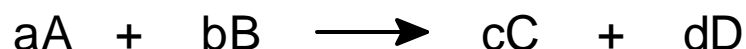Equilibrium Reactions –

In any reaction the reactants react to give products.

In the generic reaction below, a moles of reactant A react with b moles of reactant B to give c moles of product C and d moles of product D.

aA + bB $\longrightarrow$ cC + dD

The reaction will stop when either A or B is completely used up. A reaction of this type is said to "go to completion." Most reactions are not of this type.

Most reactions are equilibrium reactions. In an equilibrium reaction the reactants react to give products, but the products, in turn, react with each other to give the reactants. We indicate this by using forward and reverse reaction arrows –

aA + bB $\rightleftharpoons$ cC + dD
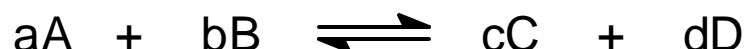
The rate of the forward reaction is –
$rate_{forward} = k_{forward}[A]^a [B]^b$, where $k_{forward}$ is the rate constant of the forward reaction. The larger $k_{forward}$ the faster a molecule of A will react with one of B.

The rate of the reverse reaction is –
$rate_{reverse} = k_{reverse}[C]^c [D]^d$, where $k_{reverse}$ is the rate constant of the reverse reaction. The larger $k_{reverse}$ the faster a molecule of C will react with one of D.

At equilibrium, $rate_{forward} = rate_{reverse}$ and the concentrations of A, B, C, and D do not change with time even though reaction is taking place.   At

equilibrium, since $\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$,

$$k_{\text{forward}}[A]^a [B]^b = k_{\text{reverse}}[C]^c [D]^d,$$

or $\dfrac{k_{\text{forward}}}{k_{\text{reverse}}} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$. The ratio $\dfrac{k_{\text{forward}}}{k_{\text{reverse}}}$ is known

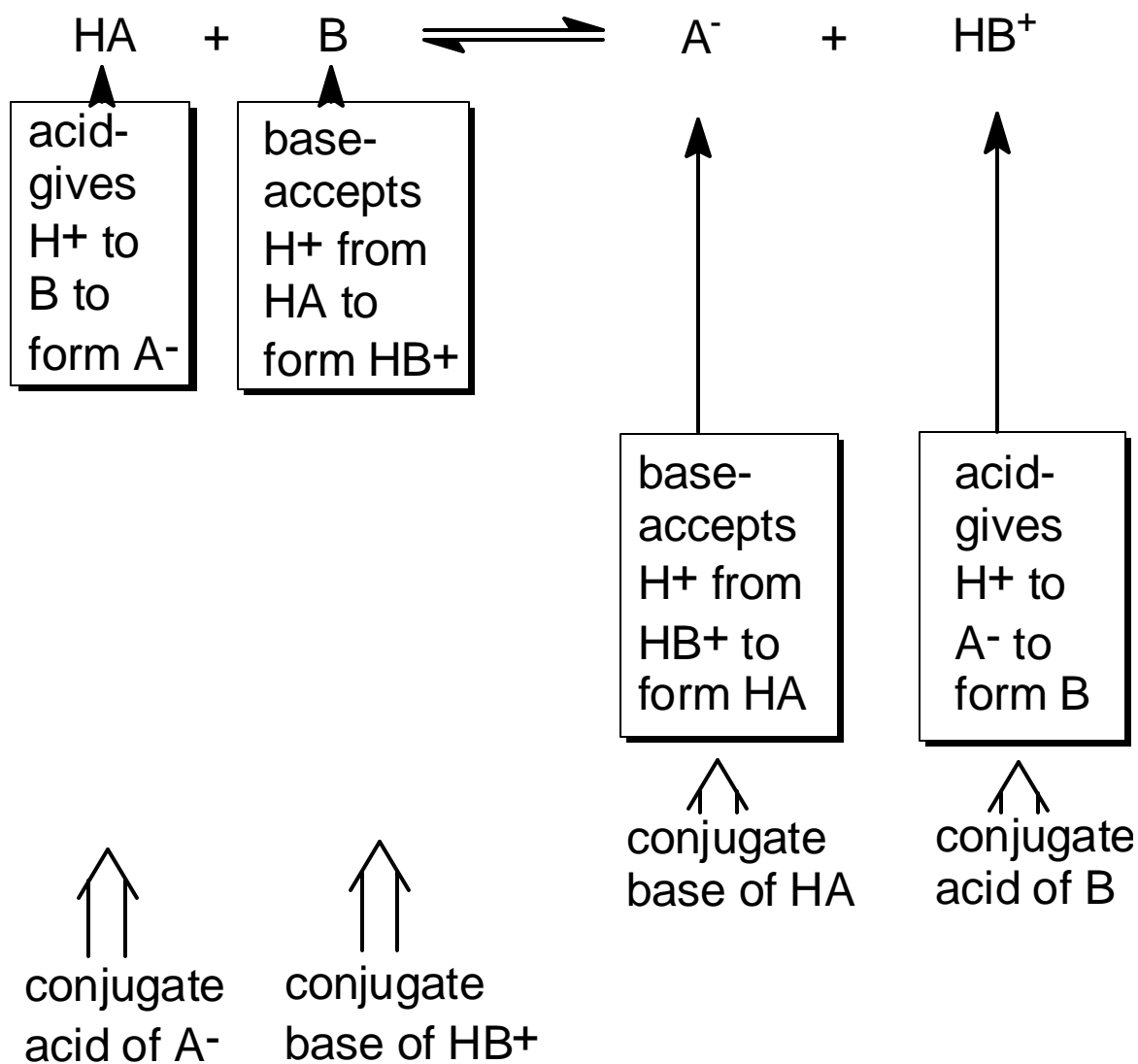as the equilibrium constant, K_{eq}, for the reaction. So,

