## Acidity

$$H_2O \rightleftharpoons H^+ + HO^-$$

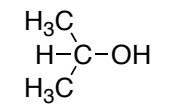
$$K_a = \frac{[H^+]\,[HO^-]}{[H_2O]} = 10^{-15.7}$$

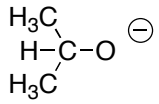
$$pK_a = -\log(K_a) \quad \text{, for } H_2O \text{ , } pK_a = 15.7$$

i) Acidity of simple alcohols:

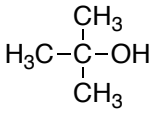
$CH_3$-OH (methanol) $\rightleftharpoons$ $H^+$ + $CH_3$-$O^\ominus$ (methoxide) pKa = 16

$H_3C$–$CH_2$-OH (ethanol) $\rightleftharpoons$ $H^+$ + $CH_3$-$CH_2$-$O^\ominus$ (ethoxide) pKa = 17

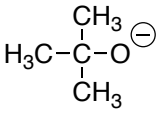



isopropyl alcohol $\rightleftharpoons$ $H^+$ +  pKa = 18





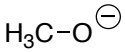

2-methyl-2-propanol
tert-butyl alcohol

$\rightleftharpoons$ $H^+$ + 

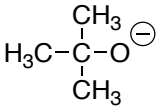


tert-butoxide
(strong base)

pKa = 19



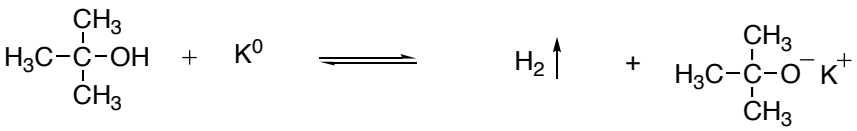

1 R (alkyl) group donates $e^-$
more likely to form, more stable




3 R (alkyl) groups donate $e^-$
less likely to form, less stable

Due to inductive electron donating effect of alkyl groups that make anion less stable (corresponding alcohol less acidic)

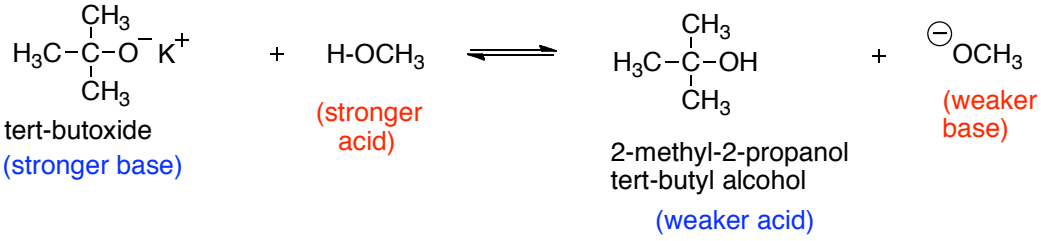
ii) Preparation of potassium tert-butoxide (equation not balanced):



2-methyl-2-propanol
tert-butyl alcohol

tert-butoxide
(strong base)

iii) Acid-Base equilibrium:



tert-butoxide
(stronger base)

(stronger acid)

2-methyl-2-propanol
tert-butyl alcohol
(weaker acid)

(weaker base)

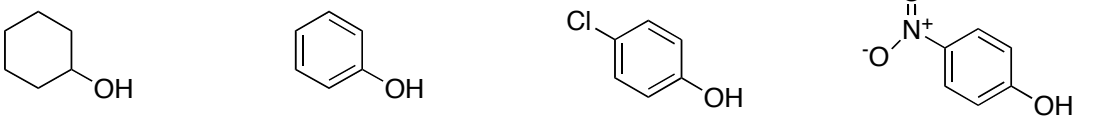
equilibrium lies to the RIGHT

Remember:

| | | | | | | |
|---|---|---|---|---|---|---|
| NaCl | + | $H_2O$ | ⇌ | HCl | + | NaOH |
| Weak Base | | Weak Acid | | Strong Base | | Strong Acid |

