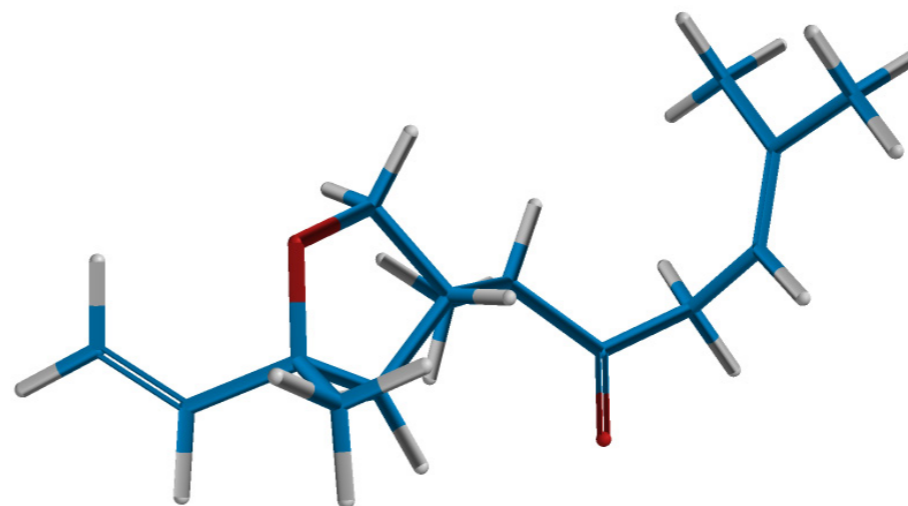


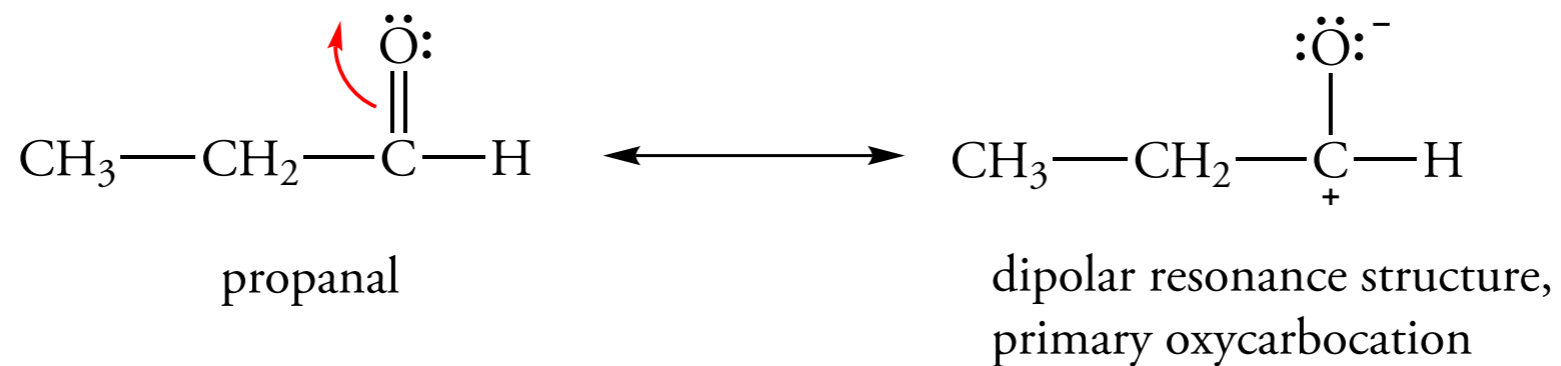
19

ALDEHYDES AND KETONES: NUCLEOPHILIC ADDITION REACTIONS

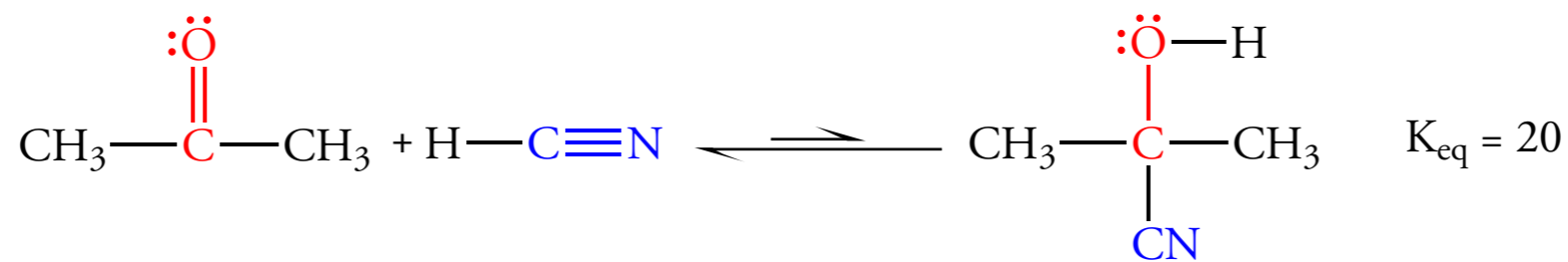
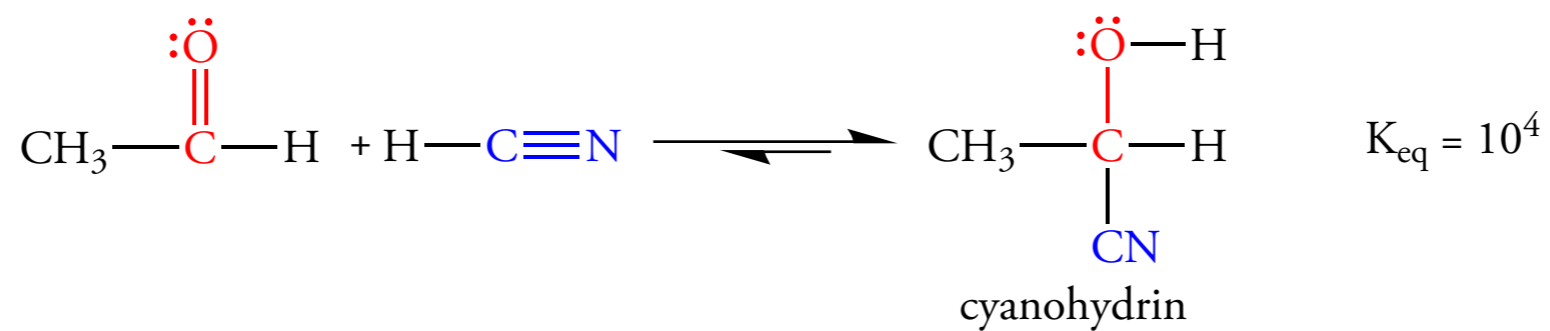


Davanone

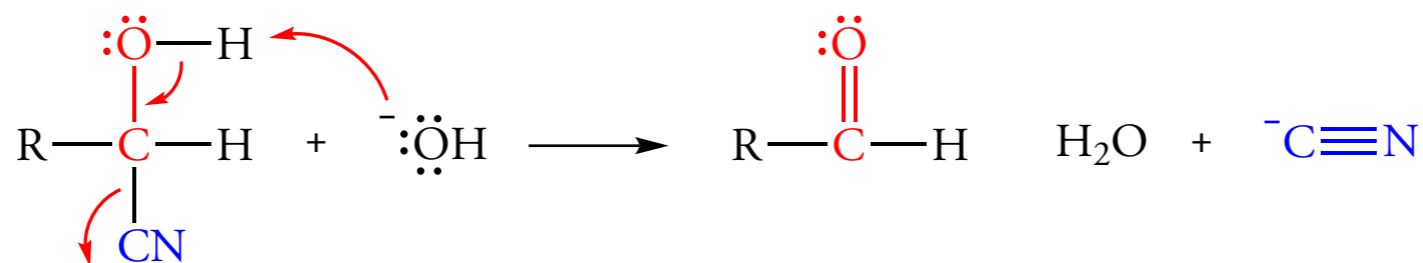
19.1 RELATIVE STABILITIES OF ALDEHYDES AND KETONES



19.2 FORMATION OF CYANOHYDRINS



+



19.2 FORMATION OF CYANOHYDRINS

Table 19.1
Equilibrium Constants for
Cyanohydrin Formation

Compound	K_{eq}
acetaldehyde	10,000
acetone	20
benzaldehyde	210
p-methoxybenzaldehyde	30
acetophenone	0.8

19.3 HYDRATION OF CARBONYL COMPOUNDS

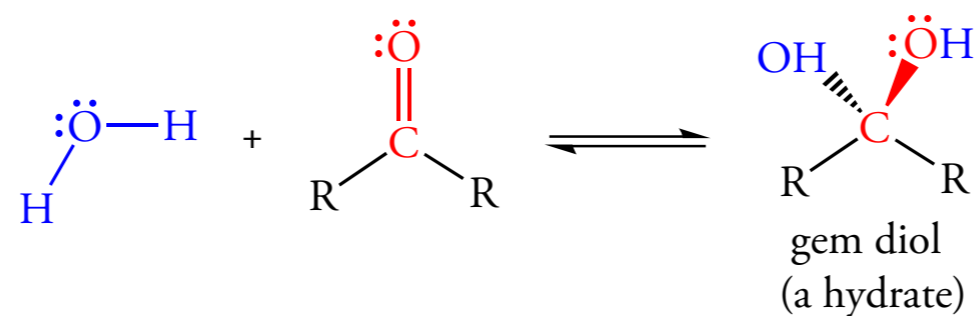


Table 19.2
Equilibrium Constants for
Hydrate Formation

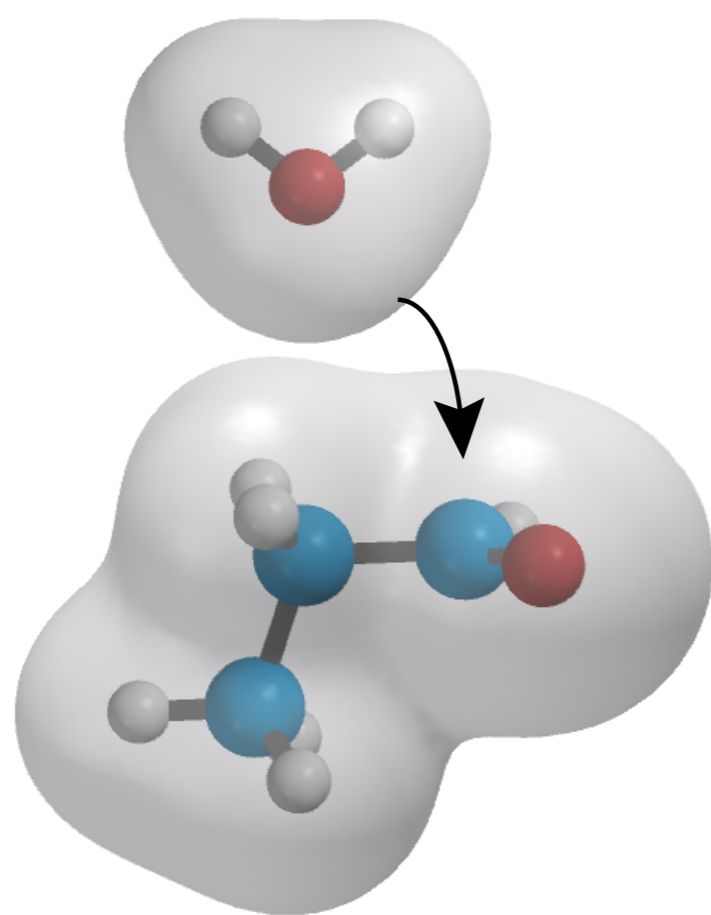
Compound	K_{eq}
methanal	2.2×10^3
ethanal	1
chloroacetaldehyde	40
acetone	1.4×10^{-3}
benzaldehyde	8×10^{-3}
acetophenone	6.6×10^{-6}