$$K_{eq} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b} \ .$$

Acids & Bases

Bronsted/Lowry:

acid: substance which gives up a proton
base: substance which accepts a proton

$$HA \quad + \quad B \rightleftharpoons A^- \quad + \quad HB^+$$

acid-
gives
H+ to
B to
form A-

base-
accepts
H+ from
HA to
form HB+

base-
accepts
H+ from
HB+ to
form HA

acid-
gives
H+ to
A- to
form B

conjugate
base of HA

conjugate
acid of B

conjugate
acid of A-

conjugate
base of HB+

Acids and bases may be charged or uncharged ---

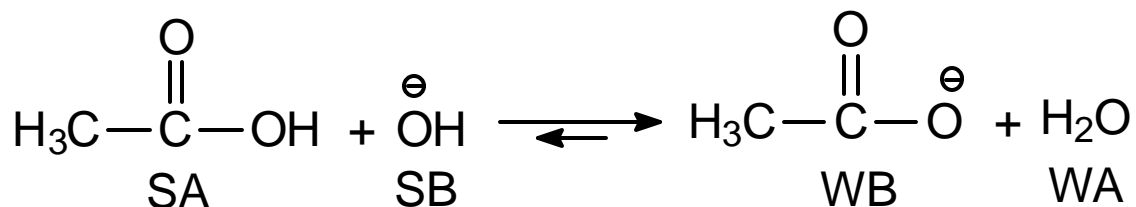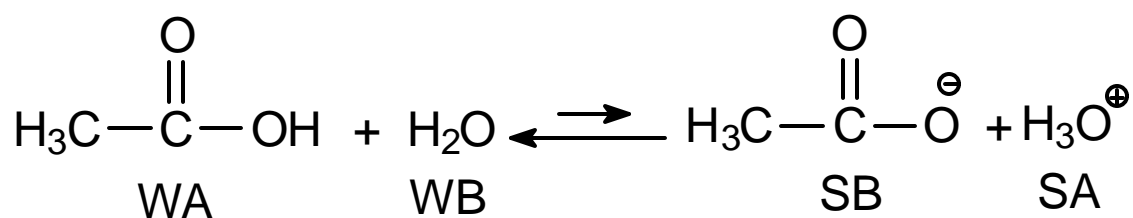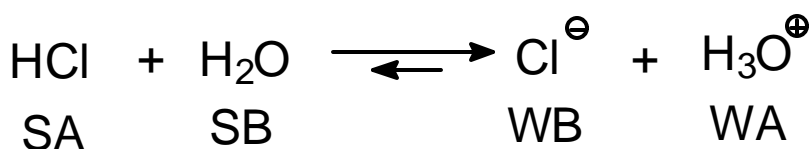| Acid		Base		Acid		Base
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	SH^-
HS^-	+	OH^-	$\rightleftharpoons$	H_2O	+	S^{-2}
$HCl + H_2N(CH_2)_4NH_3^+$			$\rightleftharpoons$	$H_3N(CH_2)_4NH_3^{+2}$	+	Cl^-
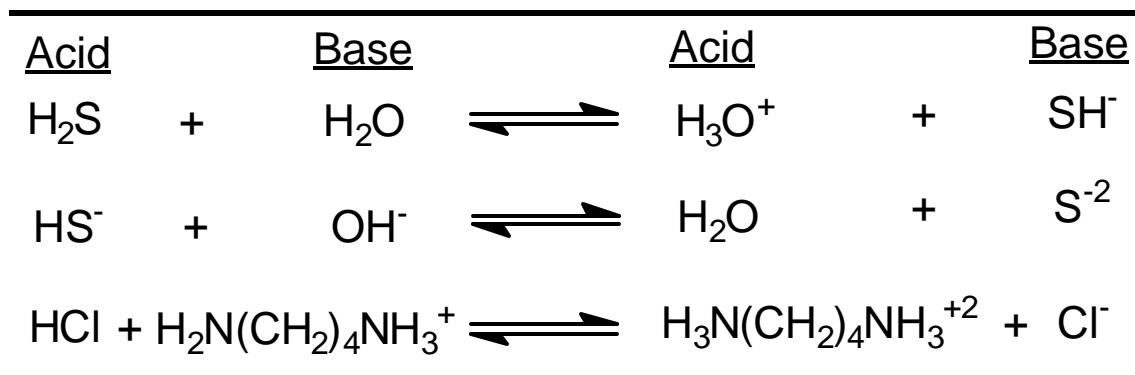
Typically, acids are neutral or positive, bases are neutral or negative.

Acid and Base Strength:
At equilibrium the weaker acid and base are favored.

SA=stronger acid   SB=stronger base
WA=weaker acid   WB=weaker base

$$HCl + H_2O \rightleftharpoons Cl^{\ominus} + H_3O^{\oplus}$$

SA   SB   WB   WA

