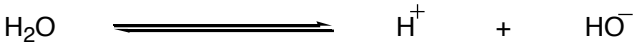
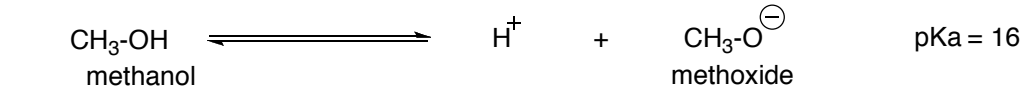
Acidity:

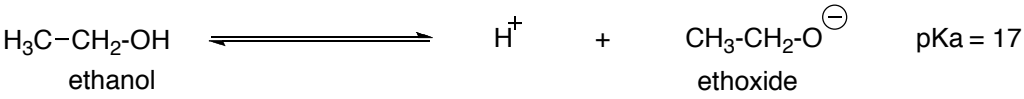


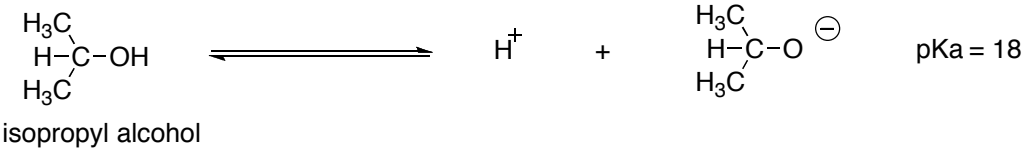
$$K_a = \frac{[H^+]\,[HO^-]}{[H_2O]} = 10^{-15.7}$$

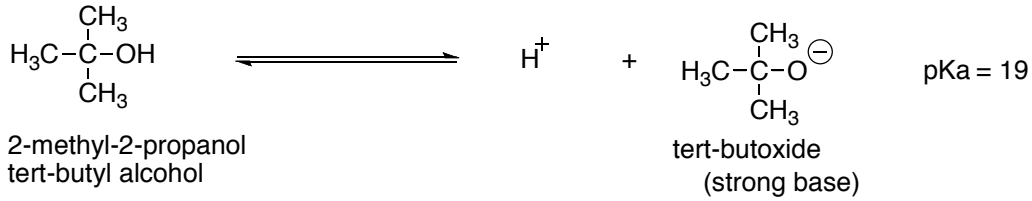
$pK_a = -\log(K_a)$, for H_2O , $pK_a = 15.7$

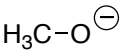
i) Acidity of simple alcohols:



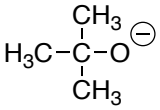








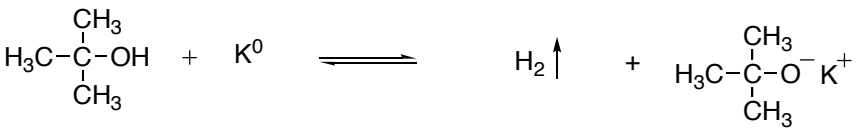
1 R (alkyl) group donates e^-
more likely to form, more stable



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)

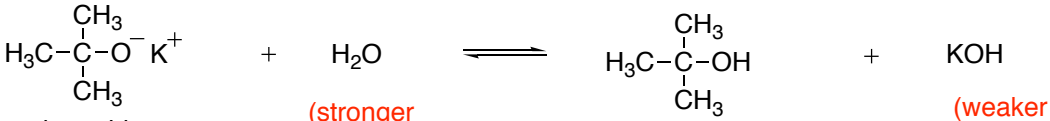
ii) Preparation of potassium tert-butoxide (equation not balanced):



2-methyl-2-propanol
tert-butyl alcohol

tert-butoxide
(strong base)

iii) Acid-Base equilibrium:



tert-butoxide
(stronger base)

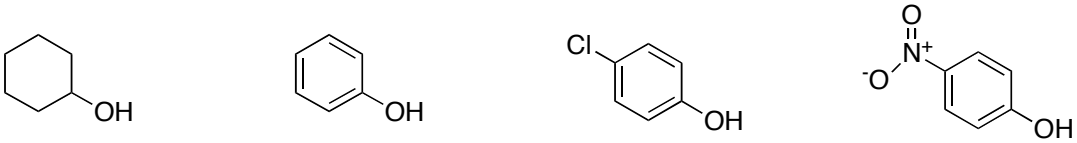
(stronger acid)