19.3 HYDRATION OF CARBONYL COMPOUNDS

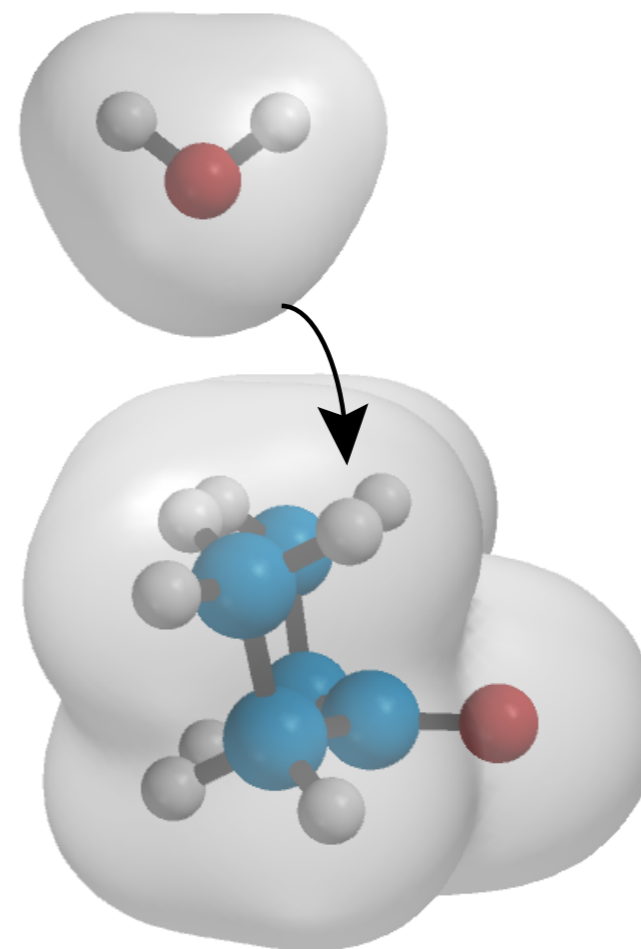
Steric Effects on Nucleophilic Addition Reactions

Figure 19.1 Steric Effects on the Equilibrium of Hydration Reactions

The carbonyl group of an aldehyde (a) is less sterically hindered than the carbonyl group of a ketone (b). Therefore, ketones react more slowly than aldehydes in nucleophilic addition reactions. The nucleophile here is water.



(a) Hydration of an aldehyde



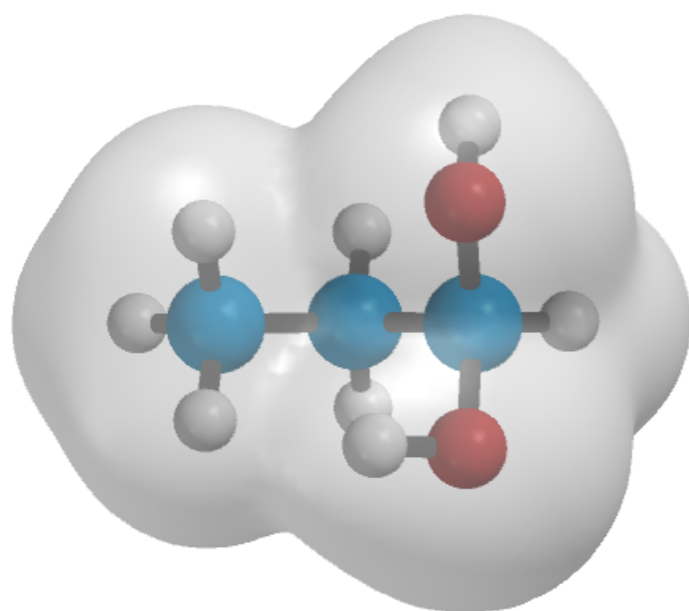
(b) Hydration of a ketone

19.3 HYDRATION OF CARBONYL COMPOUNDS

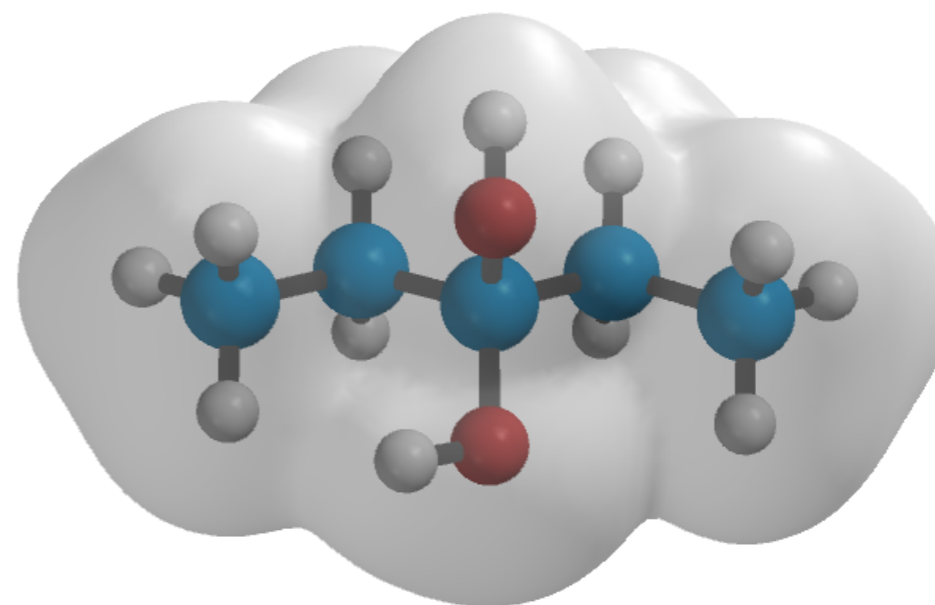
Steric Effects on Nucleophilic Addition Reactions

Figure 19.2 Steric Effects in Hydrates

The hydrate of an aldehyde (a) is less sterically hindered than the hydrate of a ketone (b).