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2O \rightleftharpoons H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + H_3O^{\oplus}$$

WA   WB   SB   SA

$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH + OH^{\ominus} \rightleftharpoons H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O^{\ominus} + H_2O$$

SA   SB   WB   WA

Therefore,

acid strength: $HCl > H_3O^+ > H_3CCOOH > H_2O$

base strength: $OH^- > H_3CCOO^- > H_2O > Cl^-$

Note that the stronger an acid is, the weaker its conjugate base is. Does this make sense to you? [It should!]

<u>Quantative measure of Bronsted-Lowry acidity</u> –

$$HA \ + \ H_2O \ \rightleftharpoons \ A^{\ominus} \ + \ H_3O^{\oplus}$$
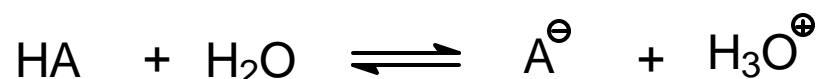
$$K_{eq} = \frac{[A^{\ominus}][H_3\overset{\oplus}{O}]}{[HA][H_2O]}$$

but in dilute solutions
$[H_2O] \sim 55.5\underline{M}$
i.e. there are ~55.5 moles of water in a liter of dilute aqueous solution, so...

$$K_{eq} = \frac{[A^{\ominus}][H_3\overset{\oplus}{O}]}{[HA](55.5)}$$

or $\quad K_{eq}(55.5) = \dfrac{[A^{\ominus}][H_3\overset{\oplus}{O}]}{[HA]} \ = \ K_a$

$pK_a = -logK_a$

The smaller (or the more negative) the pK_a, the larger the K_a, and the stronger the acid.