Equilibrium lies to the **LEFT**

iv) $pK_a$ value depends on how stable the anion formed is: most acidic



cyclohexanol — pKa = 18

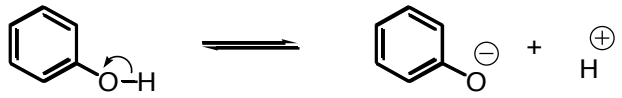
Phenol — pKa = 10

4-chlorophenol — pKa = 9.3

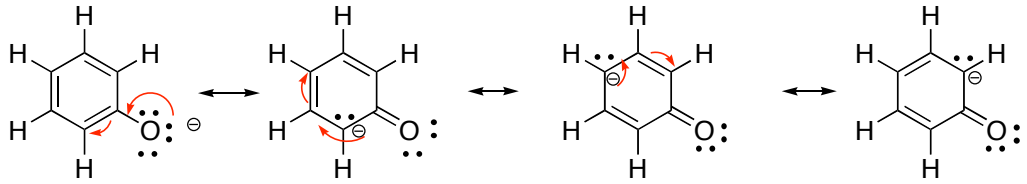
4-nitrophenol — pKa = 7

- Why phenol is more acidic?
  - the anion formed (phenoxide) can be stabilized by conjugation into benzene ring – resonance forms can be obtained

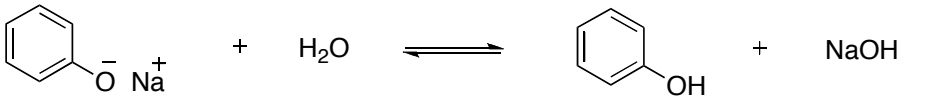
- the negative charge (electrons) on the oxygen is delocalized



- resonance forms of phenoxide anion:

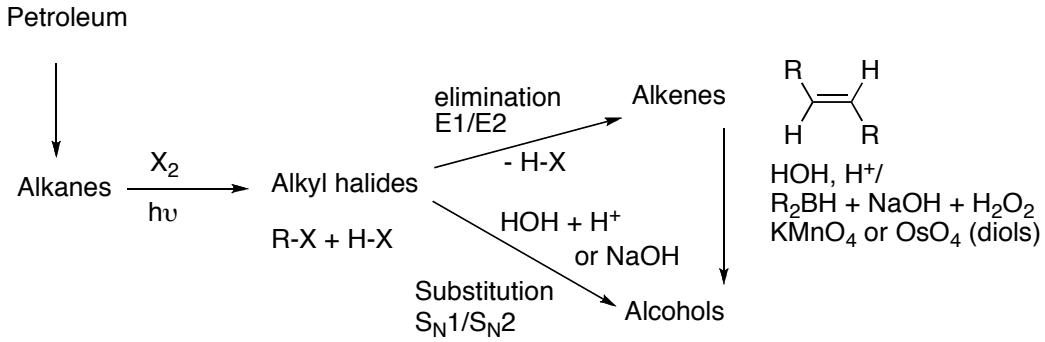


Eg.

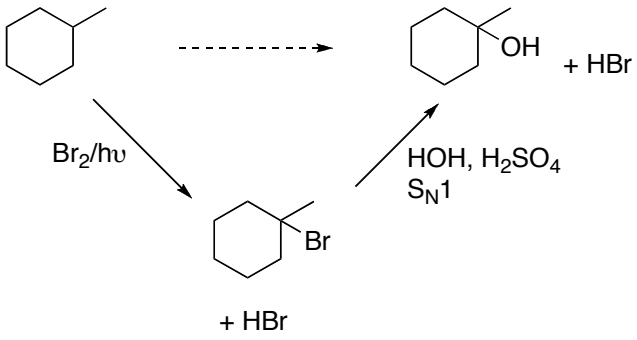



Equilibrium rapidly gives phenoxide and water from phenol and sodium hydroxide

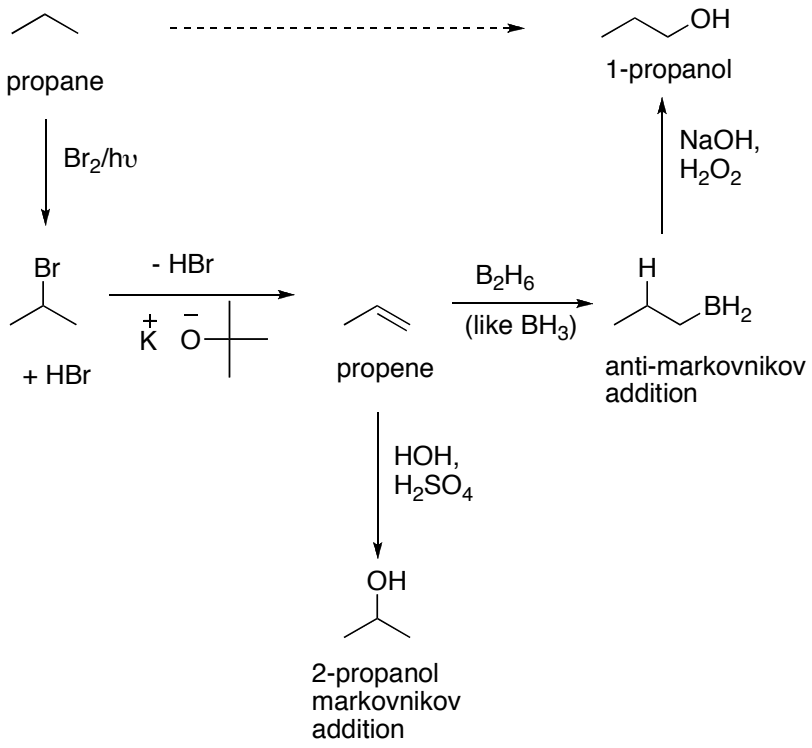
## Synthesis (Preparation) of Alcohols (Review of reactions seen earlier)