(a) 1,1-propanediol



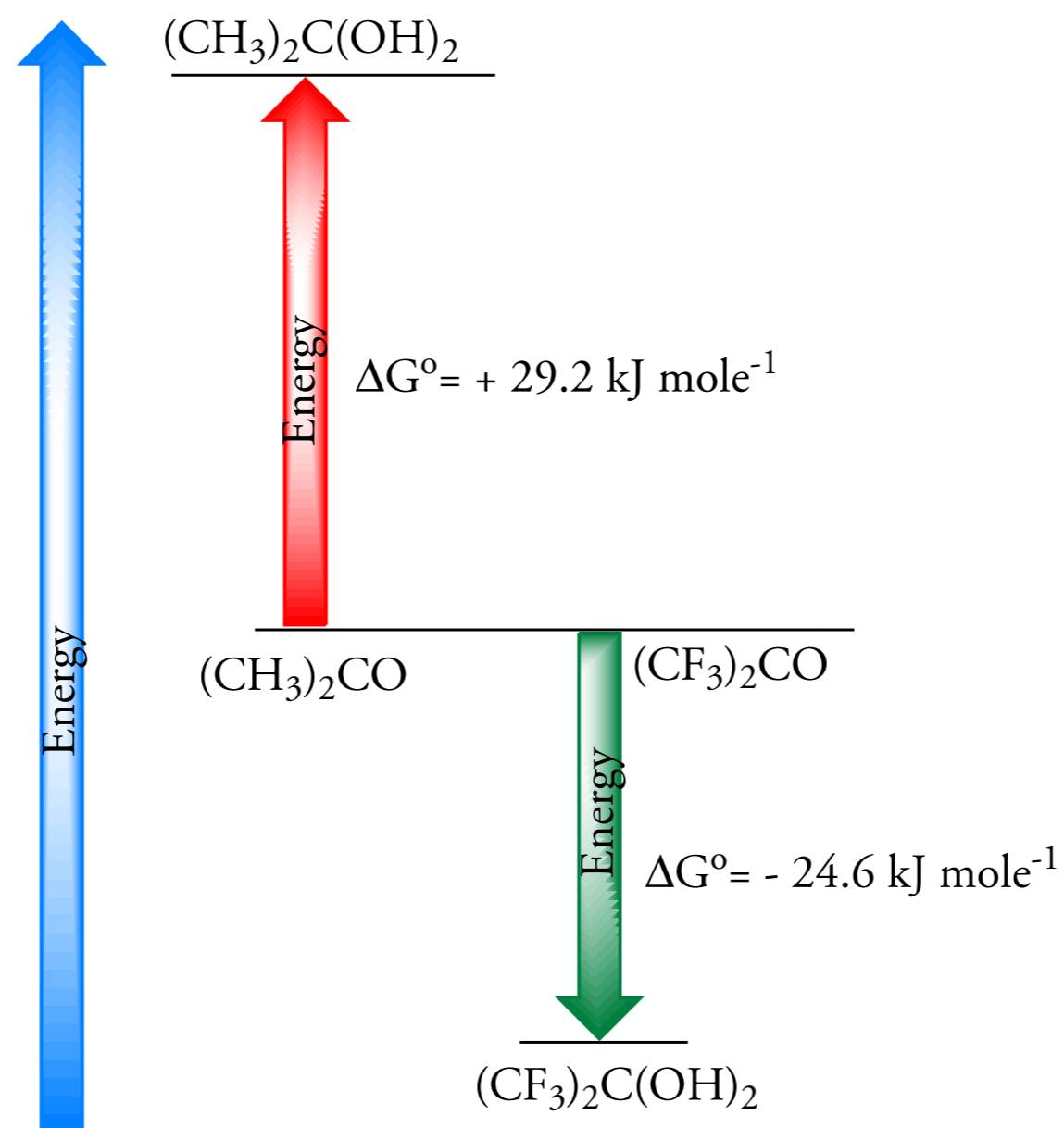
(b) 3,3-pentane-2,2-diol

19.3 HYDRATION OF CARBONYL COMPOUNDS

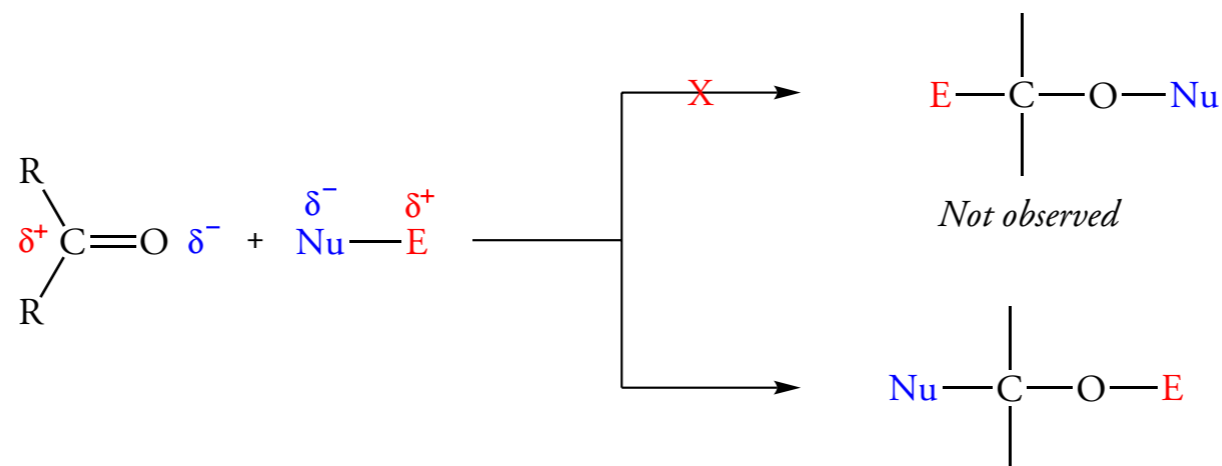
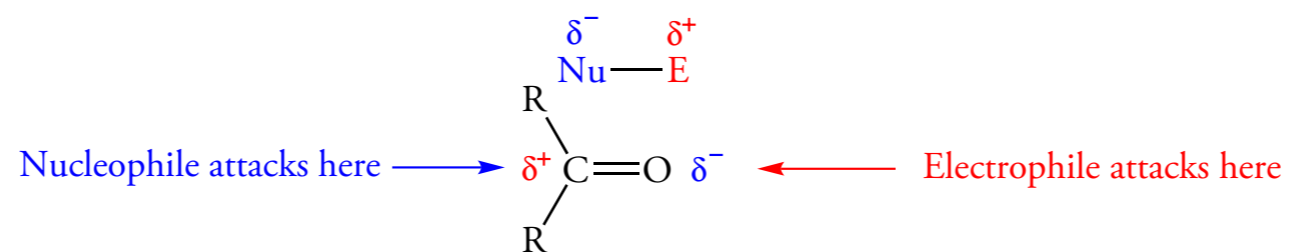
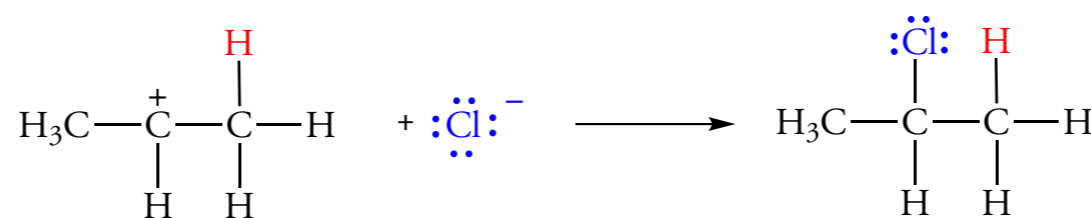
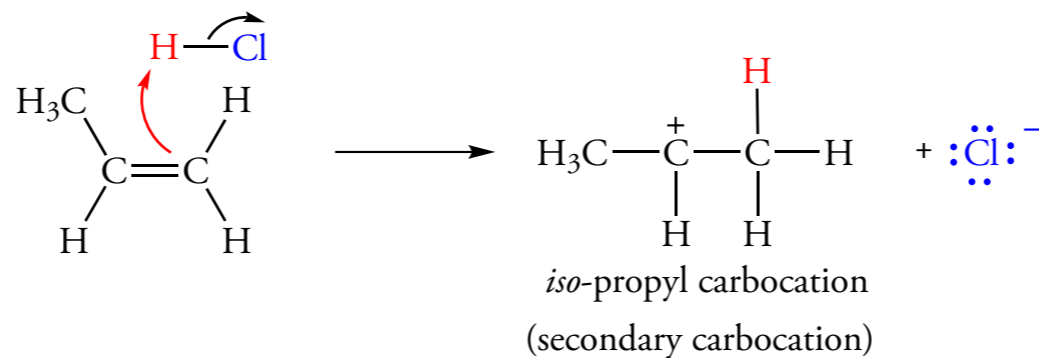
Inductive Effects on Addition Reactions

Figure 19.3 Inductive Effects on the Equilibrium of Hydration Reactions

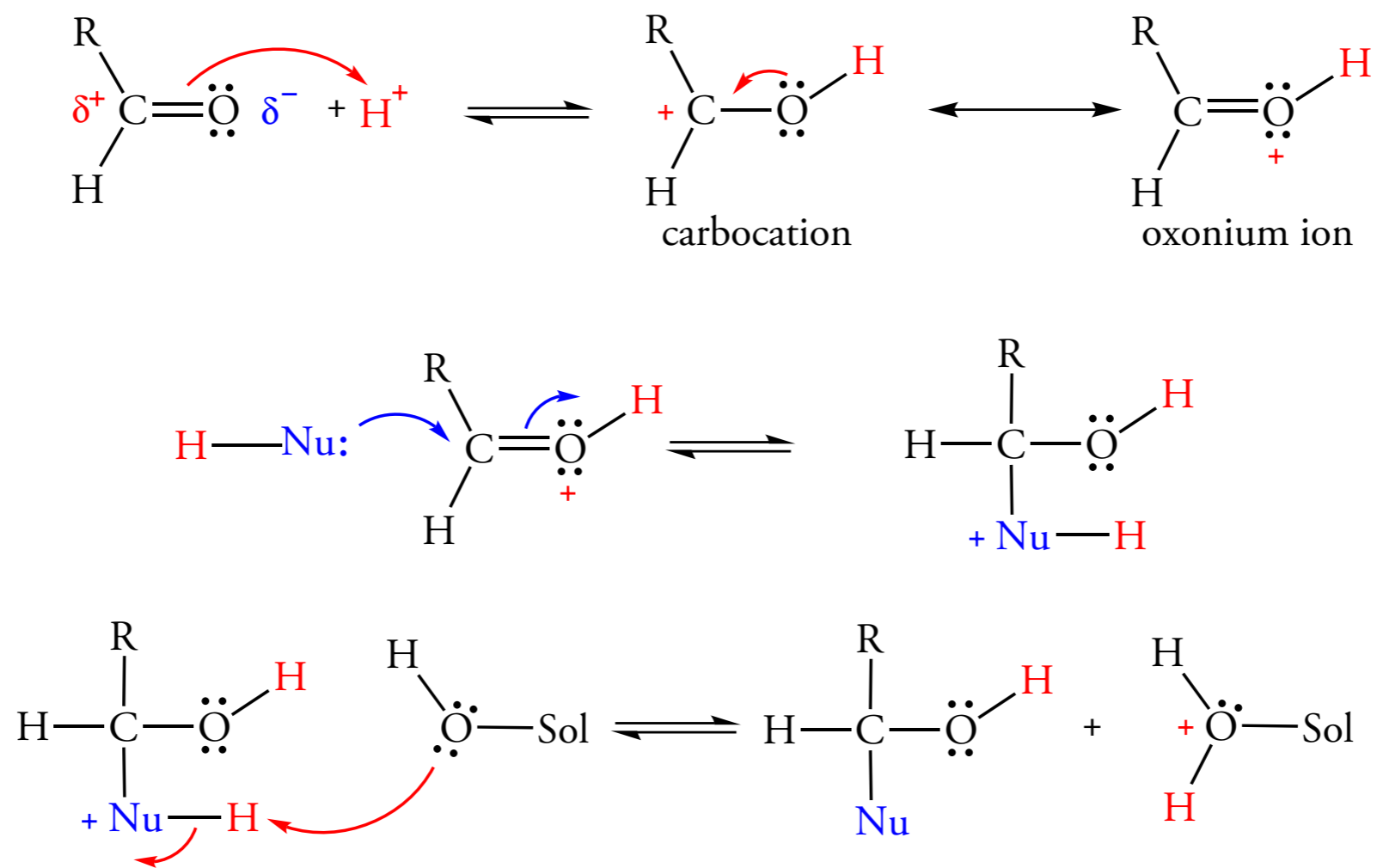
The relative energies of acetone and hexafluoroacetone are arbitrarily set as equal. The free energy of hydration of acetone is positive, whereas the free energy of hydration of hexafluoroacetone is negative.



