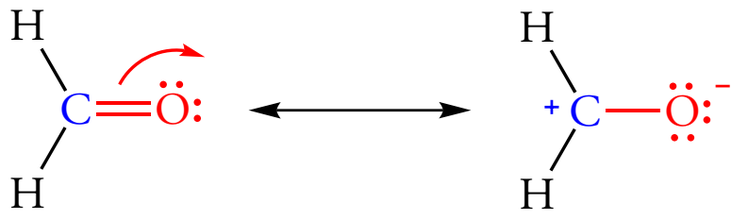
Formaldehyde, the carbonyl group, is shown in red.



formaldehyde



acetone



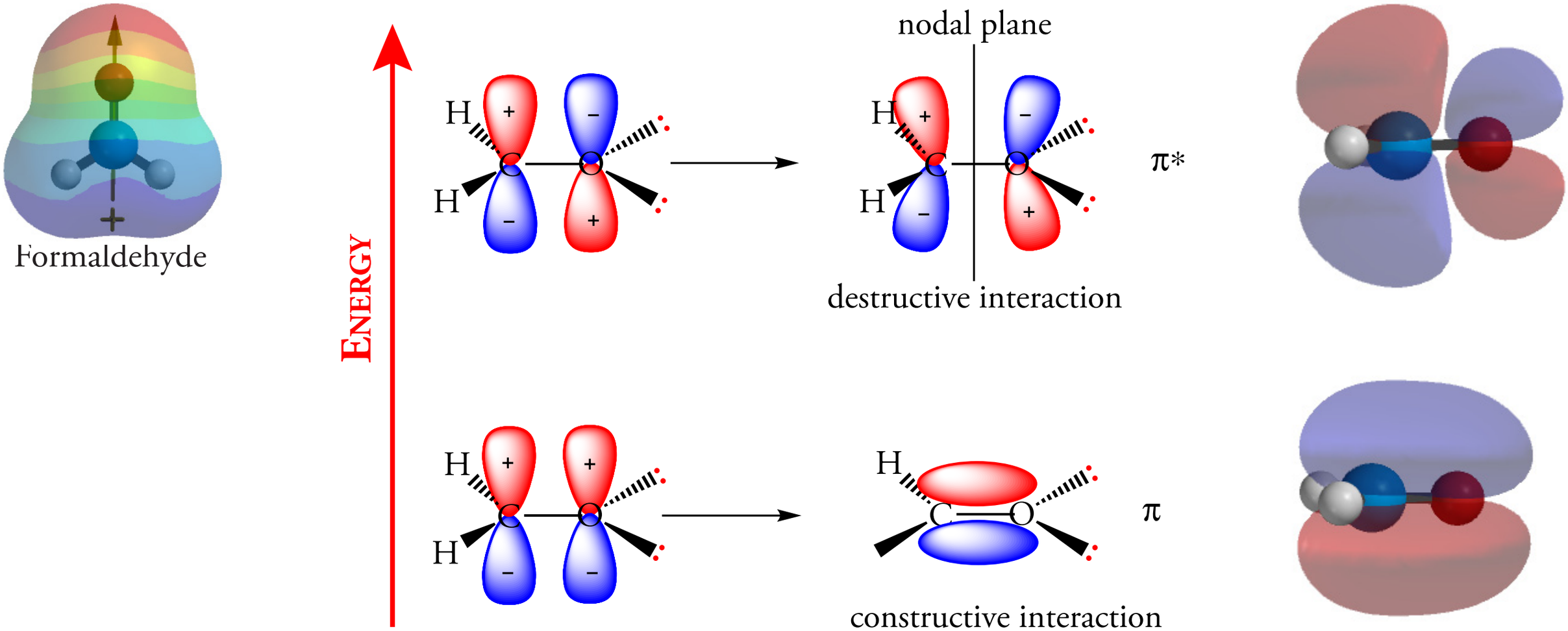
1 2

$CH_3—CH_2—CH=CH_2$
1-butene (0.2 D)

$CH_3—CH_2—CH=O$
propanal (2.5 D)

Figure 18.1 Structure of Formaldehyde

The carbonyl carbon and oxygen atoms of formaldehyde are sp^2-hybridized. The H—C—H bond angle is close to 120°. The two sets of lone pair electrons are in sp^2 hybrid orbitals that are in the same plane as the hydrogen atoms.

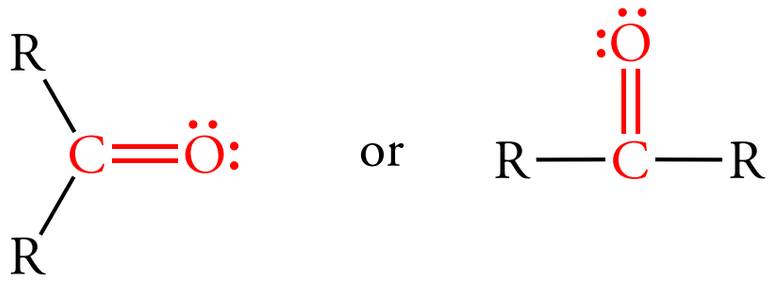


Bonding and Antibonding Molecular Orbitals of Formaldehyde

18.1 THE CARBONYL GROUP

Carbonyl Compounds

general formulas for an aldehyde

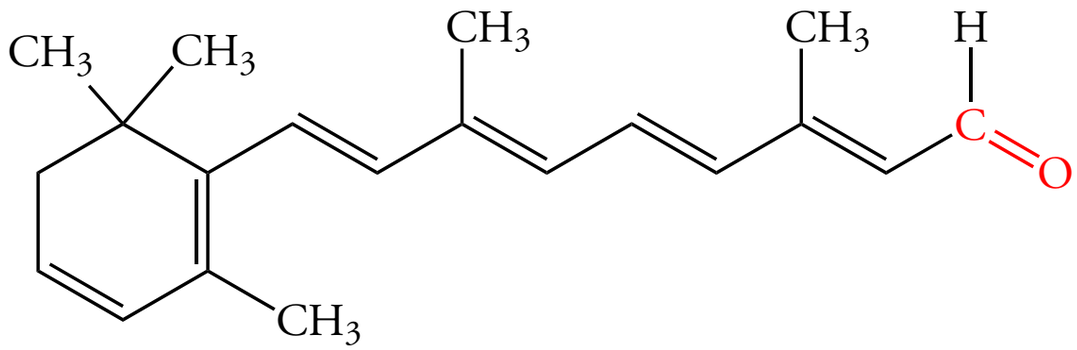


general formulas for a ketone

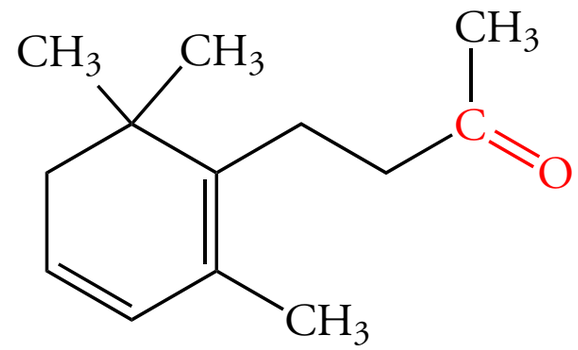
18.1 THE CARBONYL GROUP

Naturally Occurring Aldehydes and Ketones

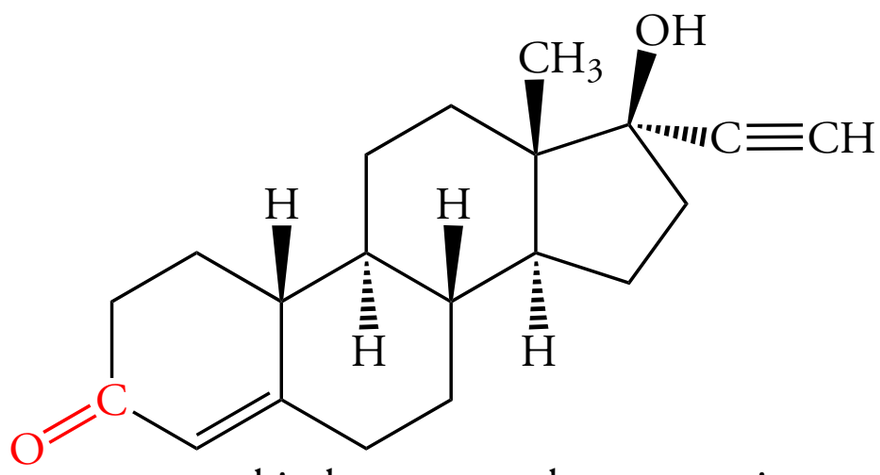
Figure 18.2 Structures of Naturally Occurring Aldehydes and Ketones