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

(weaker base)

equilibrium lies to the RIGHT

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



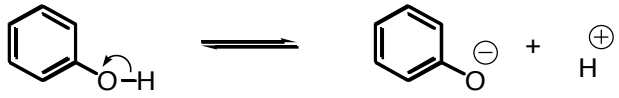
cyclohexanol — pKa = 18

Phenol — pKa = 10

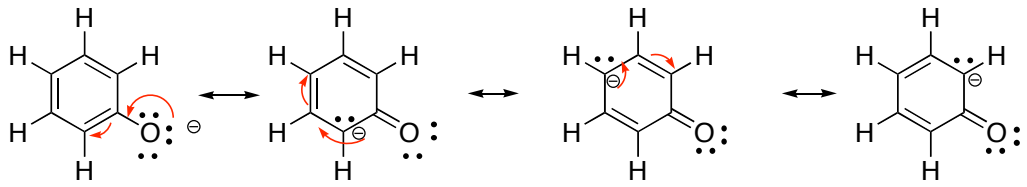
4-chlorophenol — pKa = 9.3

4-nitrophenol — pKa = 7

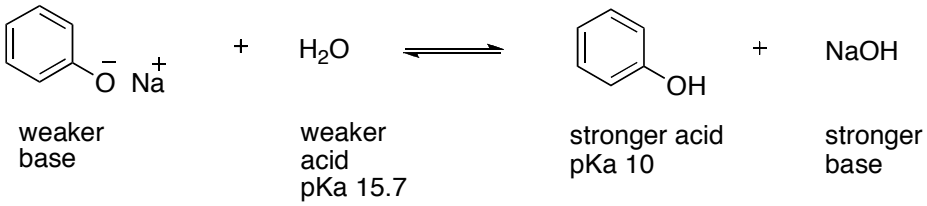
- Why phenol is more acidic?
  - the anion formed (phenoxide) can be stabilized by conjugation onto benzene ring – resonance forms can be obtained
  - the negative charge (electrons) on the oxygen is delocalized



- resonance forms of phenoxide anion:



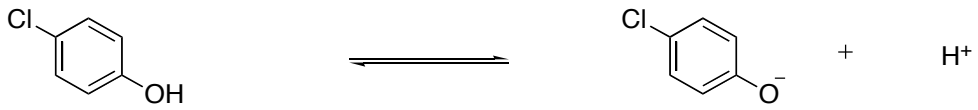
Eg.



Equilibrium rapidly gives phenoxide and water from phenol and sodium hydroxide

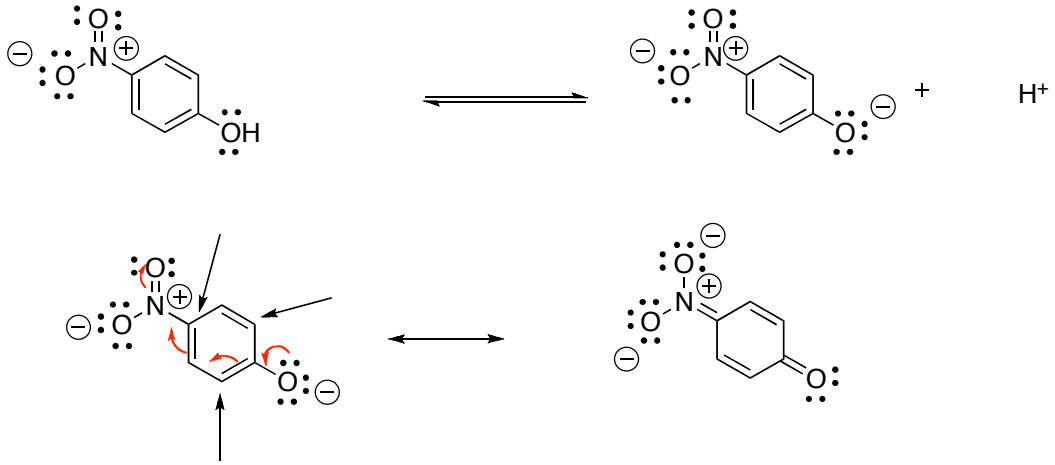
More examples:

1.