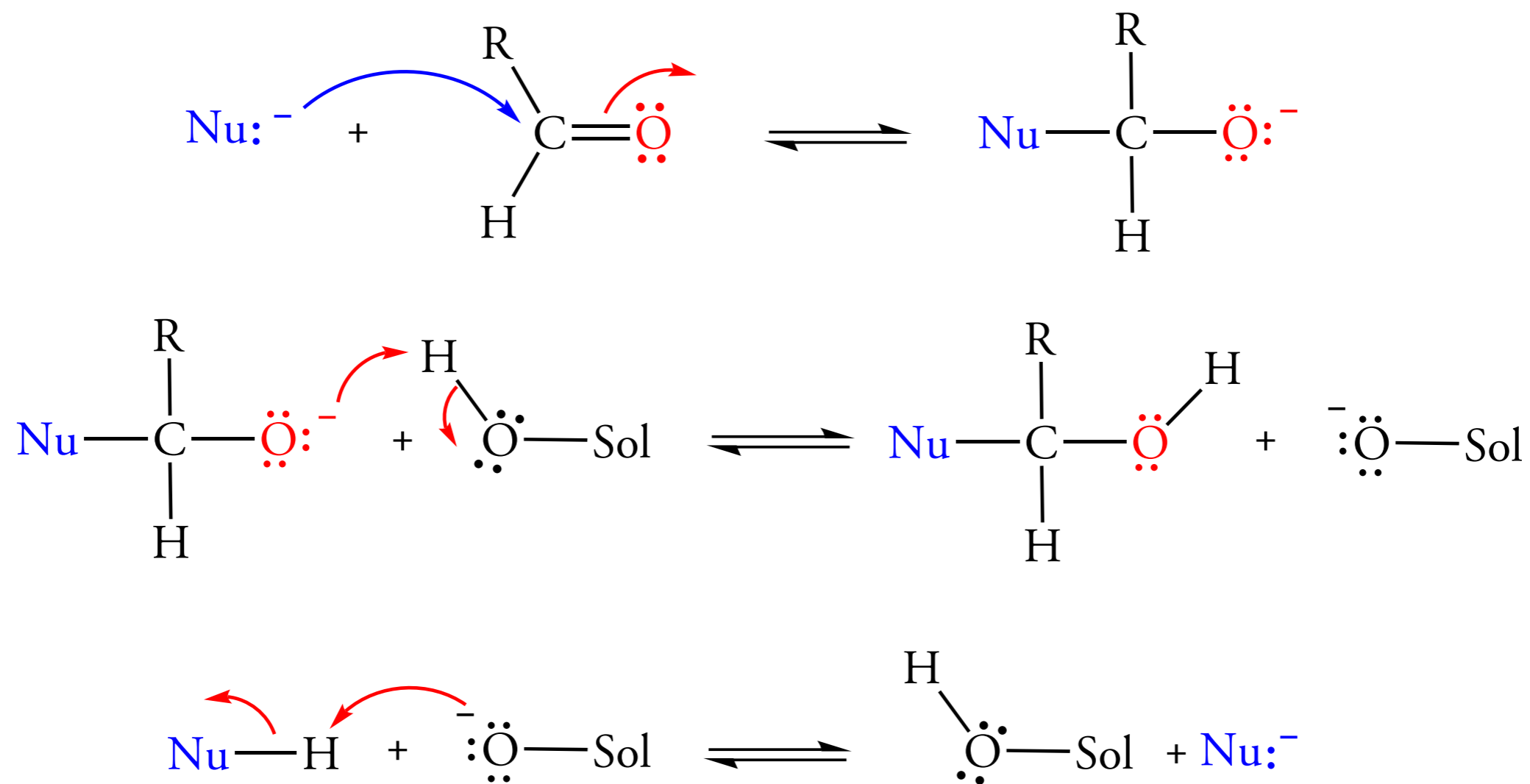
19.4 MECHANISMS OF ACID- AND BASE-CATALYZED CARBONYL ADDITION REACTIONS



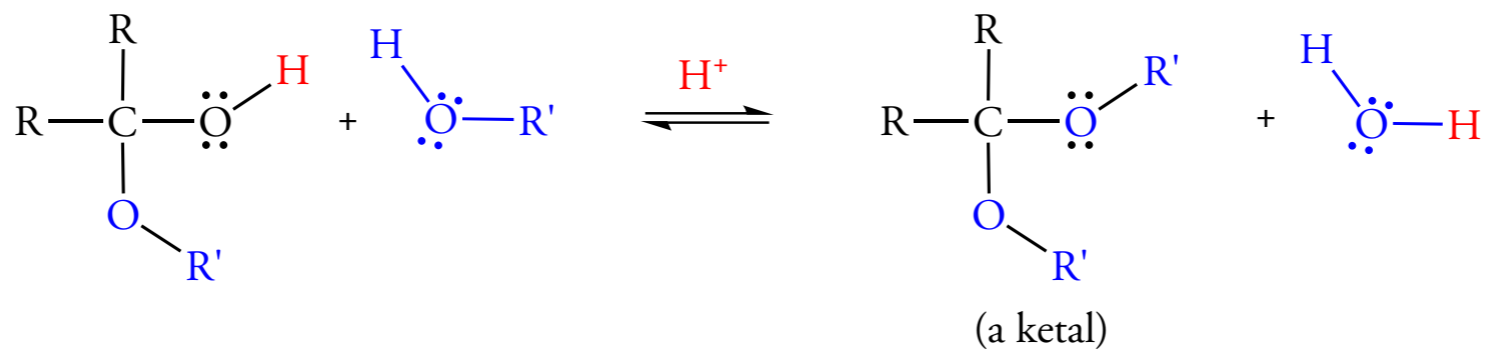
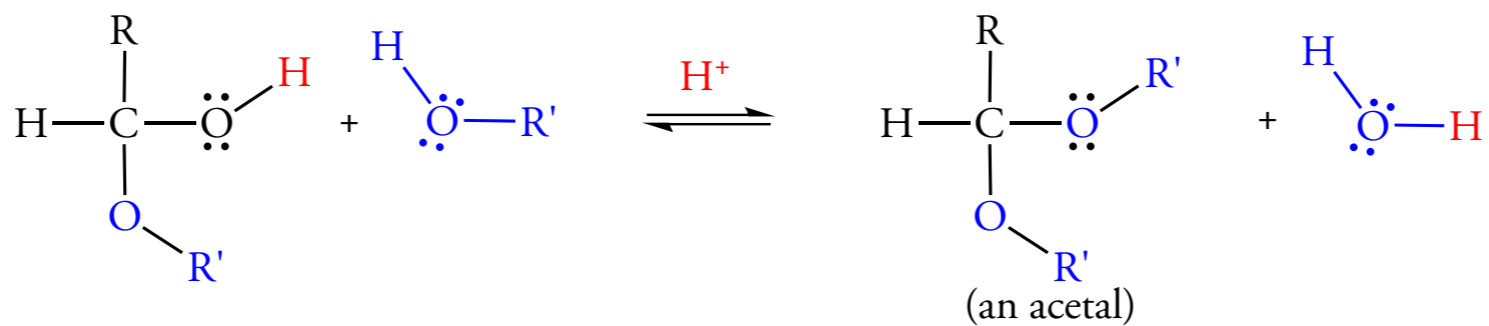
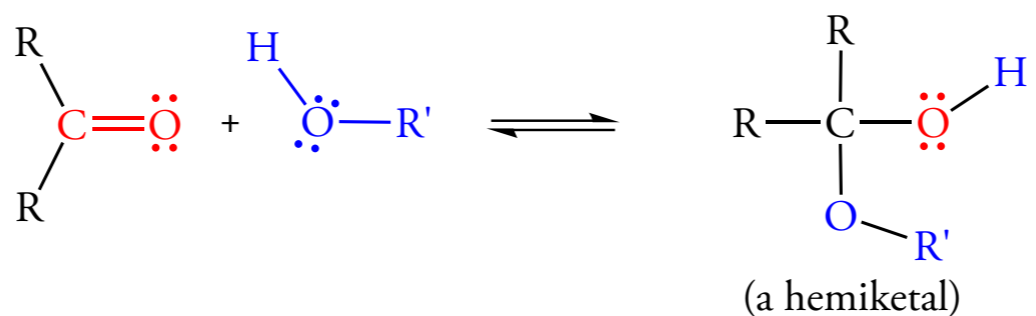
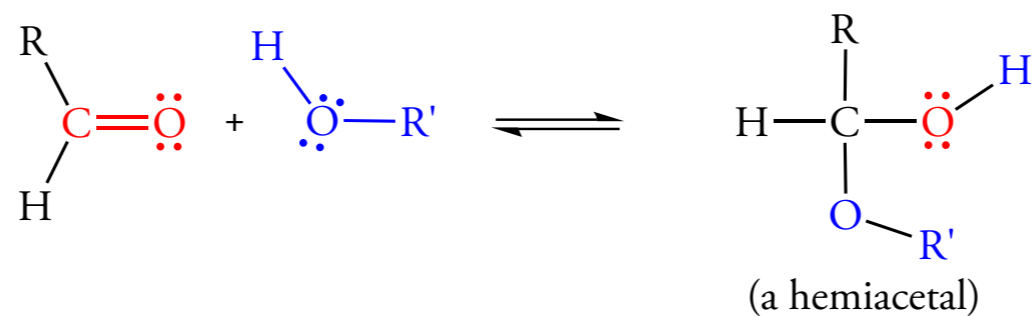
Acid-Catalyzed Nucleophilic Addition Reactions



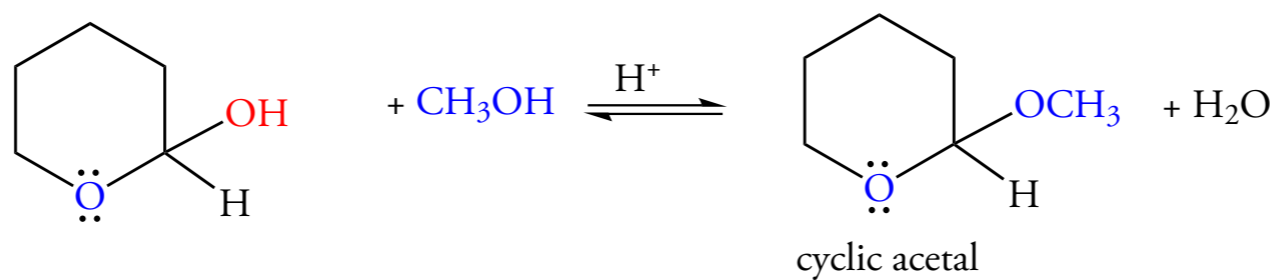
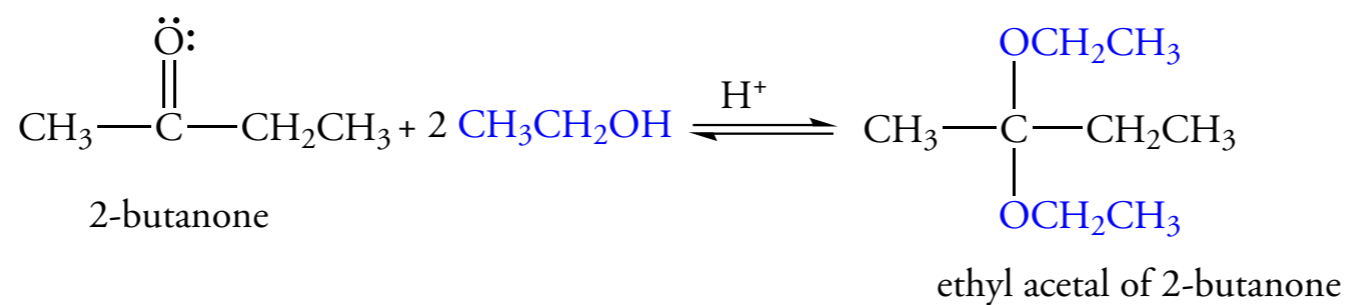
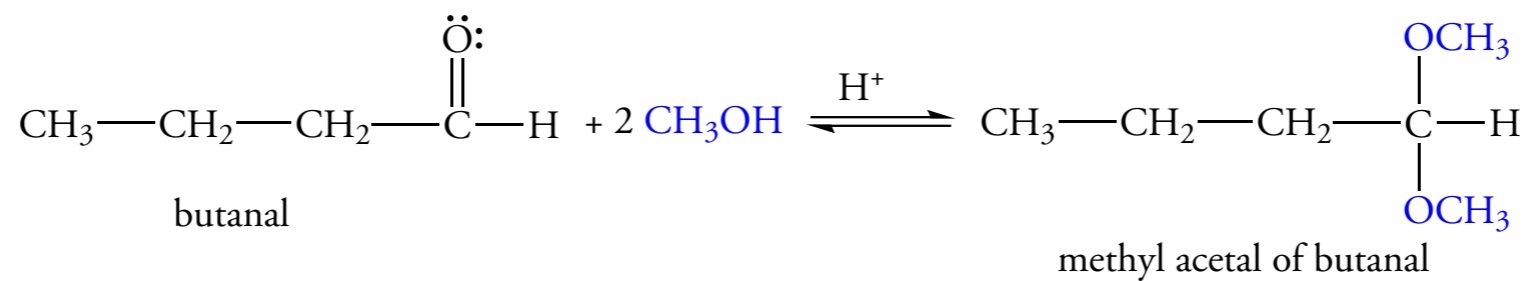
Base-Catalyzed Nucleophilic Addition Reactions



19.5 FORMATION OF ACETALS AND KETALS, II



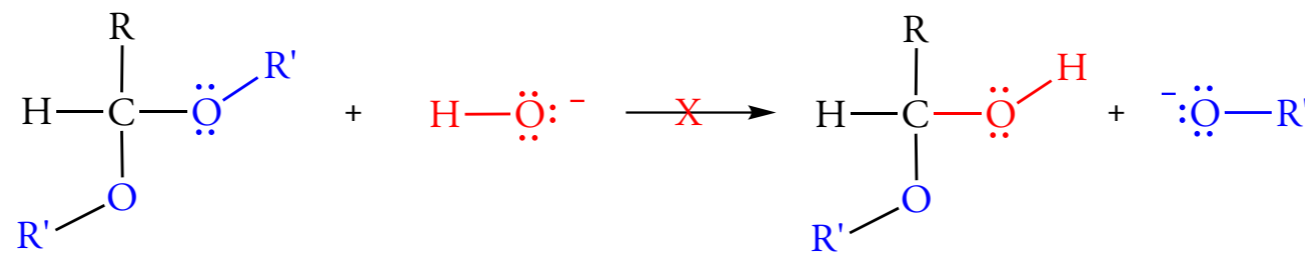
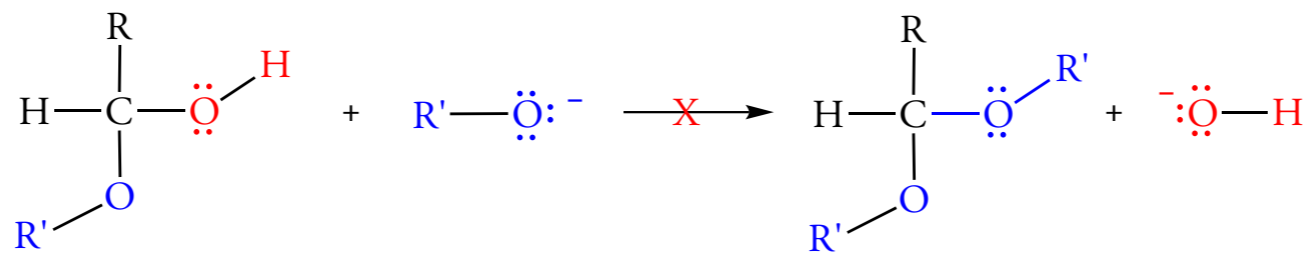
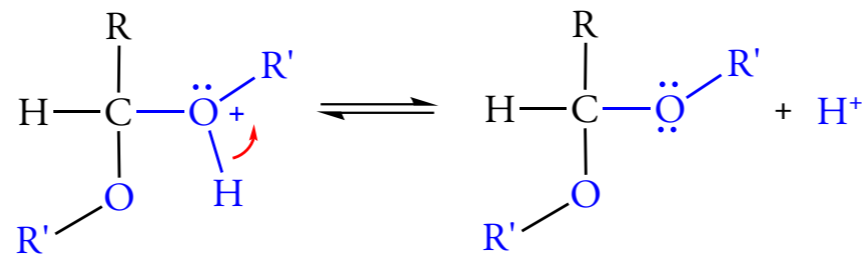
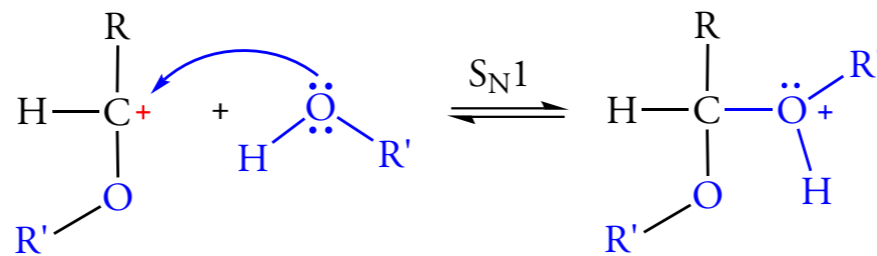
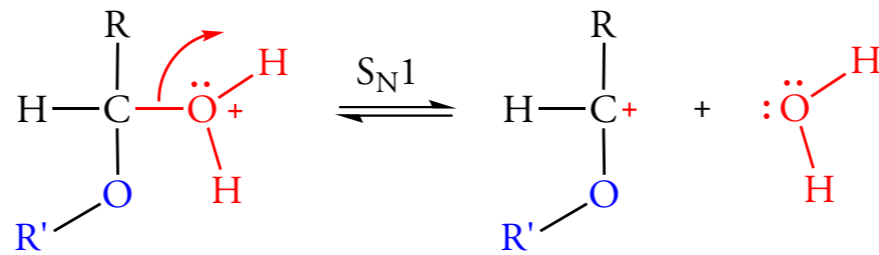
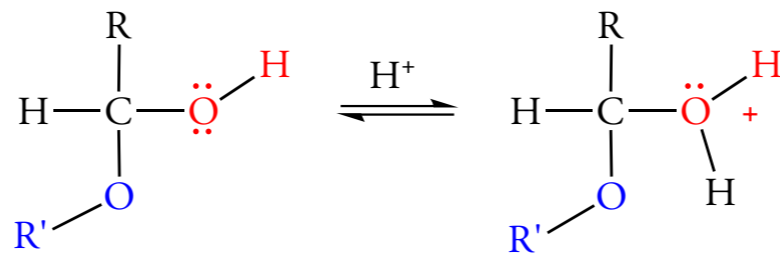
19.5 FORMATION OF ACETALS AND KETALS, II