<u>Lewis definitions of acid and base</u> –

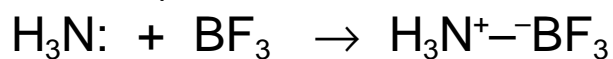Acid: an electron pair acceptor.
Base: an electron pair donor.

Lowry-Bronsted acids and bases are a subset of Lewis acids and bases; every L-B acid is a Lewis acid, every L-B base is a Lewis base.

H_3O^+ – acid by L-B and Lewis
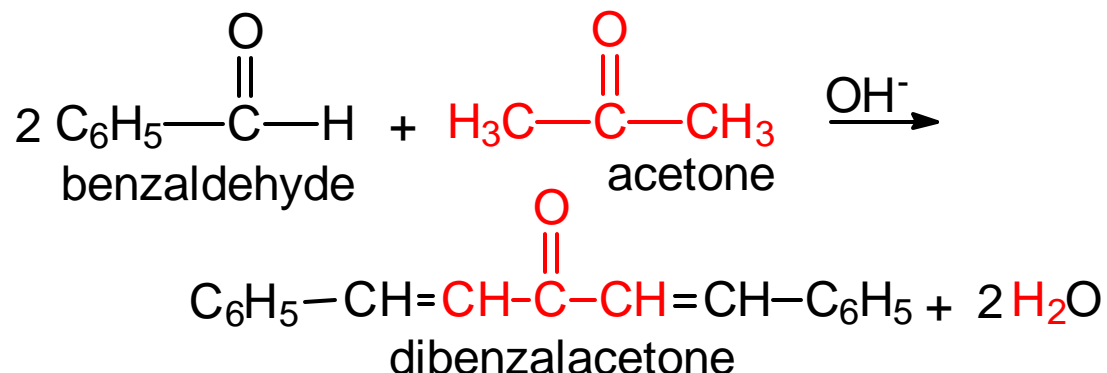$:NH_3$ – base by L-B and Lewis

BF_3 – acid by Lewis, but not by L-B (no proton to donate)
$H_3N: + BF_3 \rightarrow H_3N^+ - {}^-BF_3$

Overall reaction –

$$2\ C_6H_5\overset{\displaystyle O}{\overset{\|}{-}}C-H\ +\ H_3C\overset{\displaystyle O}{\overset{\|}{-}}C-CH_3\ \xrightarrow{\ OH^-\ }$$
benzaldehyde   acetone

$$C_6H_5-CH=CH\overset{\displaystyle O}{\overset{\|}{-}}C-CH=CH-C_6H_5\ +\ 2\,H_2O$$
dibenzalacetone

[Sometimes when we write the equations for reactions
in organic chemistry we write the formulas of one or
more of the reactants above or below the reaction
arrow. In this case the hydroxide ion (from sodium or
potassium hydroxide) is a catalyst in the reaction and,
so, is not consumed.

Color is used here to show how fragments within the
dibenzalacetone molecule derive from the two
components that react.]

The Reaction Mechanism

The equation above tells us what happens, overall, in
the reaction. The equation tells us that two molecules
of benzaldehyde react with one molecule of acetone, in
the presence of hydroxide ion, to give one molecule of
dibenzalacetone and two molecules of water; it does
not tell us how this happens. The *reaction mechanism*
tells us how the reactants are converted into products.
To use a sports analogy, knowing the overall reaction

is like knowing that the Dodgers played the Mets last night and the Mets won, 3 to 2. Knowing the details of the reaction mechanism is like knowing the play-by-play of the game.

The reaction mechanism for this reaction involves a lot of acid-base chemistry as do many, if not most, reaction mechanisms.

The Mechanism –
In the first step, acetone functions as a Bronsted-Lowry acid and hydroxide as a base. Note that the equilibrium for this step is not favorable: water (pK_a = 15.7) is a stronger acid than acetone (pK_a ~ 20). Nevertheless, the overall reaction is successful because the equilibrium for the final step in the mechanism is favorable.