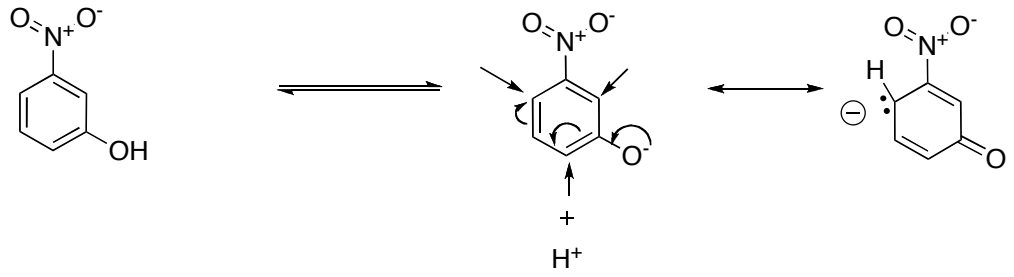
- Cl is electron withdrawing (inductive, single bond), so anion is stabilized, giving a lower pK_a value than phenol

2.



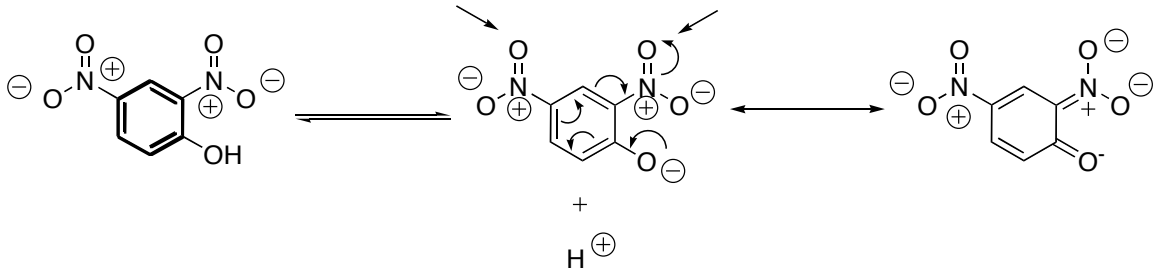
- an additional resonance form can be obtained with 4-nitrophenol (in comparison to phenoxide, three sites indicated by arrows) which gives more stability to the anion form.

3.



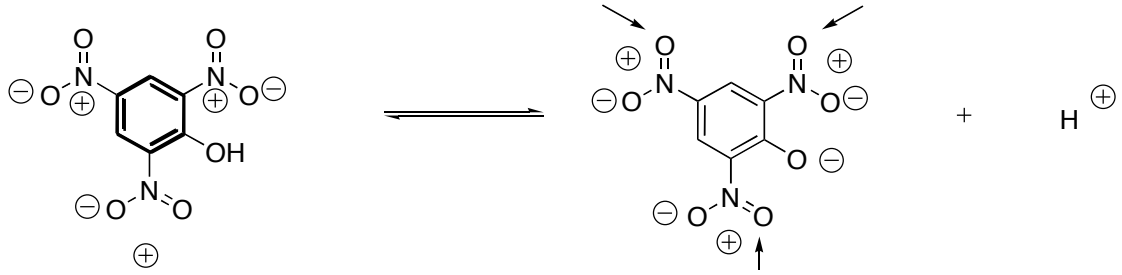
- the negative charge can only be placed on the positions shown by arrow, so that it is not possible to delocalize the negative charge onto the nitro group, thus $pK_a = 9.3$ instead of $pK_a = 7$ as for the 4-nitrophenol

4.



2,4-dinitrophenol – negative charge can be placed on two additional conjugated oxygens (indicated by straight arrows) as in the 4-nitrophenol
- $pK_a = 4.5$ (approx.)

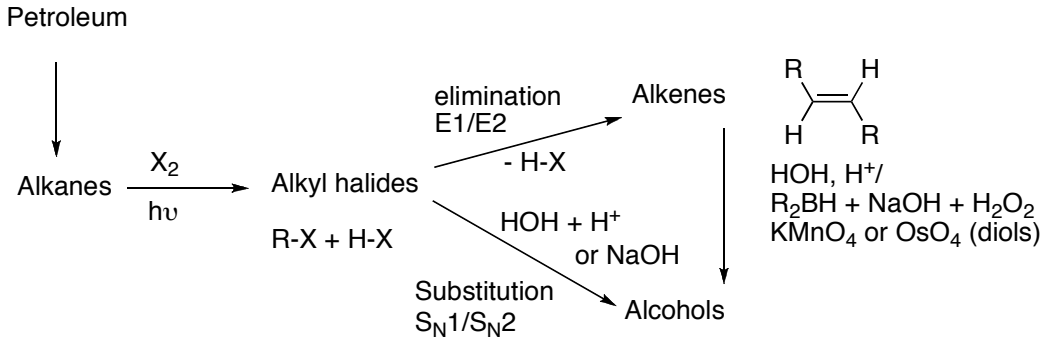
5.