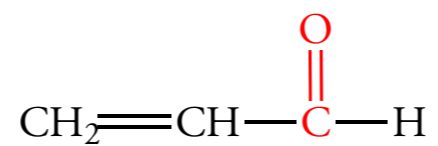
Adding alcohol pushes the equilibrium to the right.

Removing water pulls the equilibrium to the right.

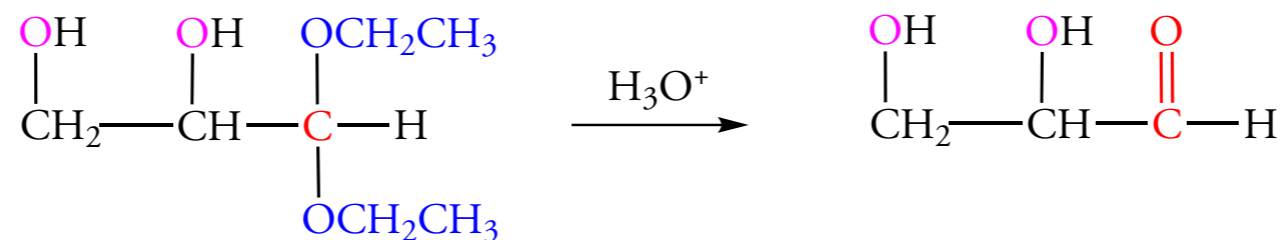
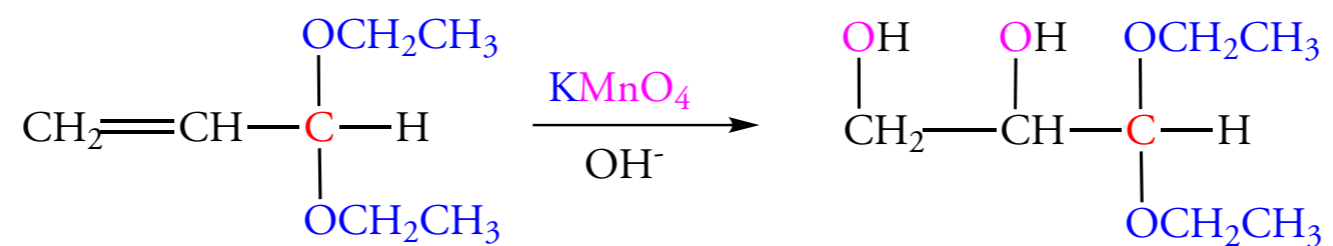
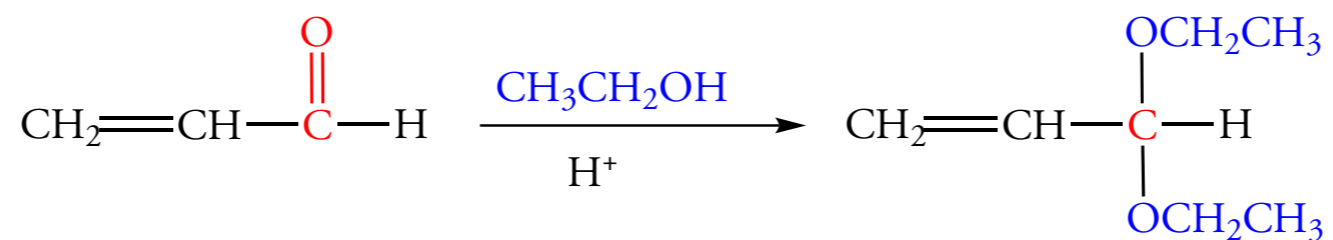
Mechanism of Acetal and Ketal Formation



19.6 ACETALS AS PROTECTING GROUPS

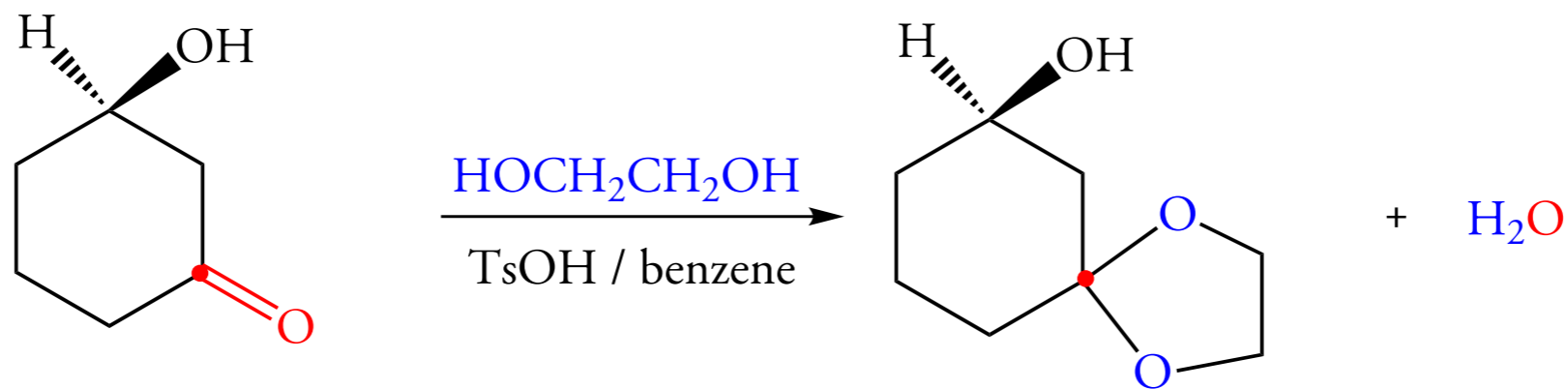
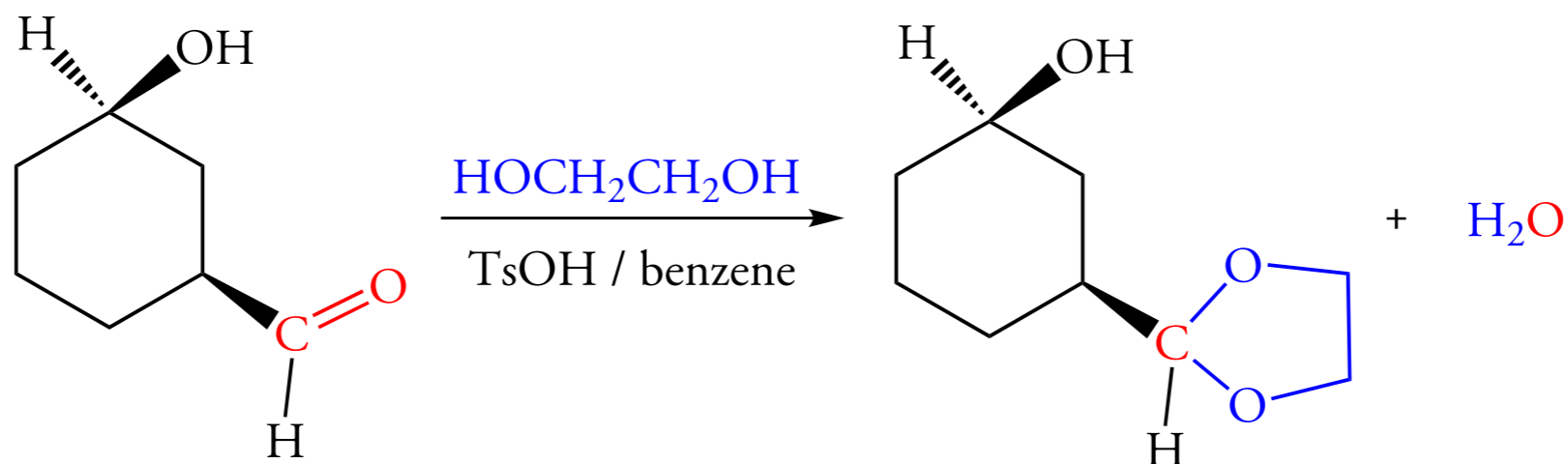


Permanganate will oxidize the double bond and the aldehyde.