Eg.

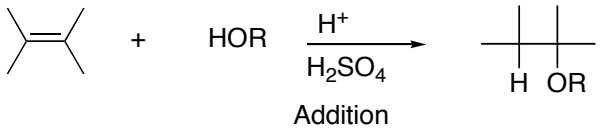



Eg.

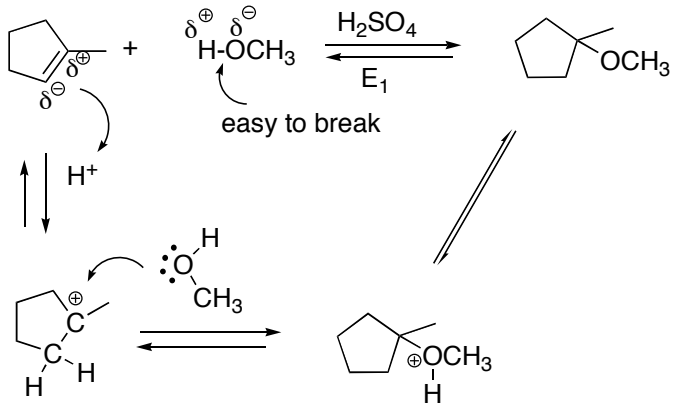


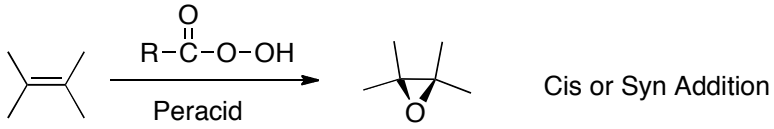

Formation of ethers

1) **From alkenes**

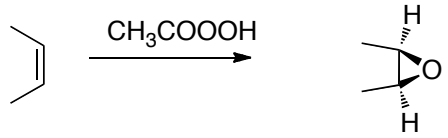



Addition

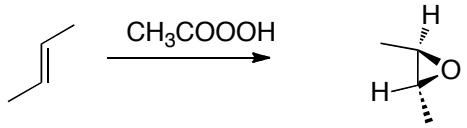


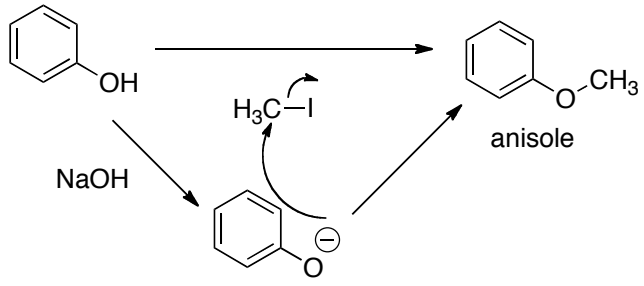

Cis or Syn Addition

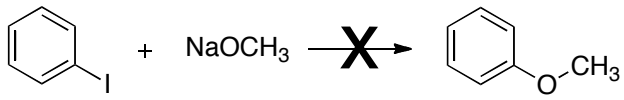



Meso Achiral




+/- racemate



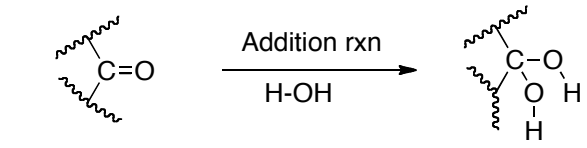

no substitution
on double bonds

**Carbonyl chemistry introduction**


carbonyl

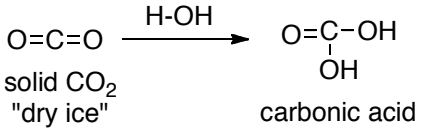

aldehyde


ketone




ketone or aldehyde hydrate

Demo:




solid $CO_2$ "dry ice" carbonic acid