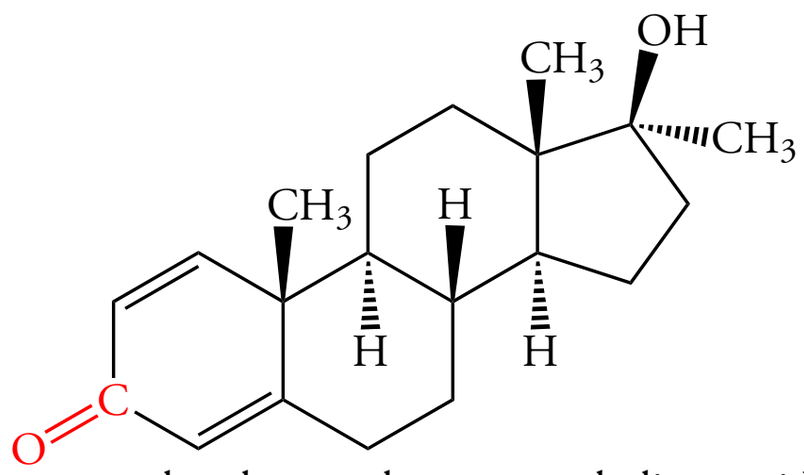
retinal



α-ionone



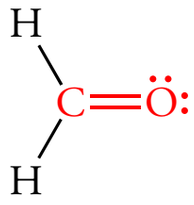
norethindrone, an oral contraceptive



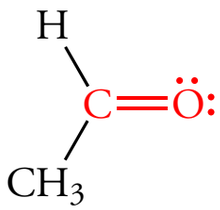
methandrostenolone, an anabolic steroid

18.2 NOMENCLATURE OF ALDEHYDES AND KETONES

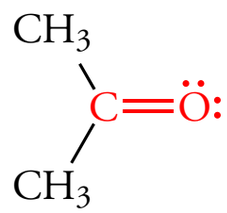
Common Names of Aldehydes



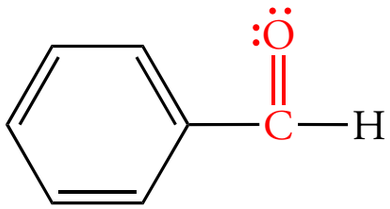
formaldehyde



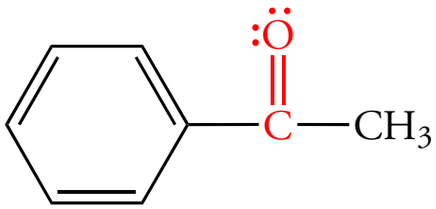
acetaldehyde



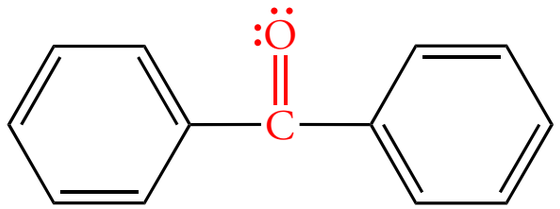
acetone



benzaldehyde



acetophenone



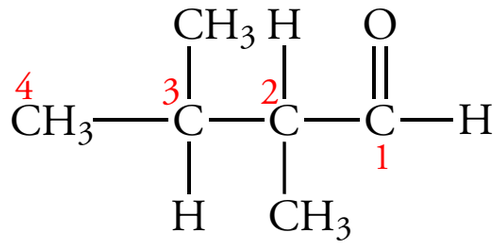
benzophenone

18.2 NOMENCLATURE OF ALDEHYDES AND KETONES

IUPAC Names of Aldehydes

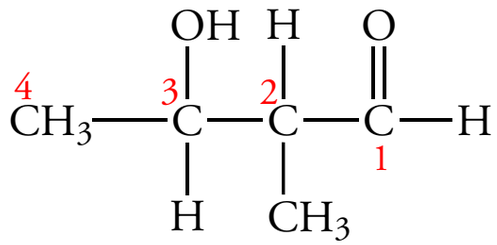
1. Name the longest continuous carbon chain that contains the carbonyl carbon atom as the parent chain. Replace the final *-e* of the parent hydrocarbon by the ending *-al*.

2. Number the parent chain to make the carbonyl carbon atom C-1. The number 1 is not required because the position of the carbonyl carbon atom must be at the end of the chain. Determine the name of each substituent and the number of the carbon atom to which it is attached. Add this information to the parent name as a prefix.



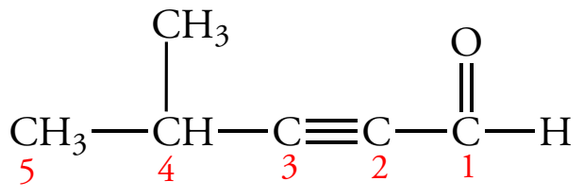
This is 2,3-dimethylbutanal, *not* 2,3-dimethyl-1-butanal.

3. The aldehyde functional group has a higher priority than alkyl, halogen, hydroxyl, and alkoxy groups. If any of these groups is present, indicate their names and positions as prefixes to the name of the parent aldehyde.



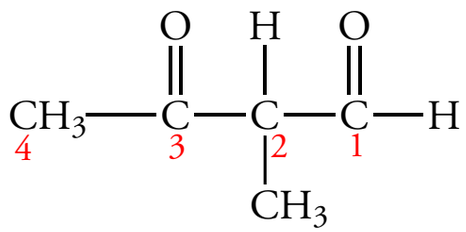
3-hydroxy-2-methylbutanal

4. The aldehyde functional group has a higher priority than double or triple bonds. When the parent chain contains a double or triple bond, replace the final *-e* of the name of the parent alkene or alkyne with the suffix *-al*. Indicate the position of the multiple bond with a prefix.



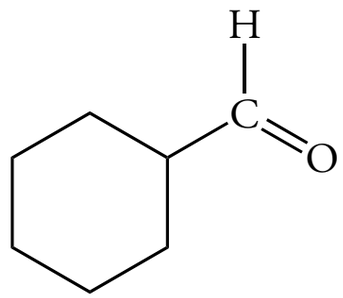
4-methyl-2-pentynal

5. If an aldehyde or ketone contains other groups with a higher priority, such as carboxylic acids, give the carbonyl group the prefix *-oxo*. Use a number to indicate the position of the *oxo* group. The priority order is carboxylic acid > aldehyde > ketone.

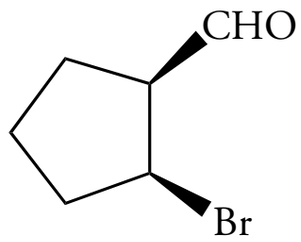


2-methyl-3-oxobutanal

6. If an aldehyde group is attached to a ring, use the suffix *-carbaldehyde*.



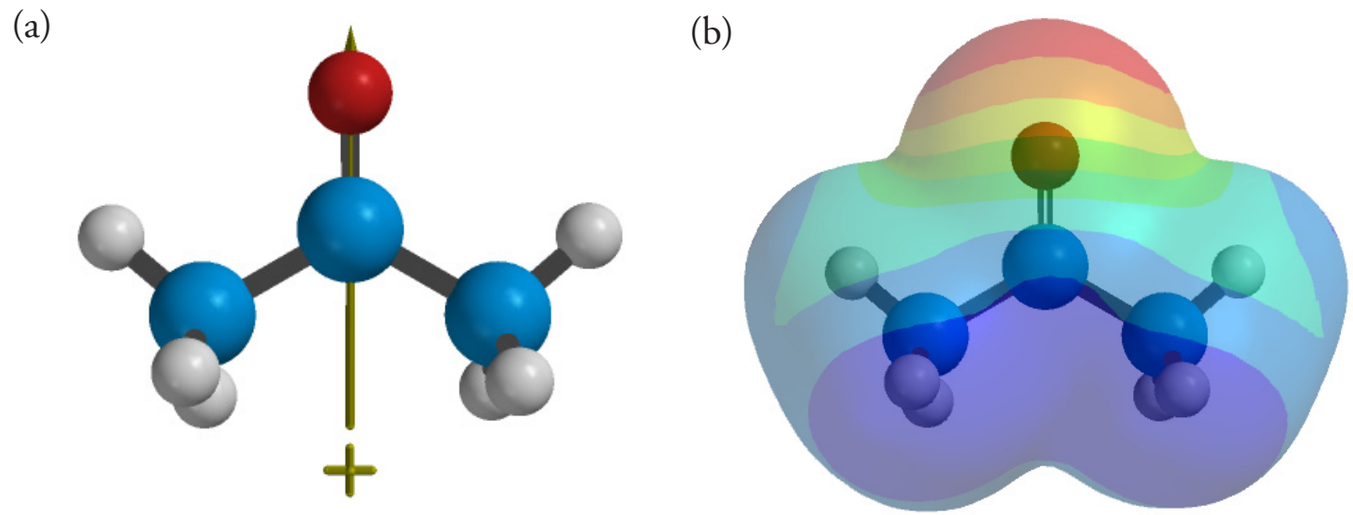
cyclohexanecarbaldehyde

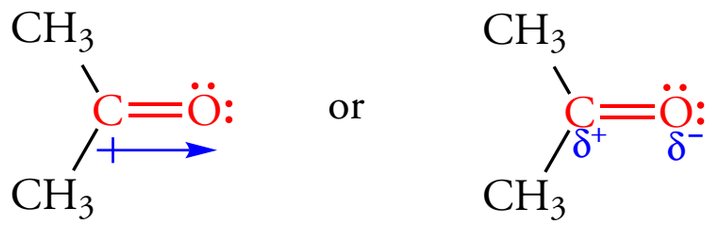


cis-2-bromocyclopentanecarbaldehyde

Figure 18.3 Electron Density Map of Acetone

(a) The carbonyl bond is highly polar. The oxygen atom, shown in red, has a large, partial negative charge; the carbonyl carbon has a partial positive charge, as do the two carbons that are α to the carbonyl group. (b) Electrostatic potential map. Regions shown in red have a partial negative charge; regions shown in blue have a partial positive charge.