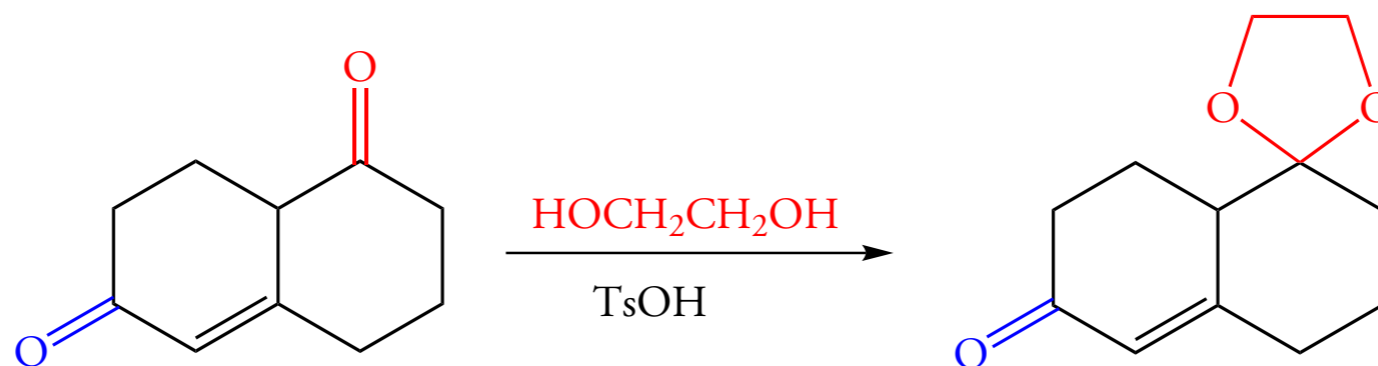
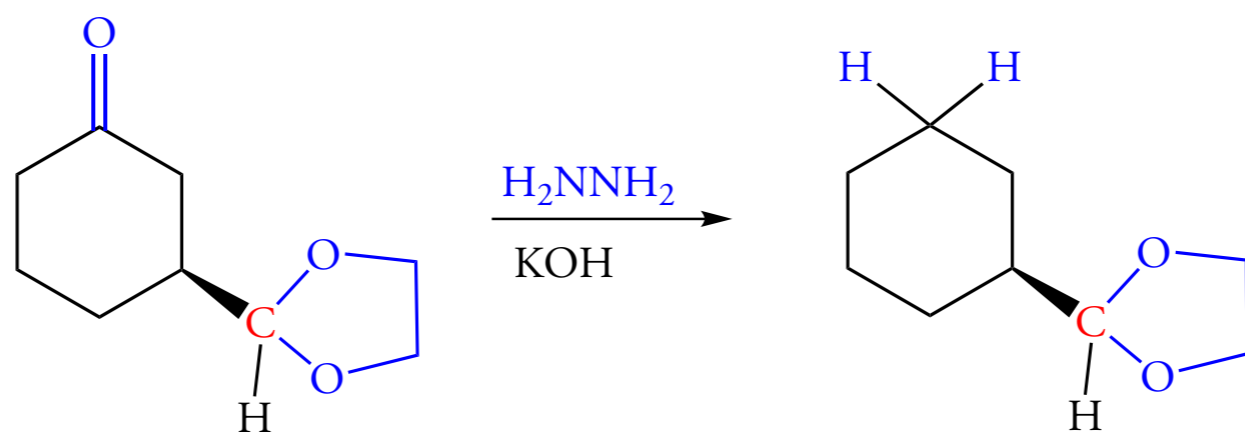
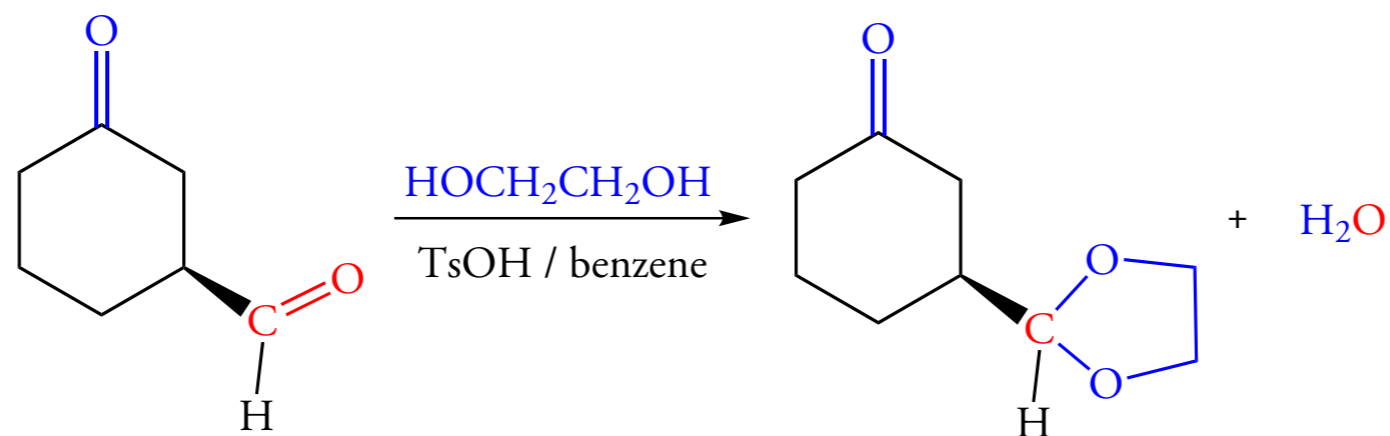
19.6 ACETALS AS PROTECTING GROUPS

Synthesis of Cyclic Acetals



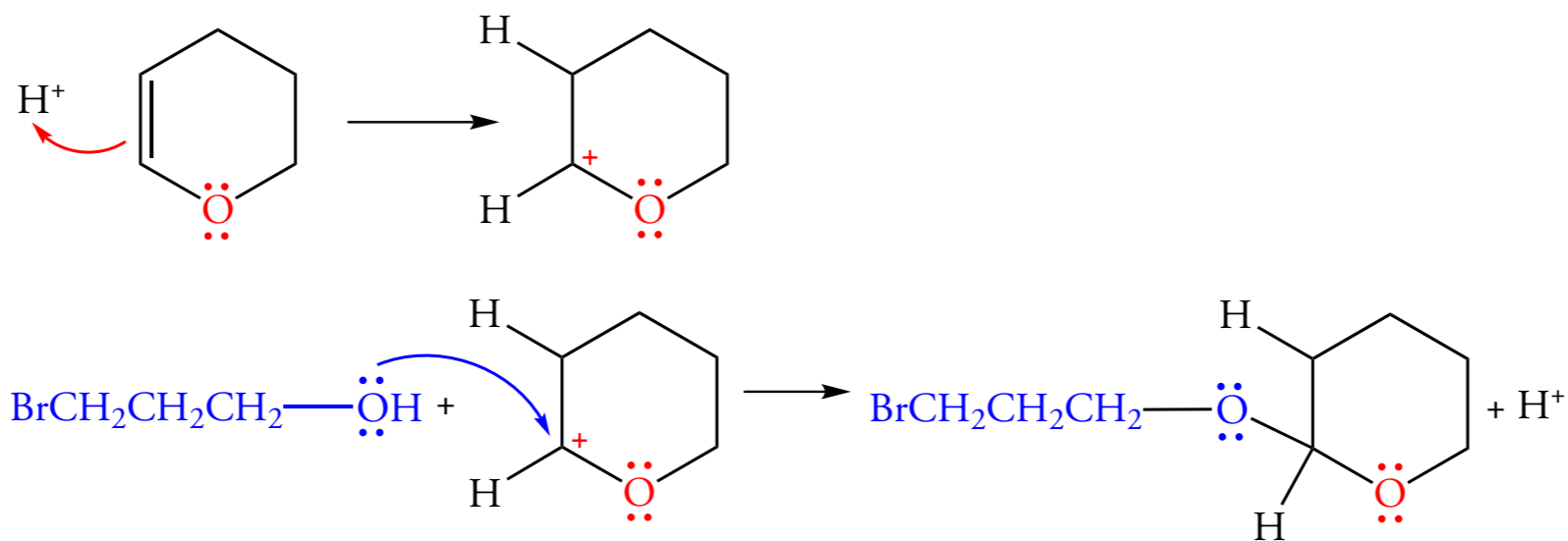
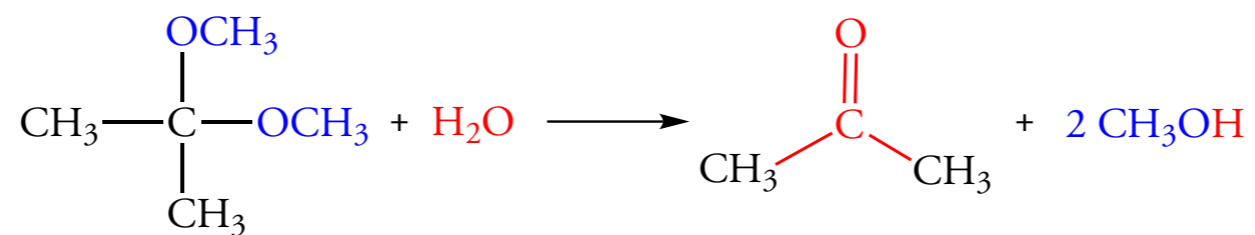
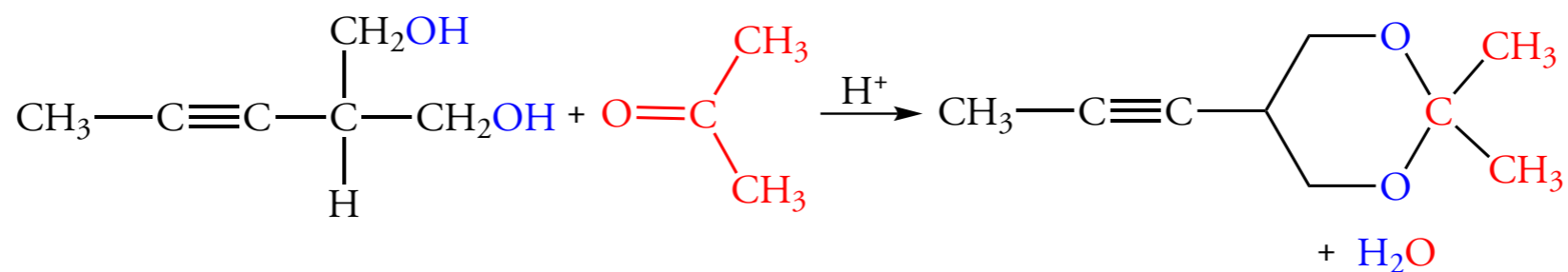
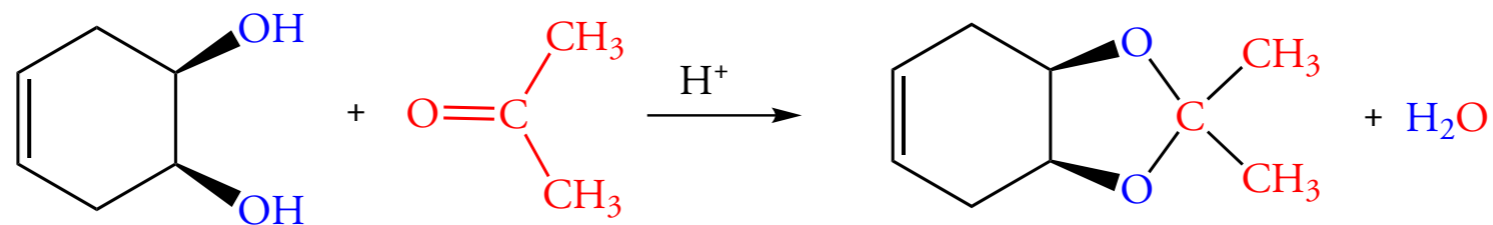
19.6 ACETALS AS PROTECTING GROUPS

