Section 16 - Reactions and Synthesis of Alcohols.

⊛ Nomenclature of Alcohols.

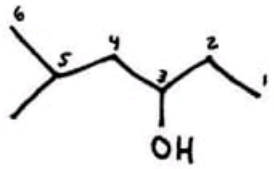
→ [Names → Structures] = most important to know.

→ **-OH** = principle group

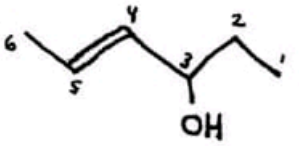
↳ principle chain contains the maximum # of -OH groups.

* alkane → alkanol, alkanediol, etc...

* when naming, -OH receives the lowest branch #.

ex: 

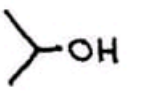
= **5-methyl-3-hexanol**

ex: 

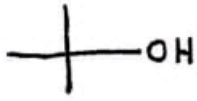
= **trans-4-hexen-3-ol**

↳ no "e"

⊛ Some Common Names of Alcohols.

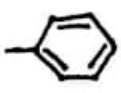
ex: 
= **isopropyl alcohol** (or 2-propanol)

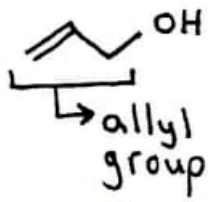
↳ IUPAC name.

ex: 
= **t-butyl alcohol**

↳ "tert"

ex: $Ph-CH_2-OH$ = **benzyl alcohol**

↳ -Ph = 

ex:  = allyl alcohol (or 2-propen-1-ol)

↳ IUPAC name.

ex:  = ethylene glycol

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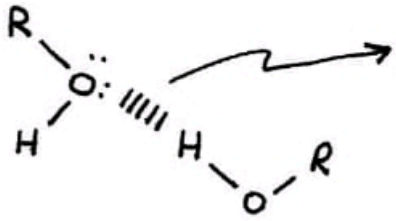
⊛ Alcohols and Hydrogen Bonding.

↳ Alcohols have relatively high boiling points due to hydrogen bonding.



hydrogen bond is worth ~ 5 kcal/mol

↳ bond dissociation energy (BDE) = 5 kcal/mol

⊛ Acidities of Alcohols.

↳ an alcohol is most acidic when it forms a stable alkoxide anion.

↳ $R\ddot{O}:^{\ominus}$

$$R\ddot{O}H \rightleftharpoons R\ddot{O}:^{\ominus} + H^{+}$$

alcohol — alkoxide

* pK_a = depends on the R-group.

↳ measure of acidity.

↳ factors that stabilize the alkoxide $RO^{\ominus}$
* make the reaction more favorable, thereby
* increasing the acidity of ROH and
* decreasing the pK_a of ROH.

↳ 3 Factors that Stabilize the Alkoxide $RO^{\ominus}$

① Inductive Effects - electronegative substituents stabilize $RO^{\ominus}$ by withdrawing e^--density through sigma bonds (σ-bonds).

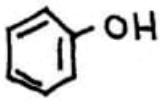
CH_3CH_2-OH $\quad pK_a = 16.0$

CF_3CH_2-OH $\quad pK_a = 12.4$ ⇝ lower; more acidic

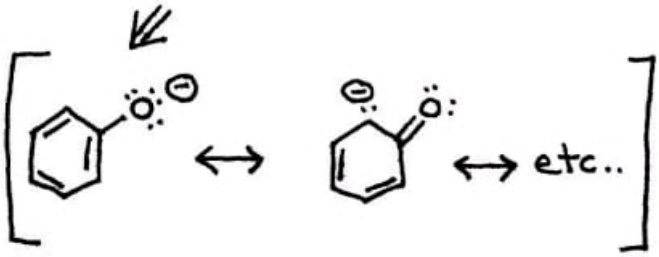
↔

② Resonance Effects. - stabilizing the resulting anion, after "H^+ is donated away, by resonance, increases acidity.

$R-OH$ $\quad pK_a = 15-19$



$pK_a = 10$ ⇝ negative charge of anion is resonance stabilized.



③ Branching.