2-propanone (2.9 D)
(acetone)

18.3 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

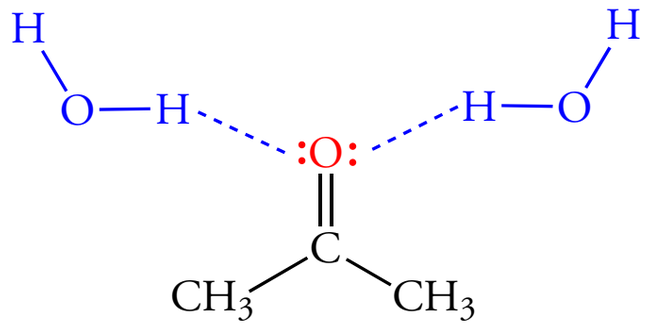
Boiling Points of Aldehydes and Ketones

Table 18.1
Effect of Functional Groups on Boiling Points

Compound	Formula	Molecular Weight	Boiling Point (°C)
ethane	CH_3CH_3	30	-89
methanol	CH_3OH	32	64.6
methanal	CH_3CHO	30	-21
propane	$CH_3CH_2CH_3$	44	-42
ethanol	CH_3CH_2OH	46	78.3
ethanal	CH_3CH_2CHO	44	20
butane	$CH_3CH_2CH_2CH_3$	58	-1
1-propanol	$CH_3CH_2CH_2OH$	60	97.1
propanal	CH_3CH_2CHO	58	48.8
methylpropane	$CH_3CH(CH_3)_2$	58	-12
2-propanol	$CH_3CH(OH)CH_3$	60	82.5
propanone	CH_3COCH_3	58	56.1

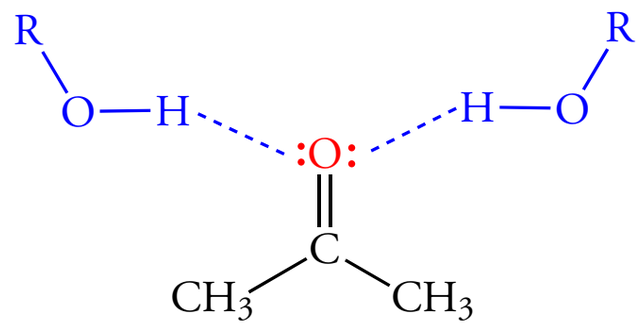
18.3 PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

Solubility of Aldehydes and Ketones in Water



The lone pair electrons of the carbonyl group act as hydrogen bond acceptors.

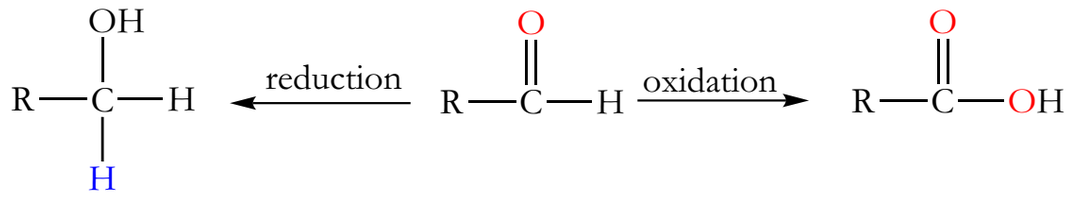
Acetone and 2-Butanone as Solvents

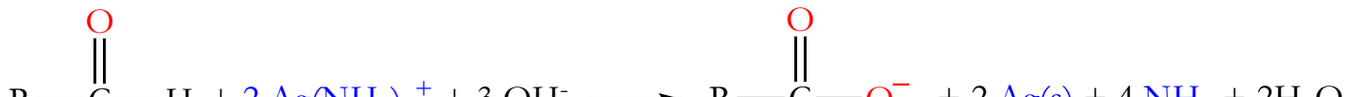


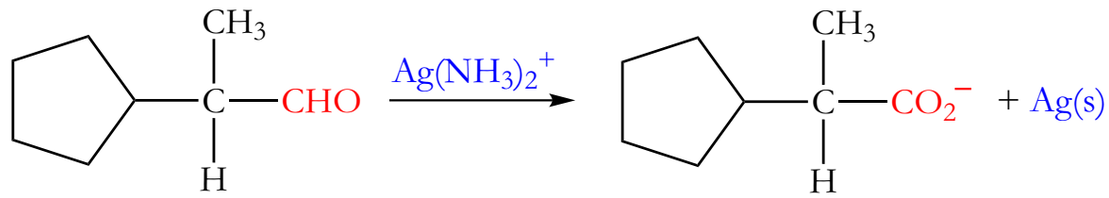
The lone pair electrons of the carbonyl group act as hydrogen bond acceptors. Hence, acetone is an excellent solvent for alcohols.

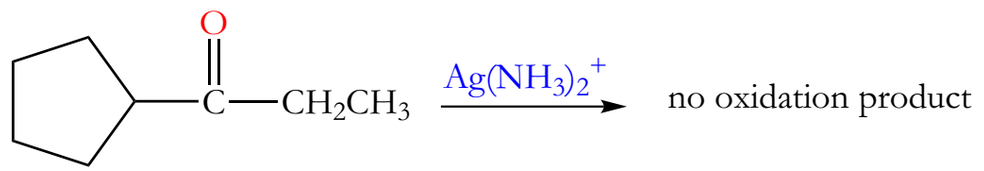
18.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS

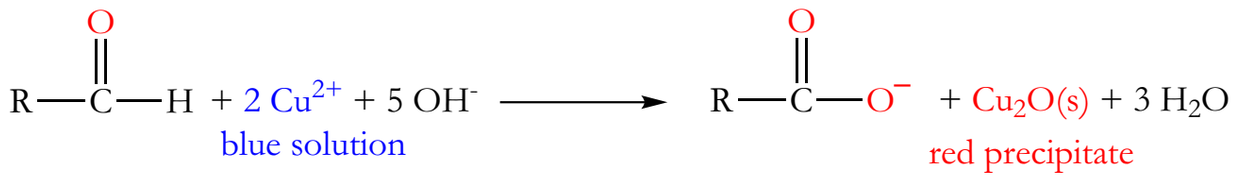
Oxidation of Aldehydes

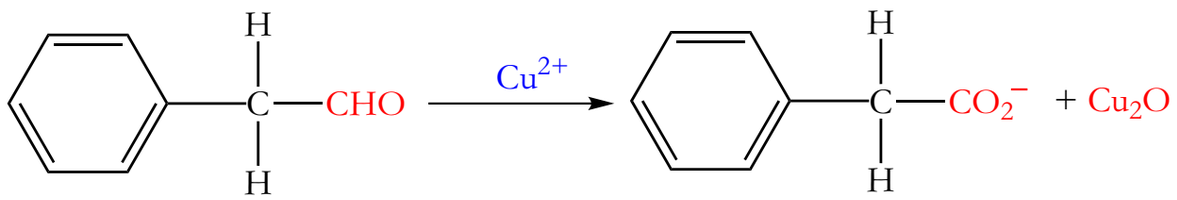


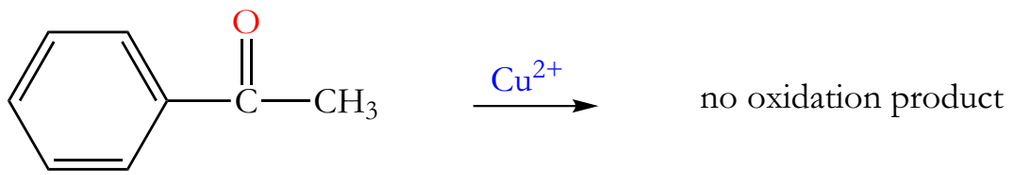






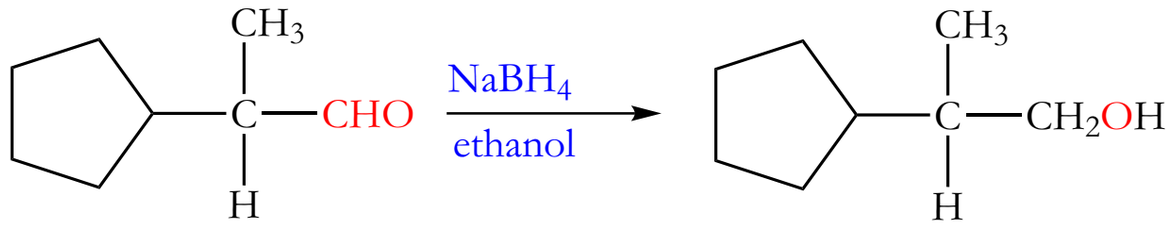


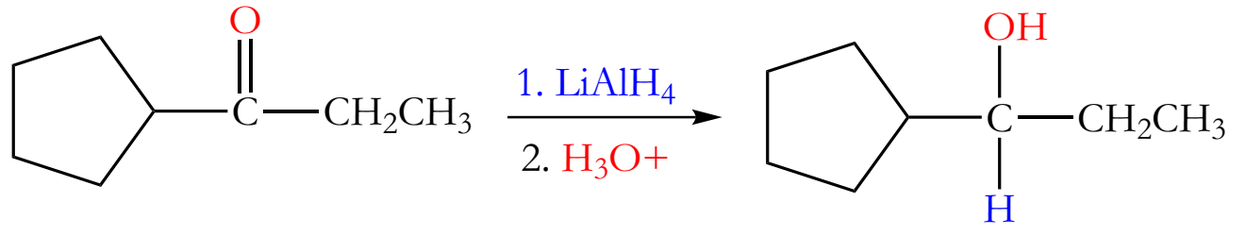




18.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS

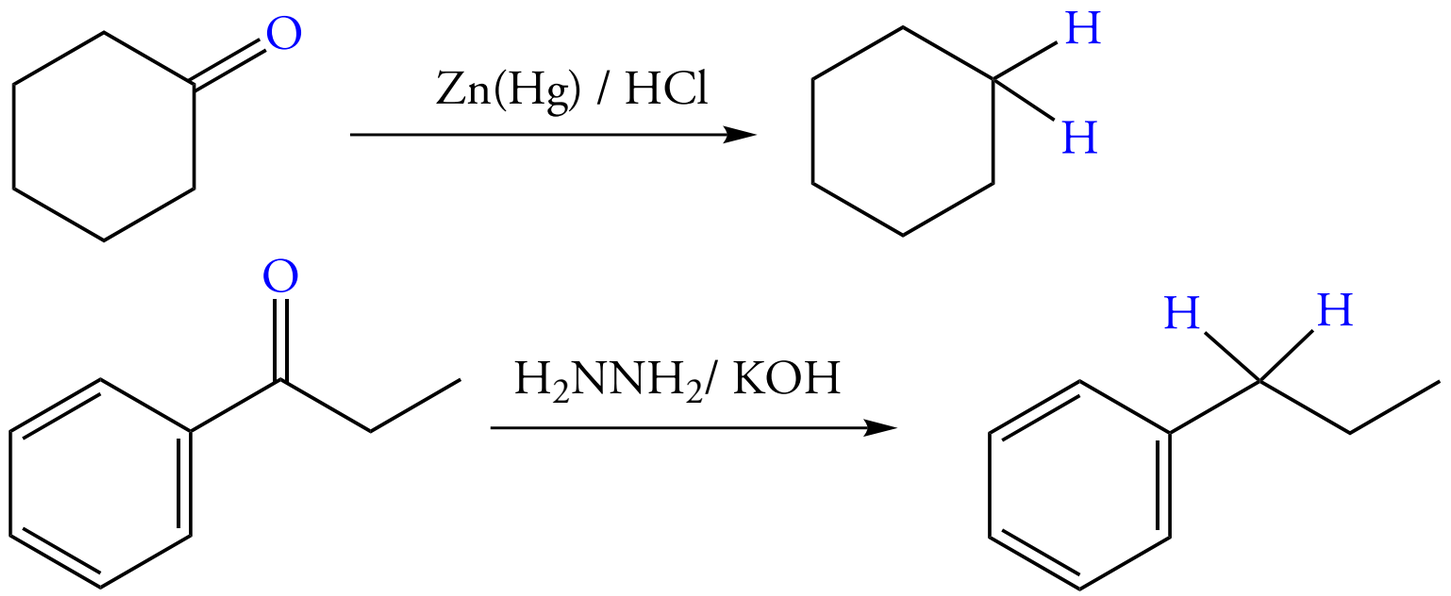
Reduction of Aldehydes and Ketones to Alcohols





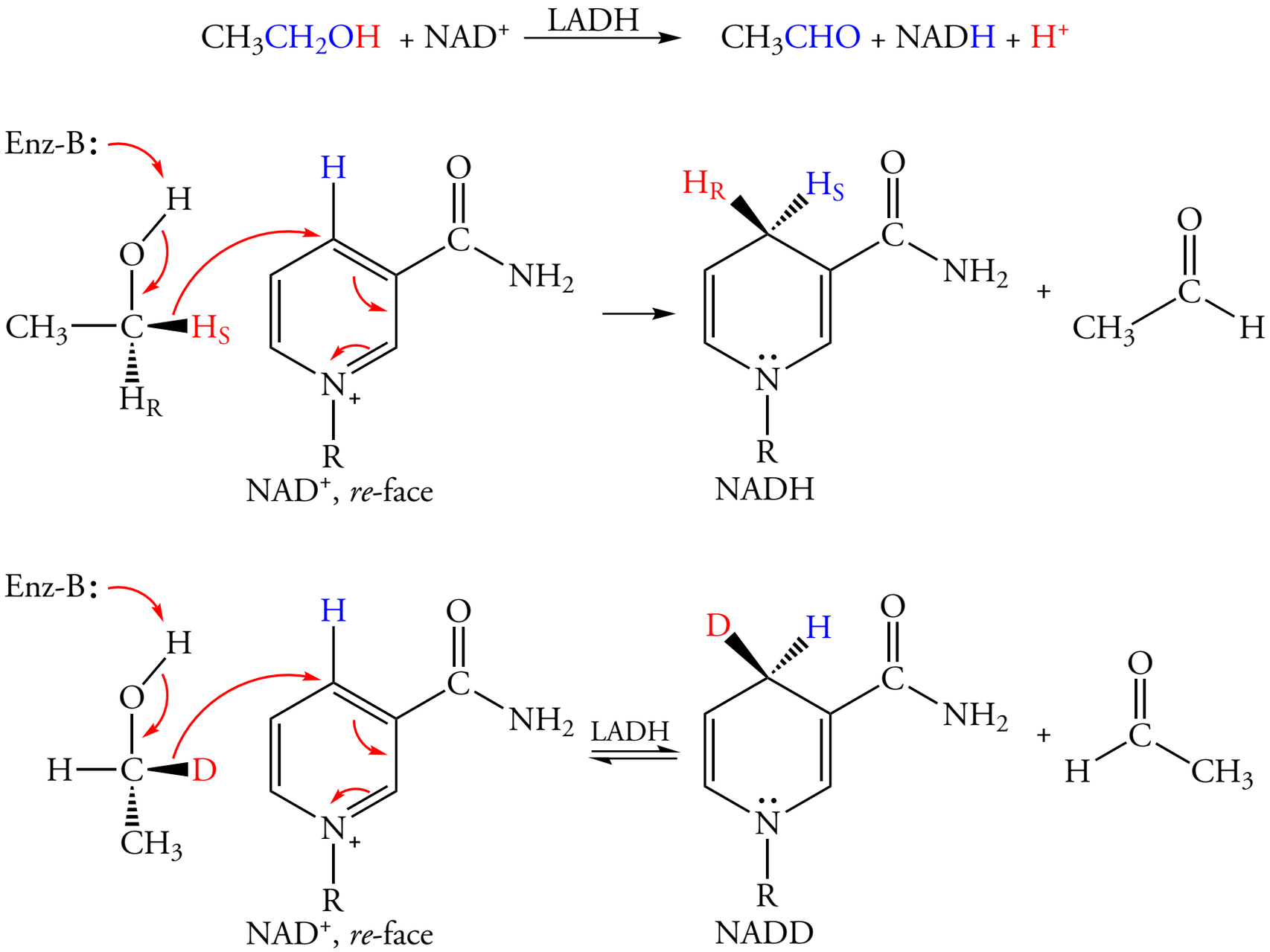
18.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS

Reduction of a Carbonyl Group to a Methylene Group



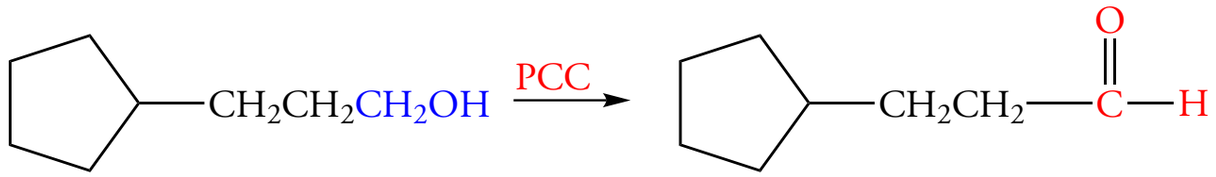
18.4 OXIDATION-REDUCTION REACTIONS OF CARBONYL COMPOUNDS

NAD-Dependent Oxidation of Ethanol

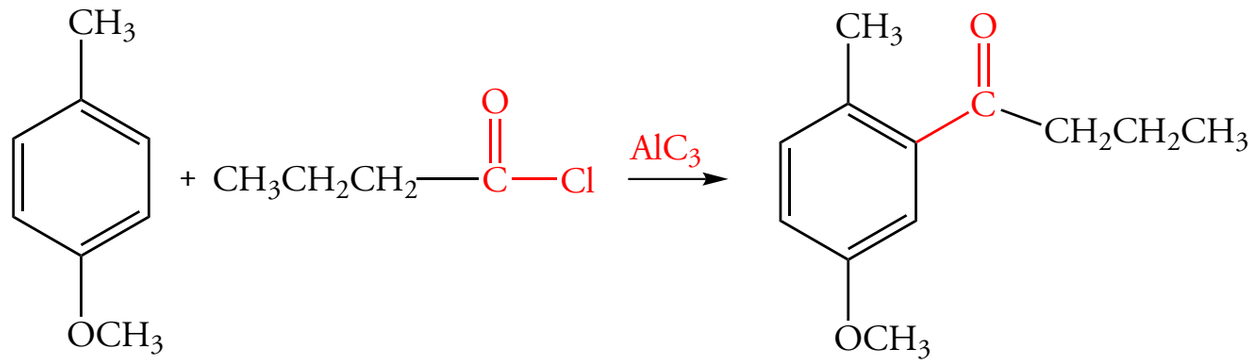


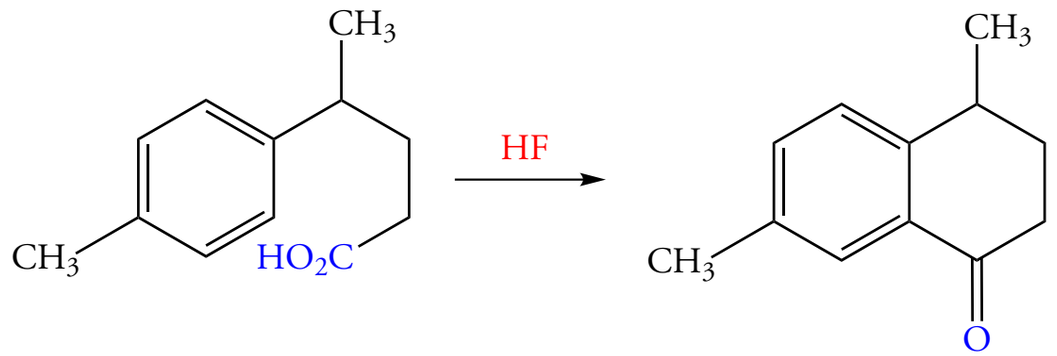
18.5 SYNTHESIS OF CARBONYL COMPOUNDS: A REVIEW

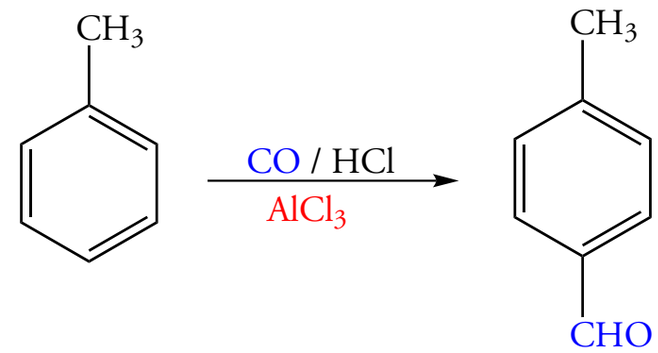
Oxidation of Alcohols



Friedel-Crafts Acylation

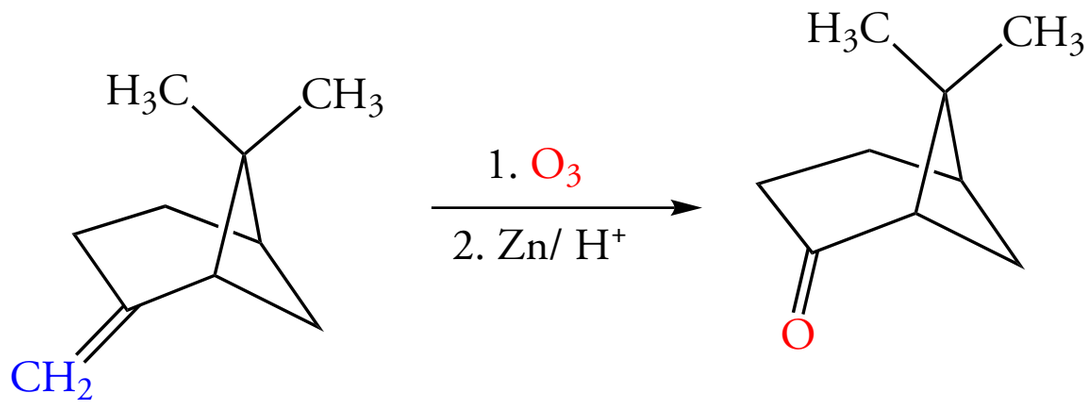




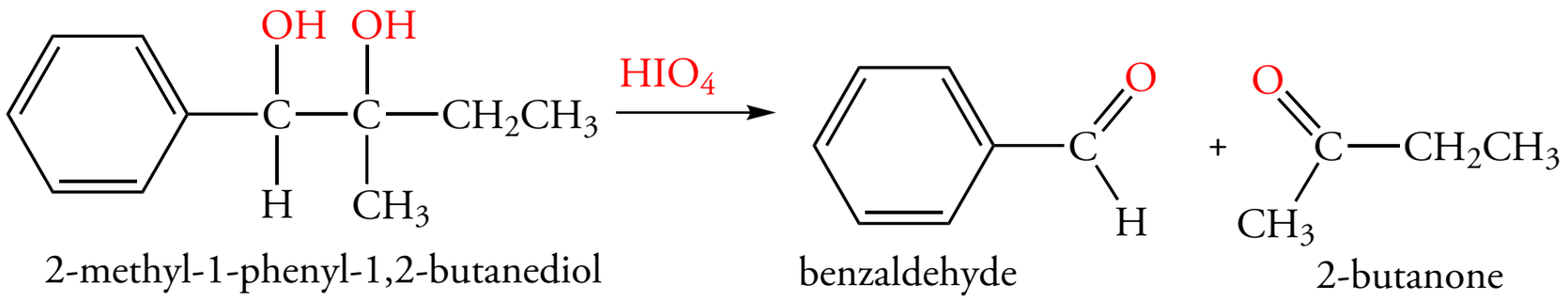


18.5 SYNTHESIS OF CARBONYL COMPOUNDS: A REVIEW

Ozonolysis of Alkenes



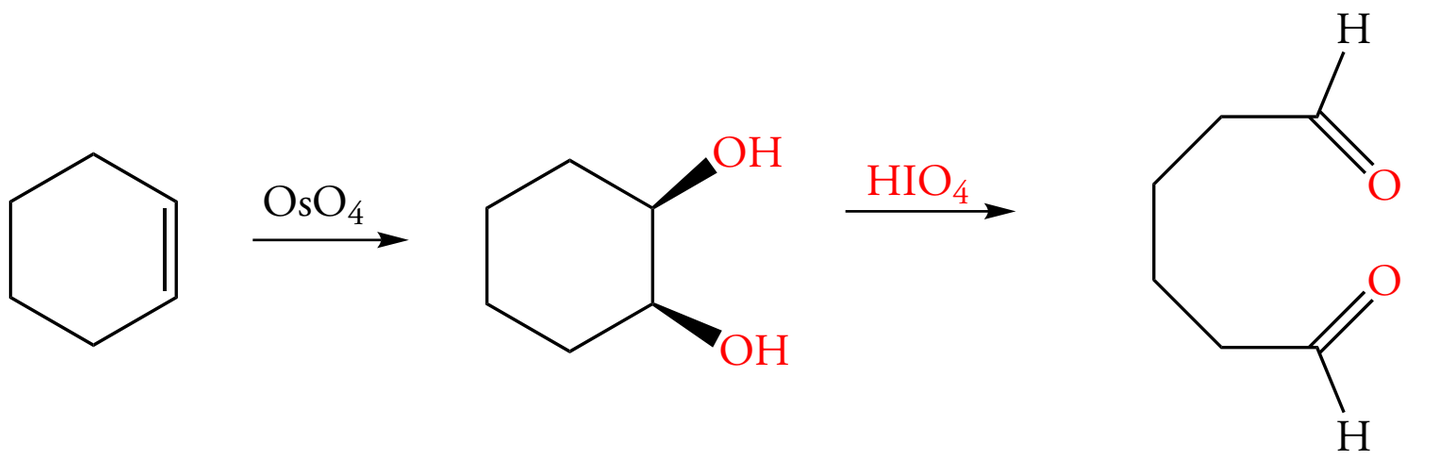
Oxidative Cleavage of Vicinal Diols



2-methyl-1-phenyl-1,2-butanediol

benzaldehyde

2-butanone