Selective Acetal Synthesis

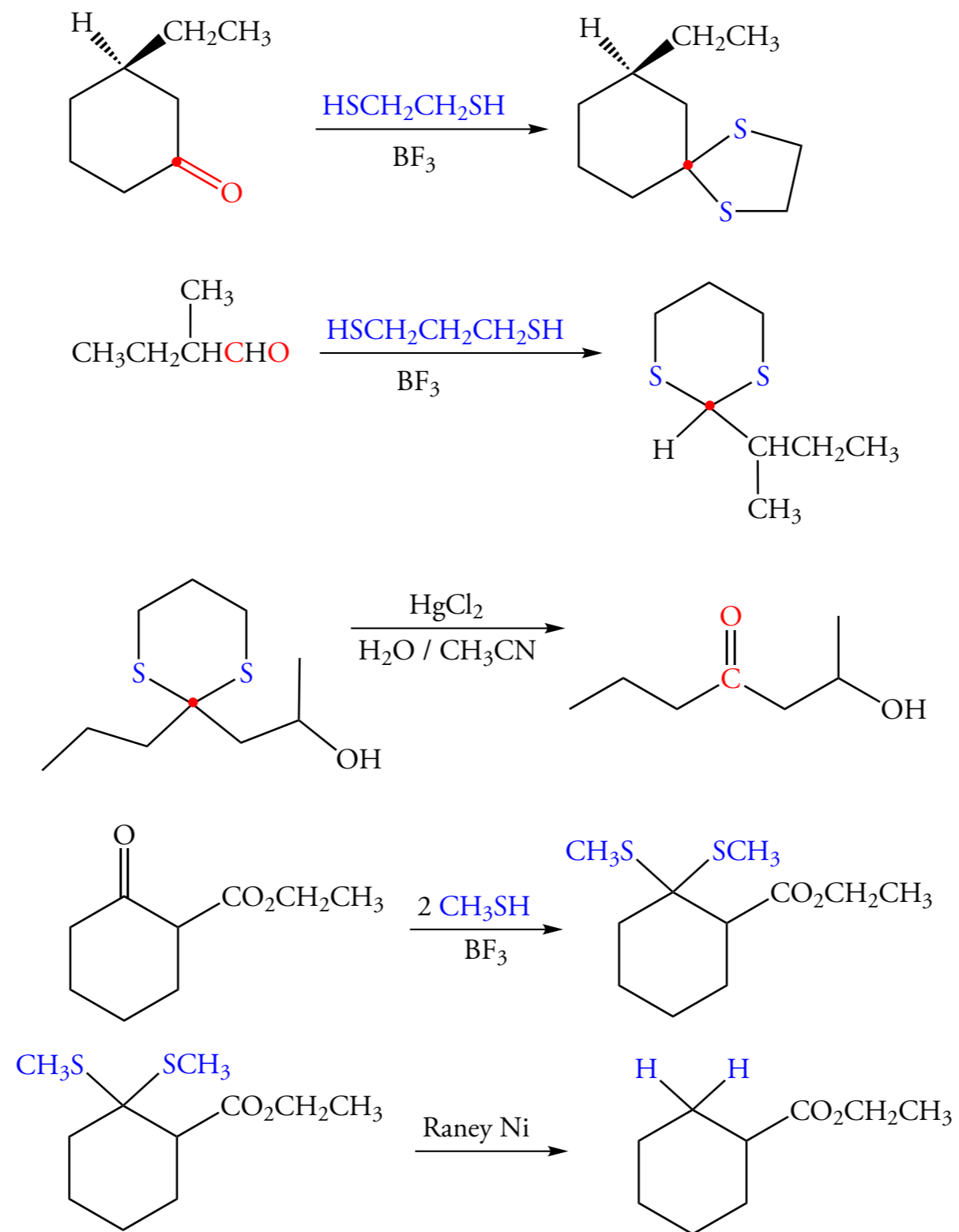


19.6 ACETALS AS PROTECTING GROUPS

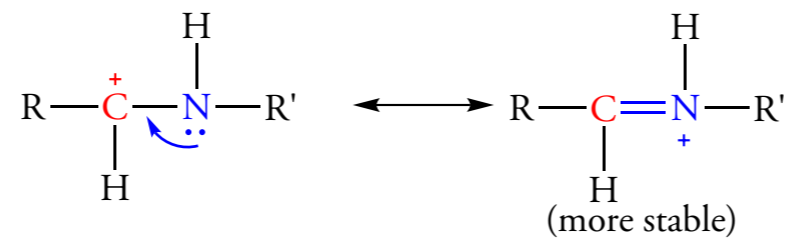
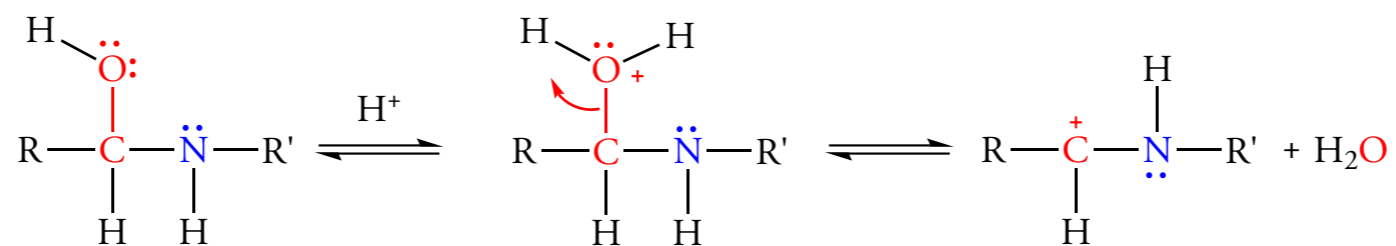
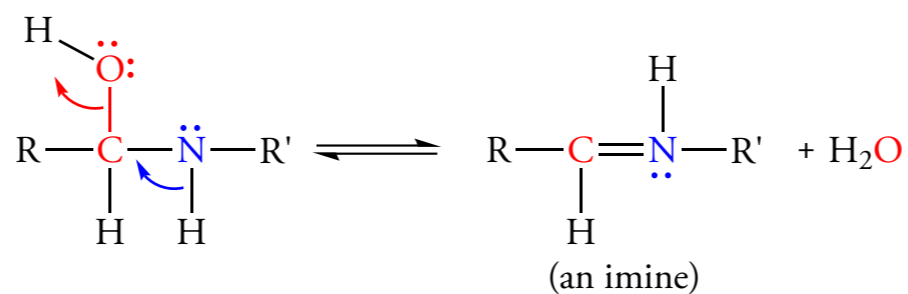
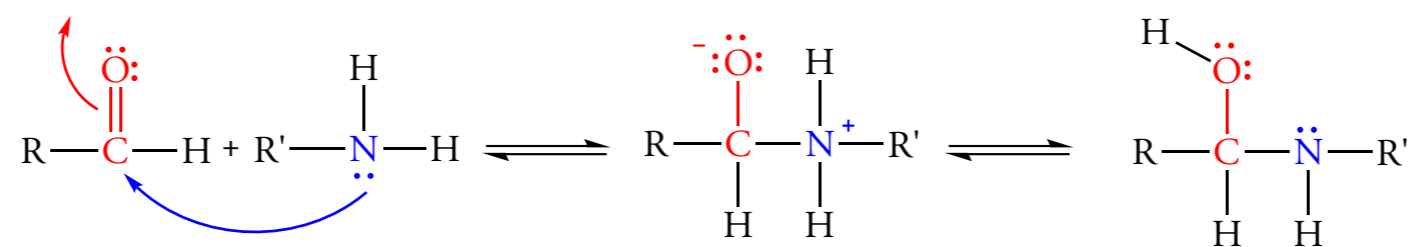
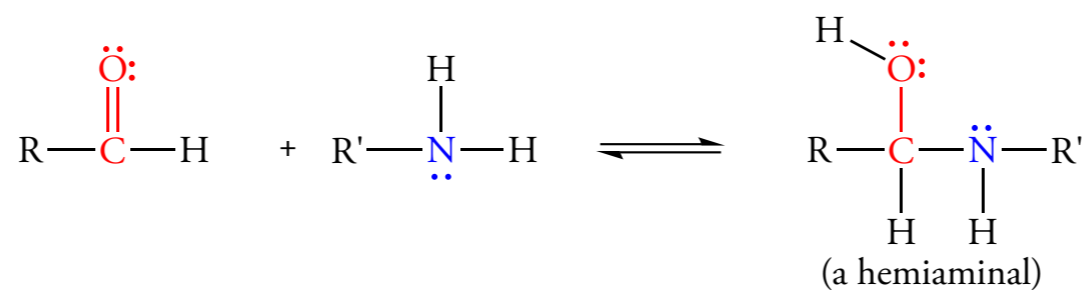
Protection of Alcohols by Acetal Formation