↳ acidity decreases with increasing branching.

↳ acid strengths:

$CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH > (CH_3)_3COH$

↳ least sterically hindered for hydrogen bonding in protic solvents.

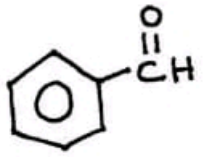
Section 18 = Aldehydes and Ketones: Nucleophilic Addition Reactions.

⊛ Nomenclature

* common names

→ Aldehydes ⇝ R–C(=O)–H

ex: $H_2C{=}O$ ⇝ formaldehyde

ex:  ⇝ benzaldehyde (= Ph–CH=O)

ex: CH_3–C(=O)–H ⇝ acetaldehyde

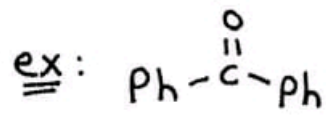
→ Ketones ⇝ R–C(=O)–R′ (sometimes R = R′)

ex: CH_3–C(=O)–CH_3 ⇝ acetone

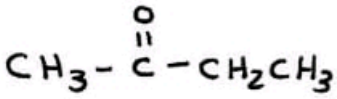
ex: Ph–C(=O)–CH_3 ⇝ acetophenone

ex: Ph–C(=O)–Ph ⇝ benzophenone

ketones sometimes named according to alkyl groups attached to >C=O

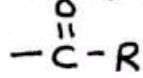
↳ ex: 

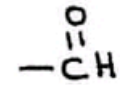
diphenyl ketone

ex: 

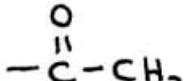
methyl ethyl ketone

* substituents or "branches" (acyl groups)

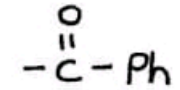
↳ 

ex: 

formyl group

ex: 

acetyl group

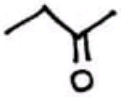
ex: 

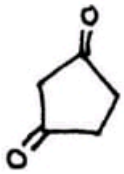
benzoyl group

* systematic (IUPAC) naming of ketones / aldehydes.

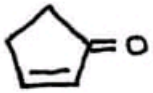
↳ the carbonyl group () is the principal group, so it must be part of the principal structure

Ketones : alkane ⟶ alkanone

ex:  ⟶ 2-butanone

ex:  ⟶ 1,3-cyclopentanedione

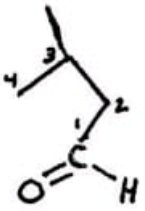
↳ a bit different here.

ex:  ⟶ 2-cyclopenteneone

Aldehydes: Alkane ⟶ Alkanal

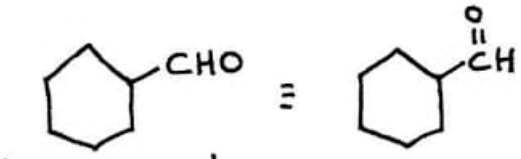
ex: $CH_3CH_2\overset{O}{\overset{\|}{C}}H$ ⟶ propanal

(common: propionaldehyde)

ex: 

⟶ 3-methylbutanal

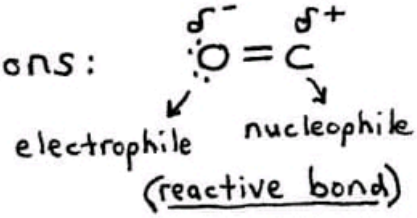
** note: when $-\overset{O}{\overset{\|}{C}}H$ is attached to a ring, use the suffix -carbaldehyde.

↳ ex: 

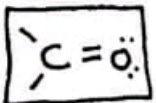
↳ = "cyclohexanecarbaldehyde

⊛ Strength.

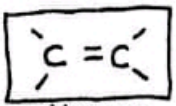
↳ structure of **C=O** is both stronger and shorter than **C=C**.

↳ due to electrostatic reasons: 

⇓



vs.



	carbonyl	alkene
length:	1.21 Å	1.34 Å
BDE for both σ and π:	177 kcal/mol	148 kcal/mol
BDE for only π:	89 kcal/mol	65 kcal/mol

BDE = bond dissociation energy