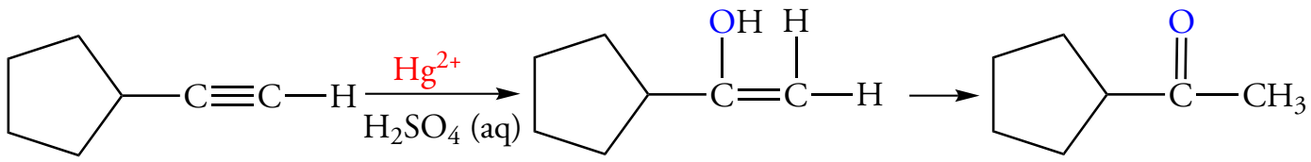


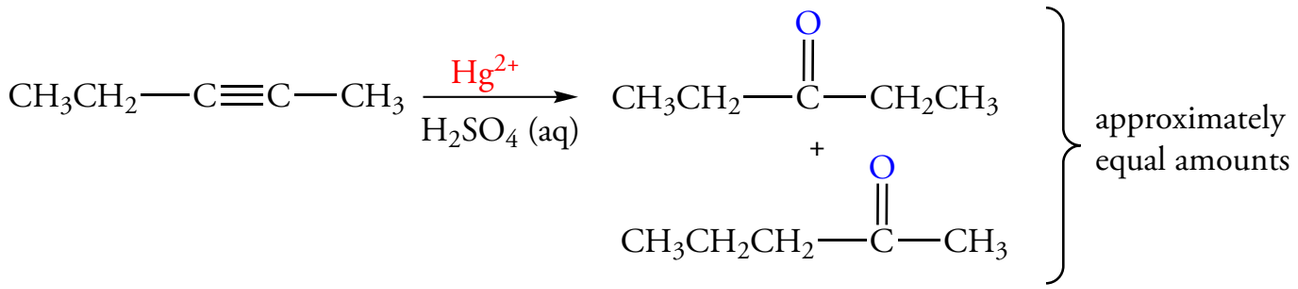
cis-1,2-cyclohexanediol

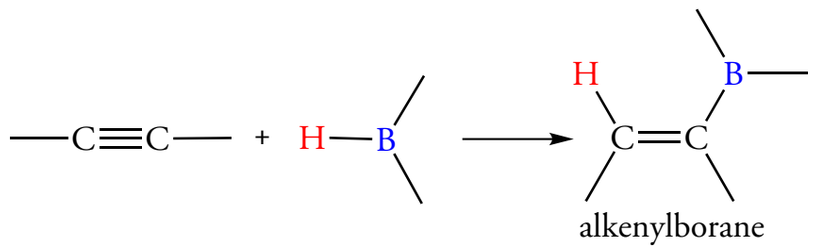
6-oxohexanal

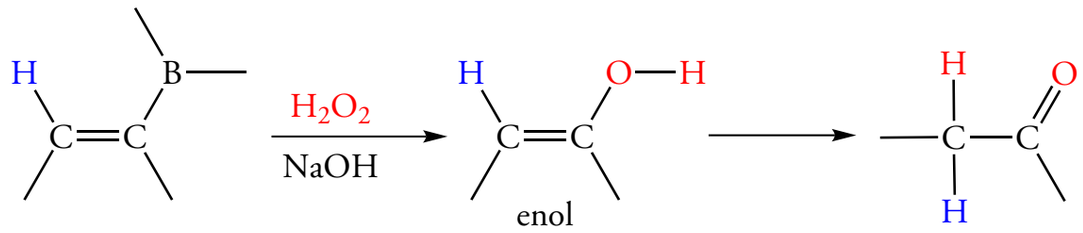
18.5 SYNTHESIS OF CARBONYL COMPOUNDS: A REVIEW

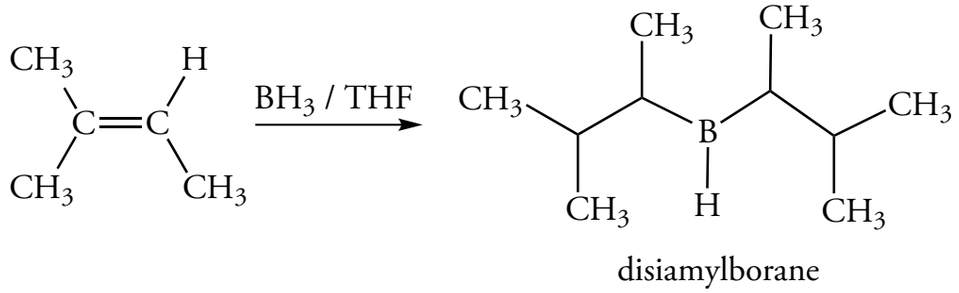
Hydration of Alkynes

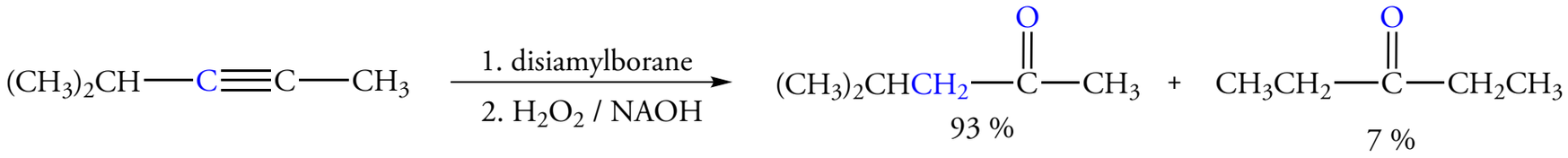






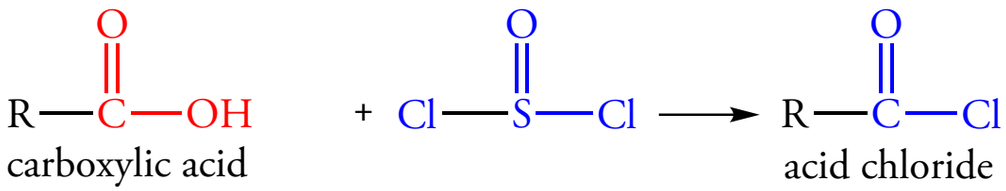


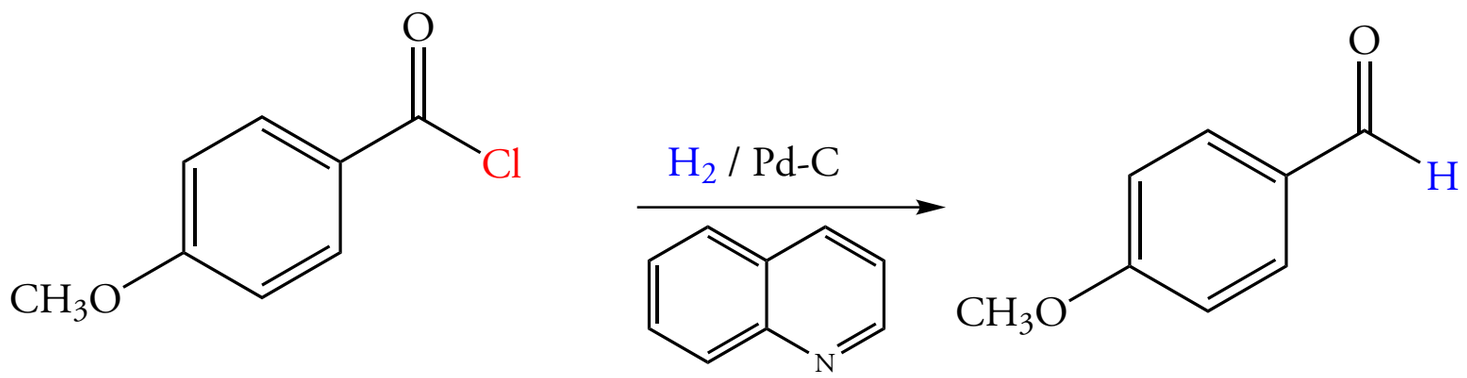




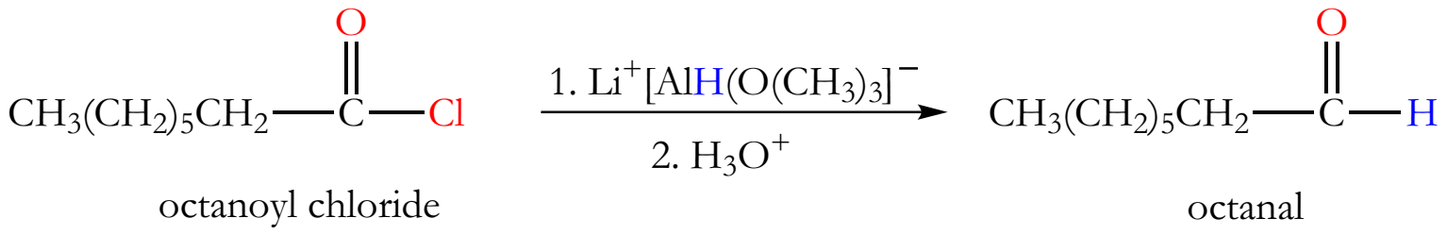
18.6 SYNTHESIS OF CARBONYL COMPOUNDS: A PREVIEW

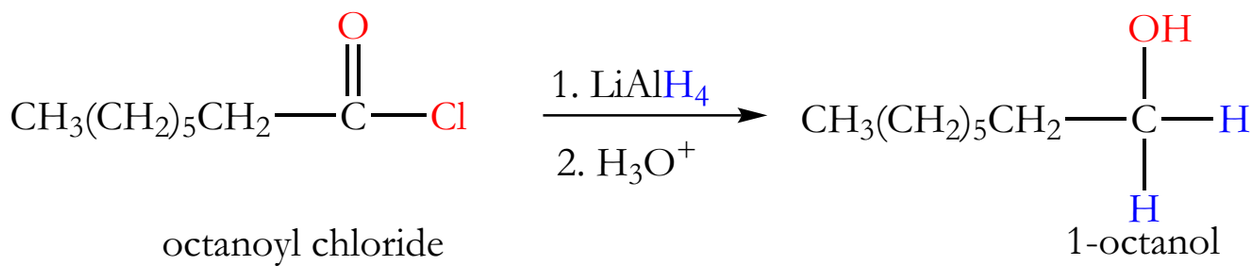
Reduction of Acid Chlorides





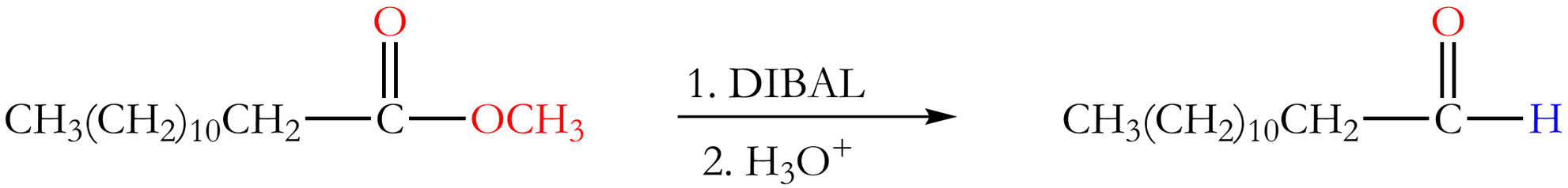
$$LiAlH_4 + 3\ (CH_3)_3COH \longrightarrow Li^+[AlH(O(CH_3)_3]^- + 3\ H_2$$