Note the use of curved arrows in the mechanism. The curves arrows are "bookkeeping" devices – they track the movements of electrons.
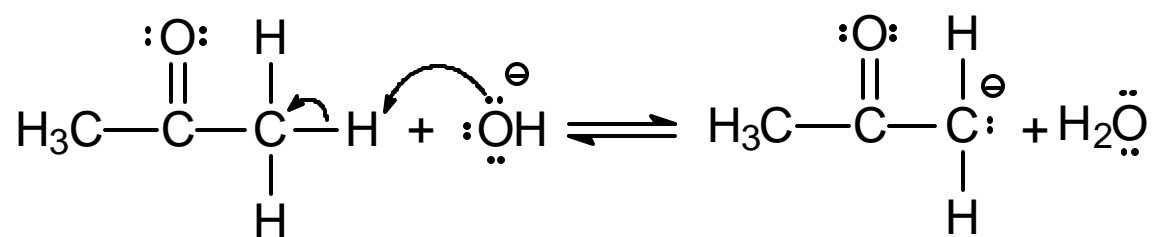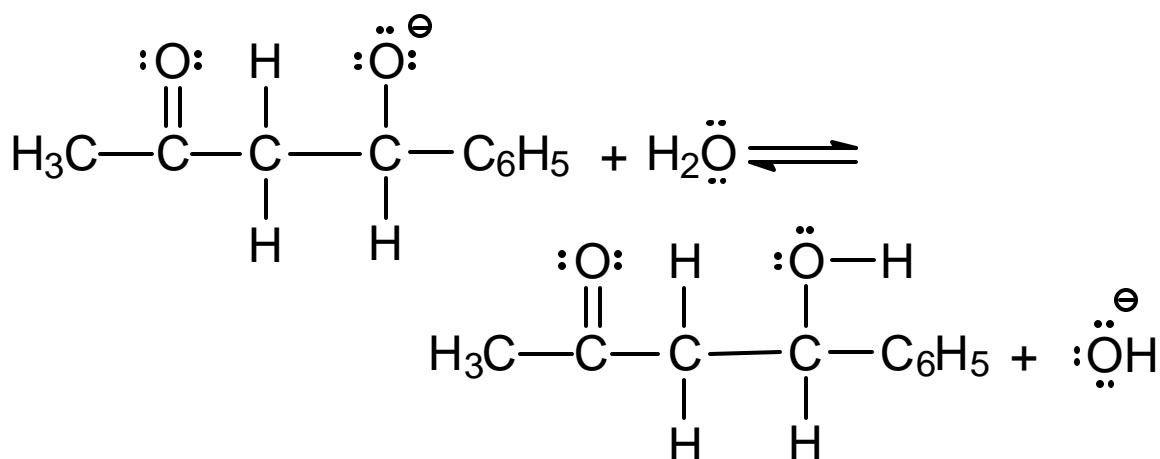

There is another resonance form for this anion. Can you draw it?

The next step involves the anion formed in the first step acting as a Lewis base in its attack on the partially positively charged C=O carbon of benzaldehyde to form a covalent bond that joins these two moieties together.
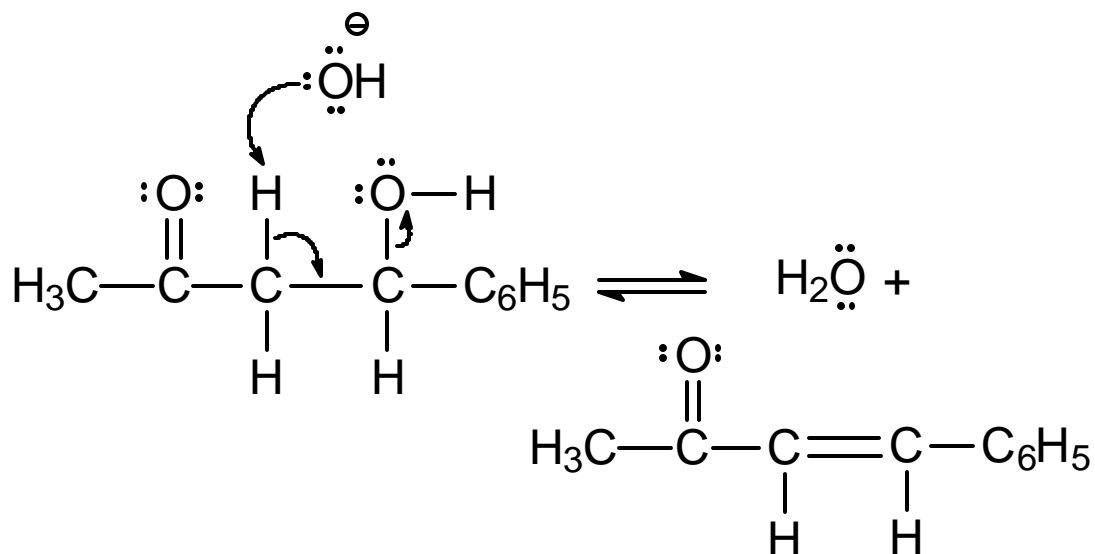
$$H_3C-\overset{\overset{\displaystyle :O:}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{:}^{\ominus} \; + \; H-\overset{\overset{\displaystyle :O:}{\|}}{C}-C_6H_5 \;\rightleftharpoons$$