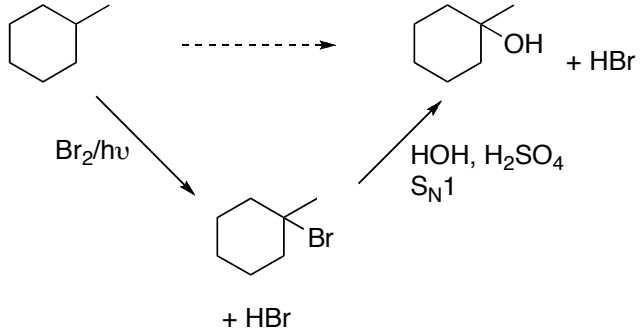
2,4,6-trinitrophenol
(picric acid – explosive – match head)
- $pK_a = 0.5$ (approx.)
- in the above two cases, the negative charge can be delocalized onto the doubly bonded oxygen of the nitro groups.

NaOH	+	HCl	→	NaCl	+	HOH
Strong Base		Strong Acid		Weak Base		Weak Acid

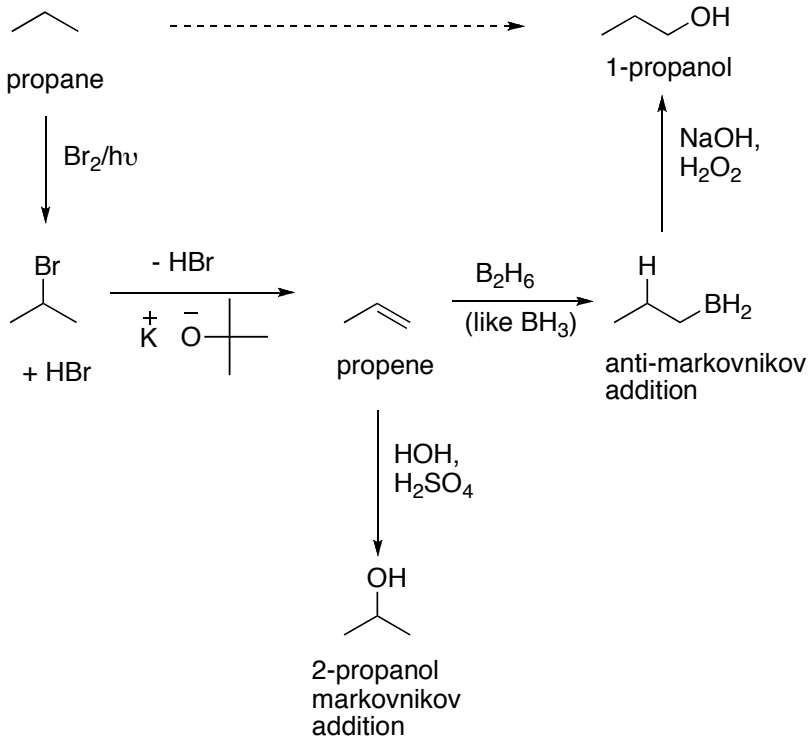
Synthesis (Preparation) of Alcohols: (Review of reactions seen earlier)

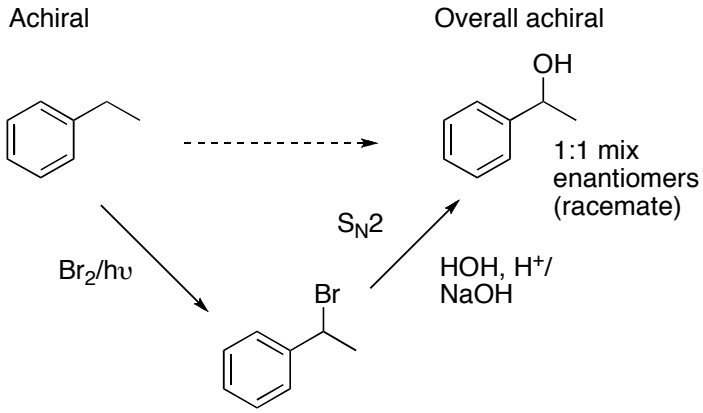


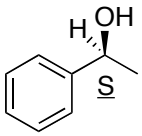
Eg 1.



Eg. 2







One enantiomer is shown above