19.7 THIOACETALS AND THIOKETALS

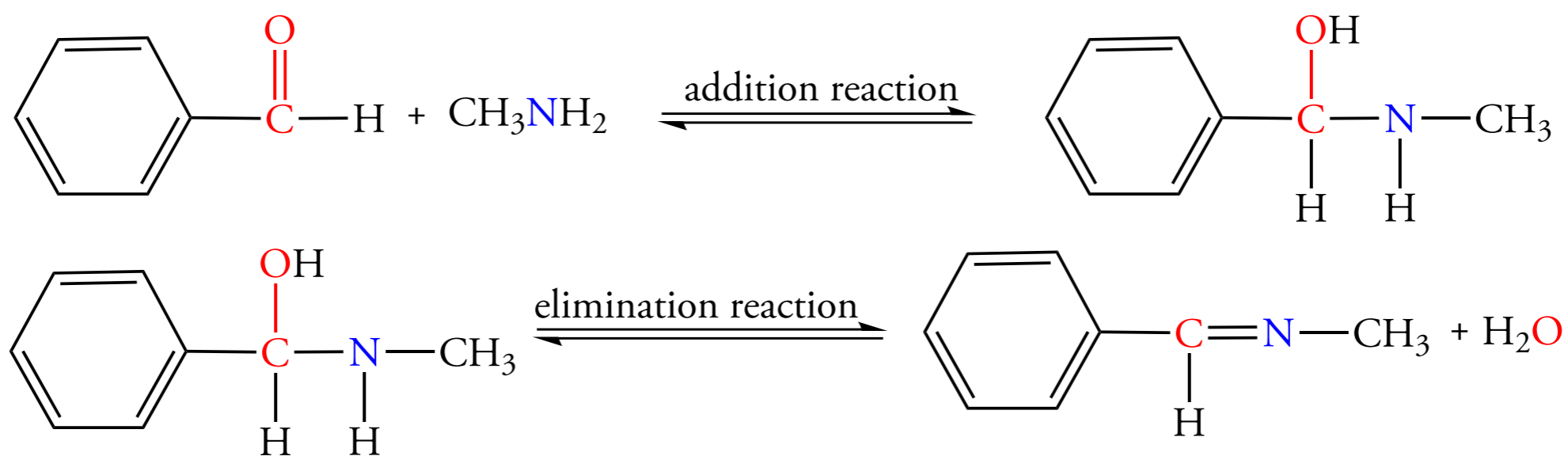


19.8 ADDITION OF NITROGEN COMPOUNDS TO ALDEHYDES AND KETONES, I



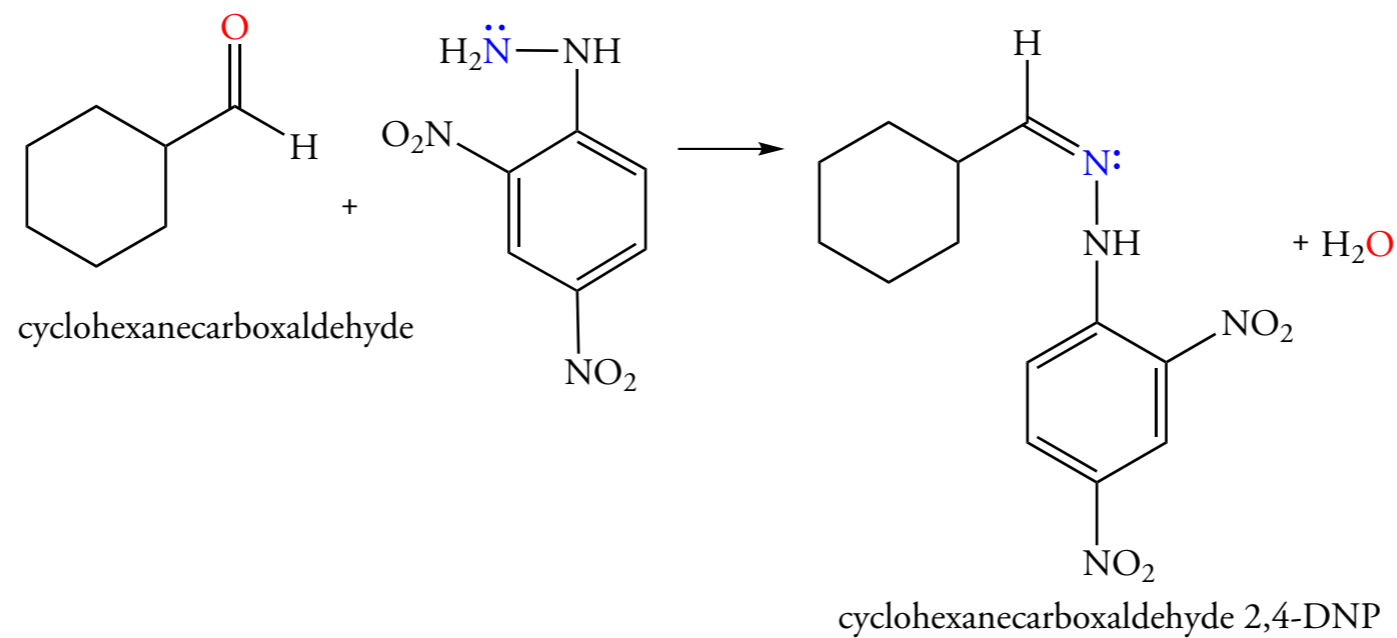
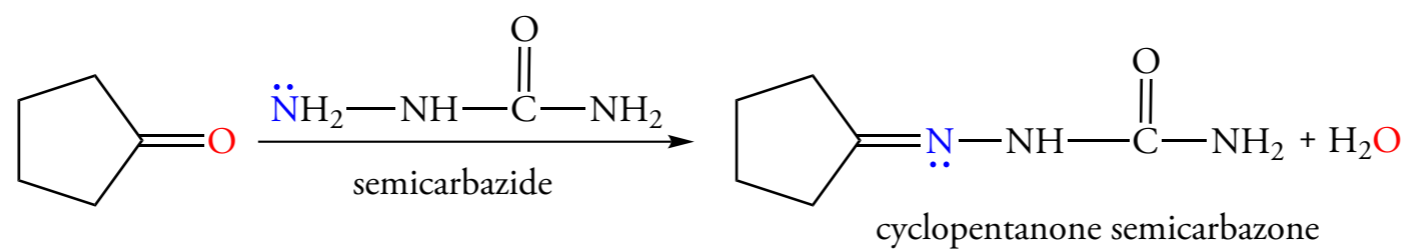
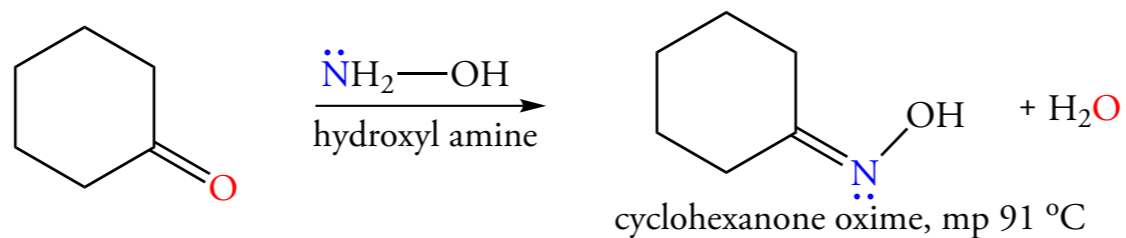
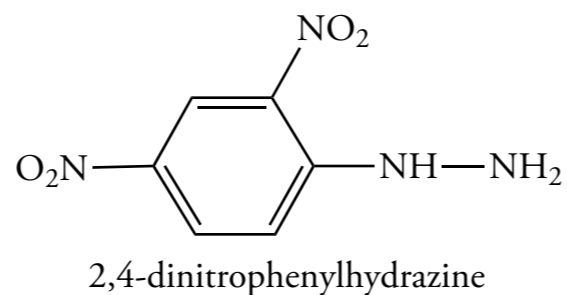
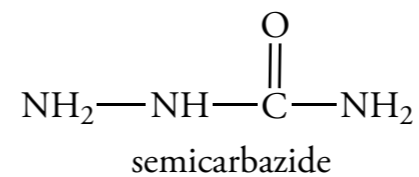
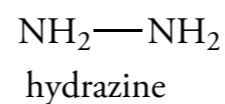
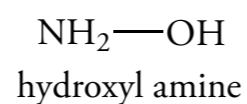
resonance forms of an iminium ion

19.8 ADDITION OF NITROGEN COMPOUNDS TO ALDEHYDES AND KETONES, II

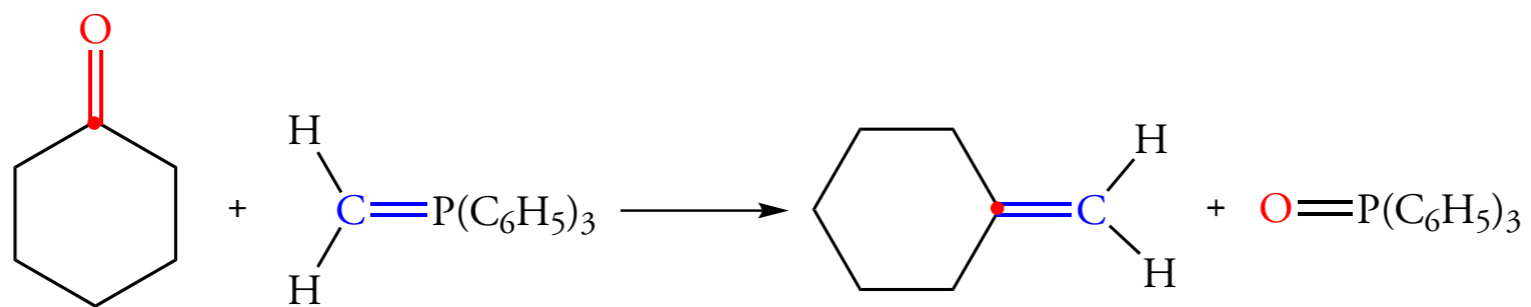
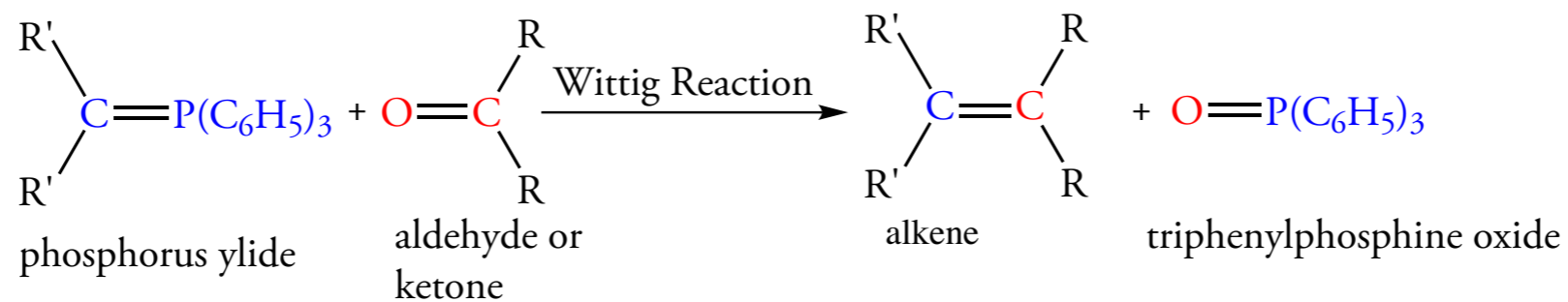


19.8 ADDITION OF NITROGEN COMPOUNDS TO ALDEHYDES AND KETONES

Stable Imine Derivatives

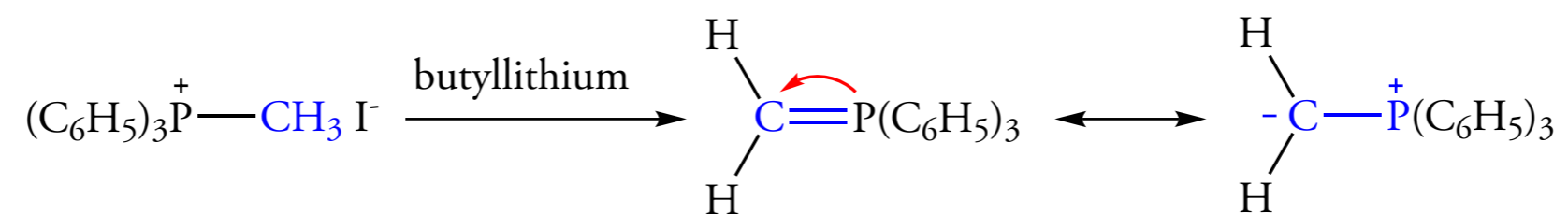


19.9 THE WITTIG REACTION



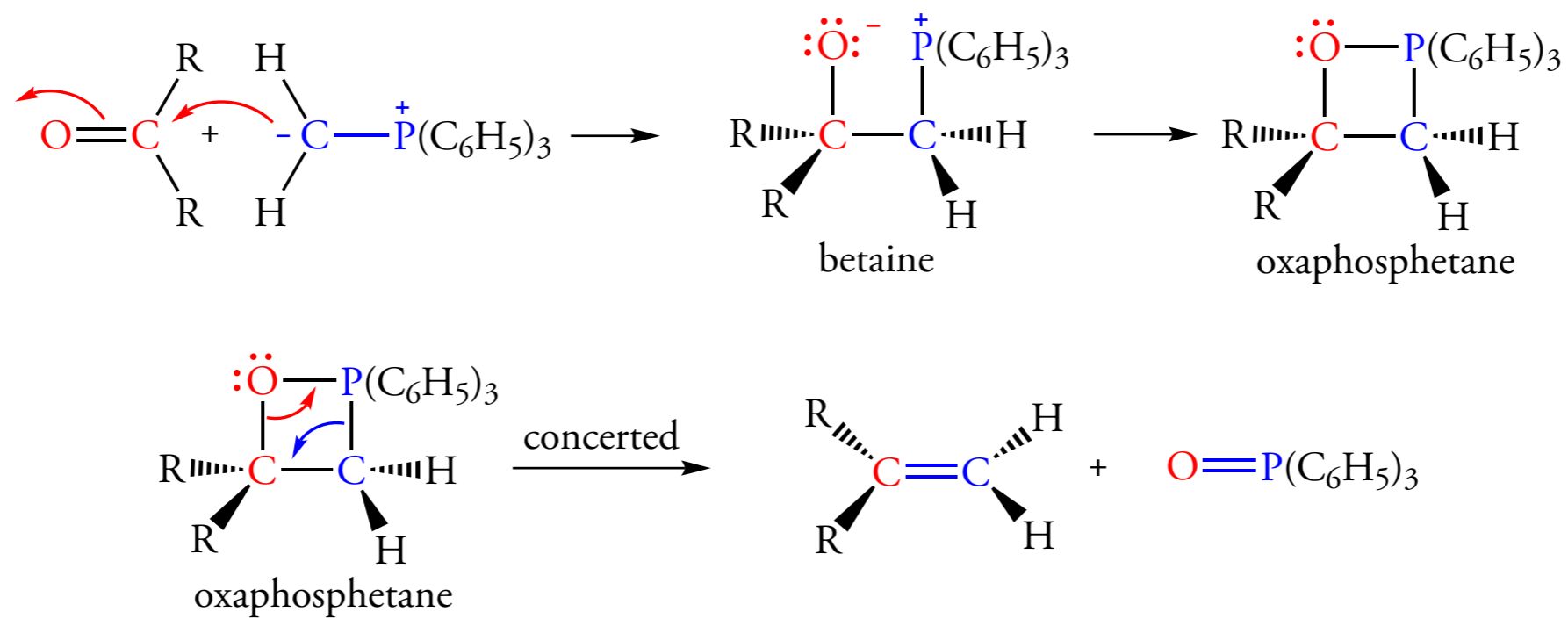
19.9 THE WITTIG REACTION

Preparation of Phosphorus Ylides



19.9 THE WITTIG REACTION

Mechanism of the Wittig Reaction



19.9 THE WITTIG REACTION

The Wittig Reaction in Organic Synthesis