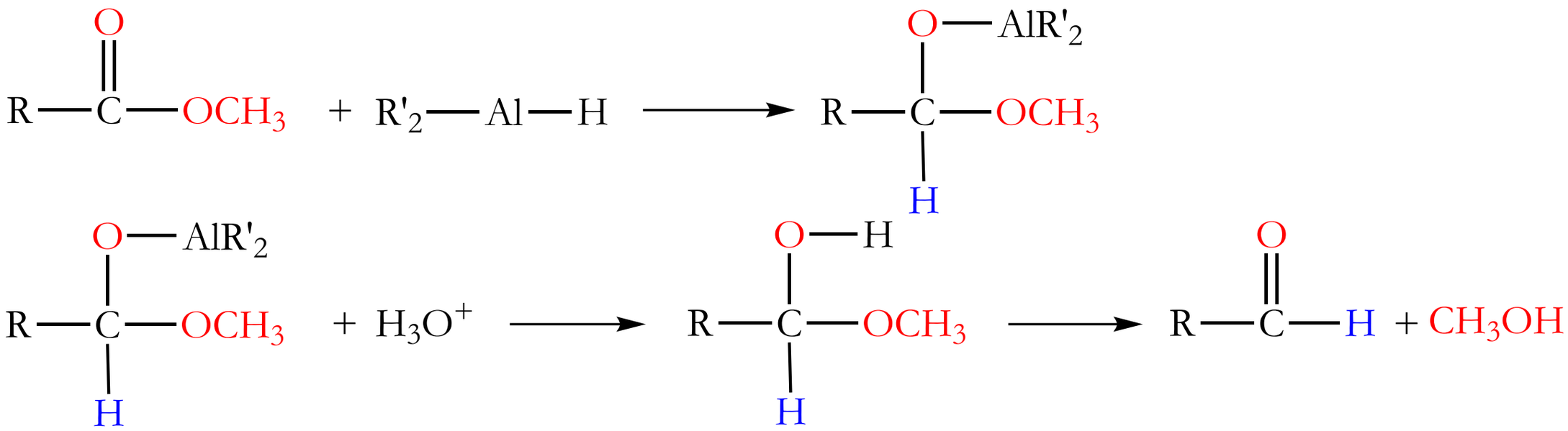
18.6 SYNTHESIS OF CARBONYL COMPOUNDS: A PREVIEW

Reduction of Esters



methyl hexadecanoate

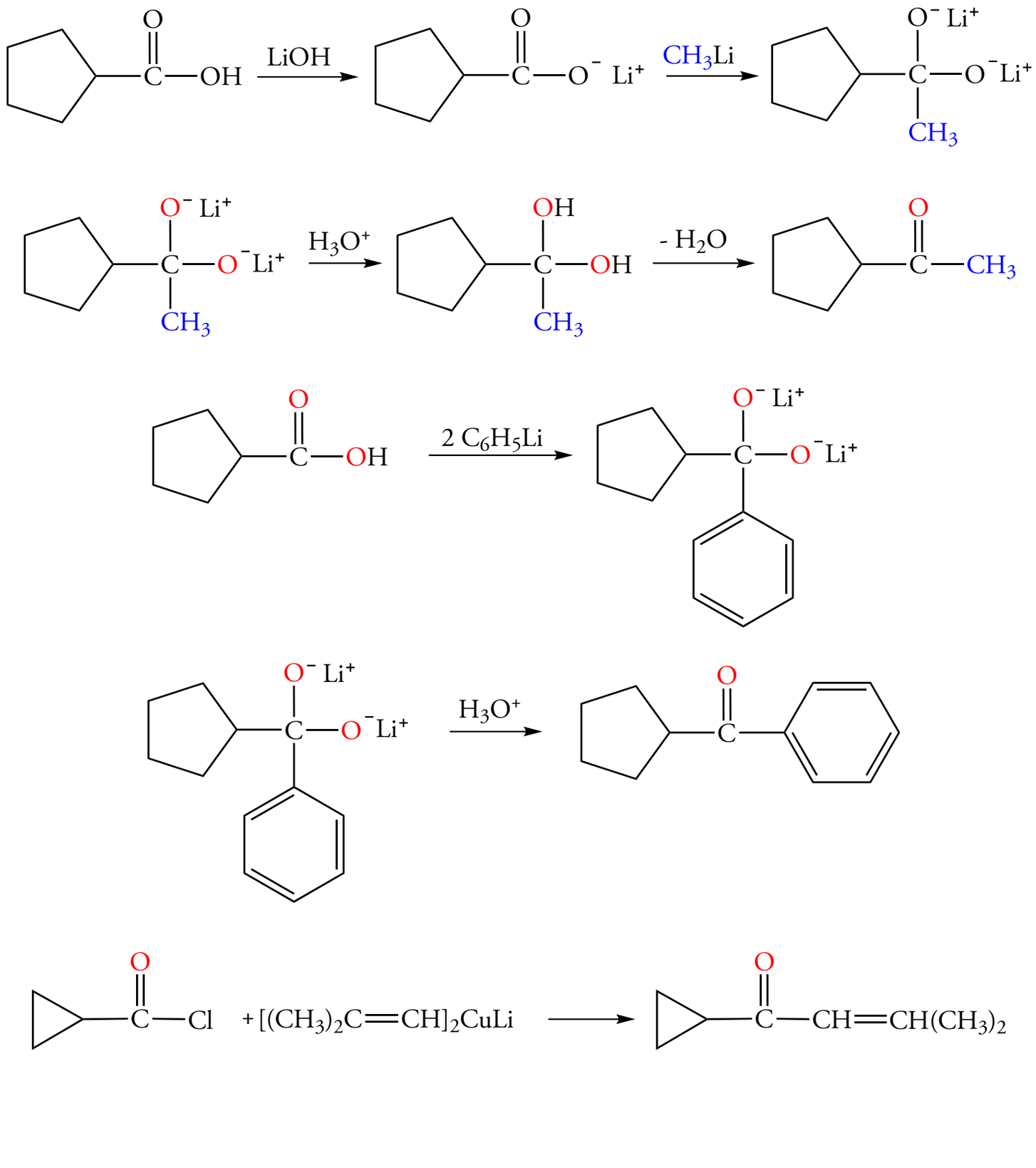
hexadecanal



a hemiacetal

18.6 SYNTHESIS OF CARBONYL COMPOUNDS: A PREVIEW

Reactions of Acid Derivatives with Organometallic Reagents



18.6 SYNTHESIS OF CARBONYL COMPOUNDS: A PREVIEW

Synthesis of Carbonyl Compounds From Nitriles

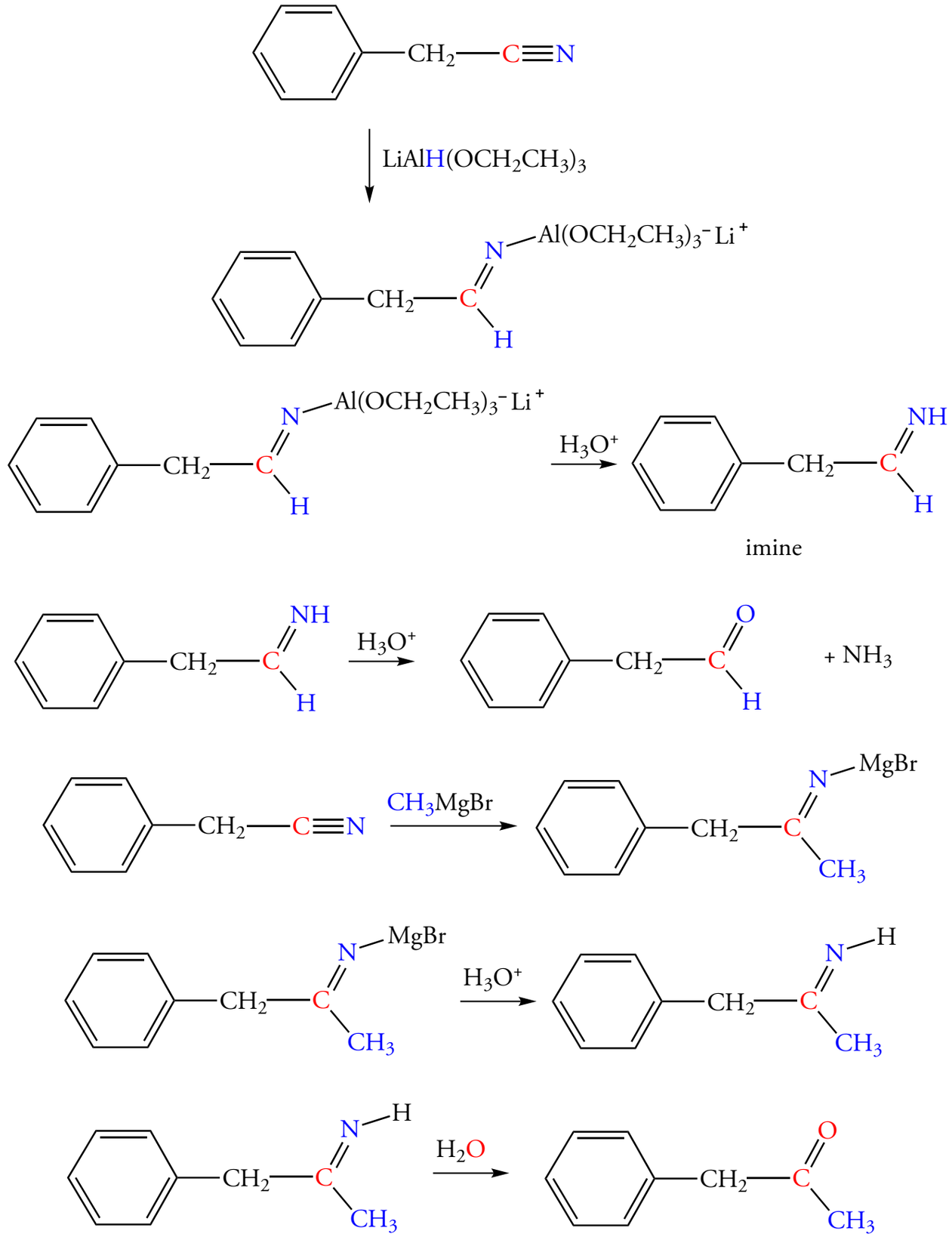