$$H_3C-\overset{\overset{\displaystyle :O:}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle :\ddot{O}:^{\ominus}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5$$
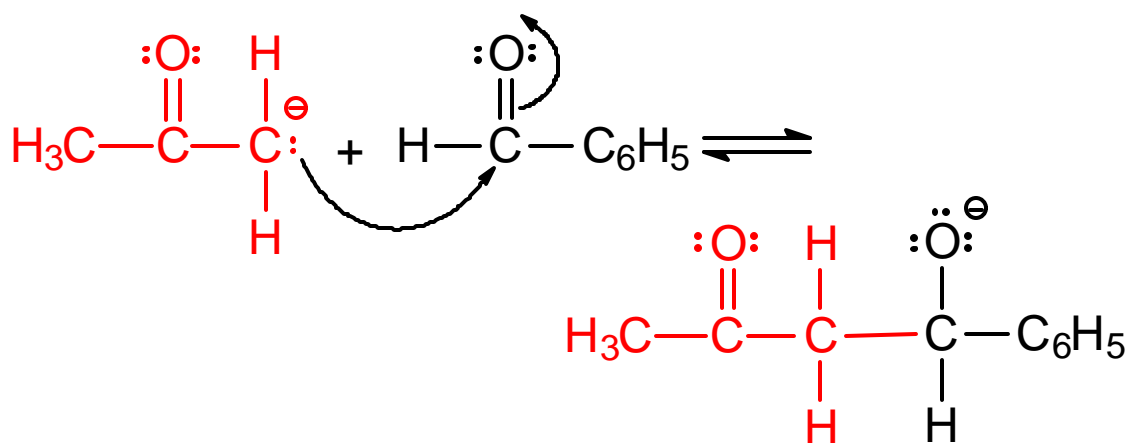
The next step is simply a B-L acid-base reaction with water functioning as the acid.

$$H_3C-\overset{\overset{\displaystyle :O:}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle :\ddot{O}:^{\ominus}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5 \; + \; H_2\ddot{O} \rightleftharpoons$$

$$H_3C-\overset{\overset{\displaystyle :O:}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle :\ddot{O}-H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C_6H_5 \; + \; :\ddot{O}H^{\ominus}$$

The next step involves what is known as an *elimination reaction*. In an elimination reaction a couple of moieties (atoms or groups of atoms) are removed from a molecule generating the products. In this case the elimination reaction involves a B-L acid-base reaction with hydroxide as the base.

:ÖH (with ⊖ charge)

$$:O: \quad H \quad :\ddot{O}-H$$
$$H_3C-\overset{\|}{C}-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-C_6H_5 \quad \rightleftharpoons \quad H_2\ddot{O} \; +$$
$$\qquad\quad H \qquad H$$

$$:O:$$
$$H_3C-\overset{\|}{C}-C=\!\!=C-C_6H_5$$
$$\qquad\qquad\quad H \quad\; H$$

At this point we are halfway to the final product. Looking back, we started with acetone and converted the -CH_3 group on the right side into a $CH=CH-C_6H_5$ group. Using the same series of steps, it is now possible to convert the remaining -CH_3 into a $CH=CH-C_6H_5$ group to produce the final product.

Do it!