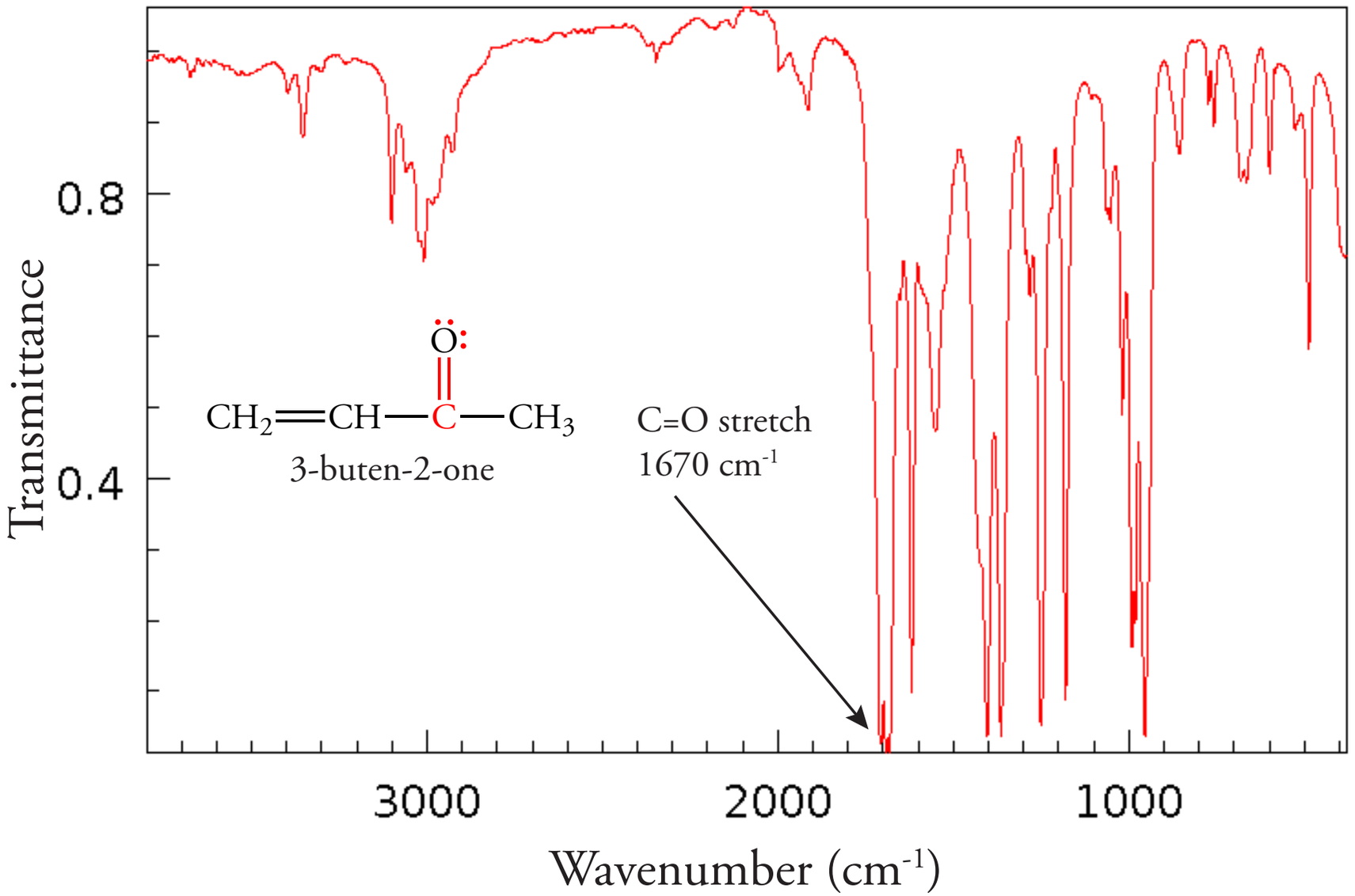


Figure 18.4 IR Spectrum of 3-buten-2-one

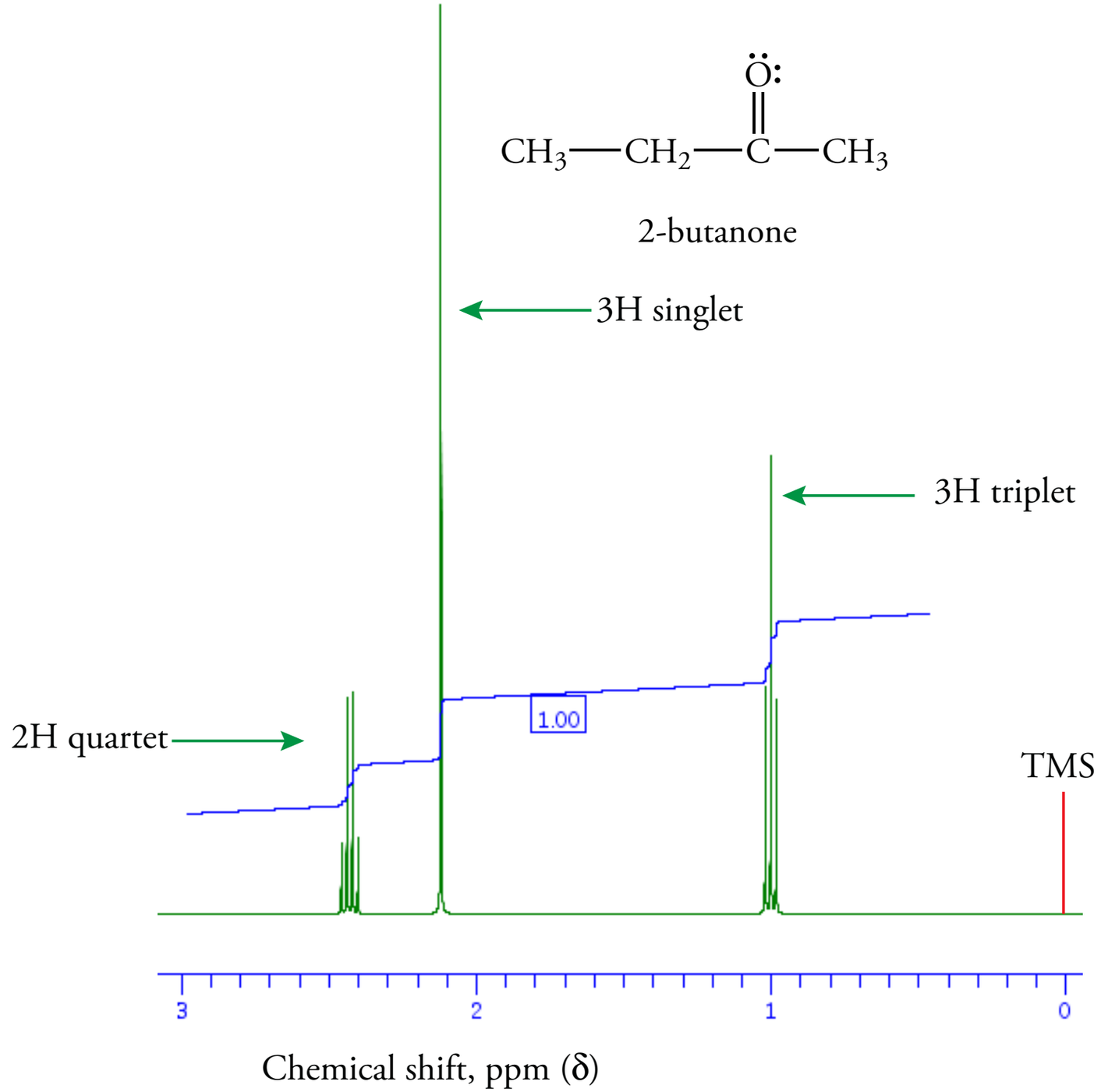
The carbonyl stretching frequency occurs at 1670 cm^{-1}.



18.7 SPECTROSCOPY OF ALDEHYDES AND KETONES

Proton NMR Spectroscopy

Figure 18.5 Proton NMR Spectrum of 2-Butanone



18.7 SPECTROSCOPY OF ALDEHYDES AND KETONES

C-13 NMR Spectroscopy

Figure 18.6 C-13 NMR Spectrum of 2-Butanone