Topics: Finding Oxidation Numbers, Alcohol Oxidation Rxns

OCSP 2020
Lecture #15 BP, AF
July 24th, 2020

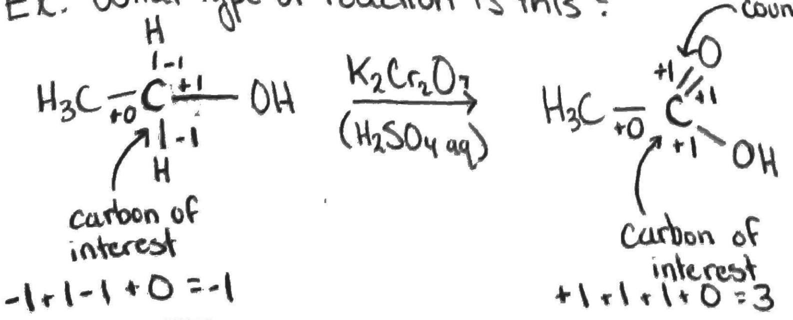
- Assigning Oxidation Numbers:

- Oil Rig or Leo the lion says ger (mnemonics to remember oxidation vs. reduction)
  1. Oil
     ↳ Oxidation = loss of electrons

     Rig
     ↳ Reduction = gain of electrons
  2. Leo ... the lion says... Ger
     ↳ Lose electrons = oxidized
     ↳ Gain electrons = reduction

- We are now moving onto reactions in which one species is reduced and another is oxidized and the fastest way to determine whether a species is oxidized or reduced is to determine oxidation numbers for the product and reactants. This process is a 3-step bookkeeping process that focuses on individual carbon atoms involved in the process.
  - Step 1: Assign oxidation level to each carbon that changes (from reactant → product)
    - For every bond from carbon to less electronegative atom, and for every negative charge on carbon, assign a "-1"
    - For every bond from carbon to another carbon atom and for every unpaired electron on the carbon, assign a "0"
    - For every bond from carbon to a more electronegative atom, and for every positive charge on carbon, assign a "+1"
    - Add all the above numbers to obtain the oxidation level of the specific carbon
  - Step 2: Determine the oxidation number (N_{ox}) of reactants + products by adding within each compound the oxidation numbers of all carbon considered in Step 1. (Only consider carbons that undergo a change in the reaction
  - Step 3: Compute the difference N_{ox} (product) - N_{ox} (reactant) to determine whether the transformation is an oxidation, reduction, or neither
    - difference = positive number (oxidation)
    - difference = negative number (reduction)
    - difference = 0 (neither)

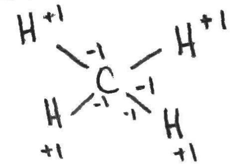
Ex. What type of reaction is this?



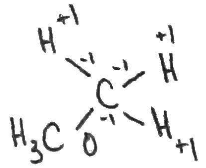
3 - (-1) = 4

∴ this rxn is a 4 e^- oxidation of ethanol to acetic acid

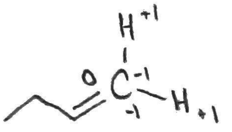
Ex. Find the oxidation state of the indicated carbon for the following molecules.



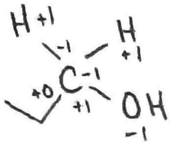
≡ Carbon Ox. state = $4(-1) = -4$



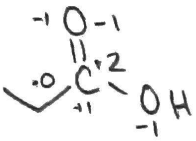
≡ Carbon Ox. state = $3(-1) = -3$



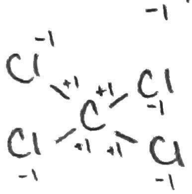
≡ Carbon ox. state = $2(-1) = -2$



≡ carbon ox. state = $2(-1) + (+1) = -1$



≡ Carbon Ox. state = $2 + 1 = +3$



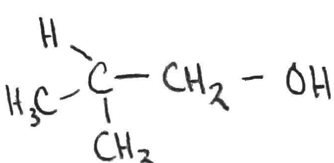
≡ carbon Ox. State = $4(+1) = +4$

↳ Note: this is a "formalism / bookkeeping" so the charge on the carbon isn't real. The oxidation state formalism is a way to help us keep track of where electrons are going (which will come in handy for our next rxns... alcohol oxidations!)

- Alcohol Oxidation Reactions: (creates carbonyl compounds typically using Cr(VI))
  - What are alcohols: compounds in which one or more hydrogen atoms in an alkane have been replaced by an OH group. Alcohols fall into different classes depending on how the OH group is positioned on the chain of carbon atoms
    - 1° (Primary) Alcohols: the carbon atom that carries the OH group is only attached to one alkyl group

CH_3-CH_2-OH
(Ethanol)

$CH_3-CH_2-CH_2-OH$
(propal-1-ol)

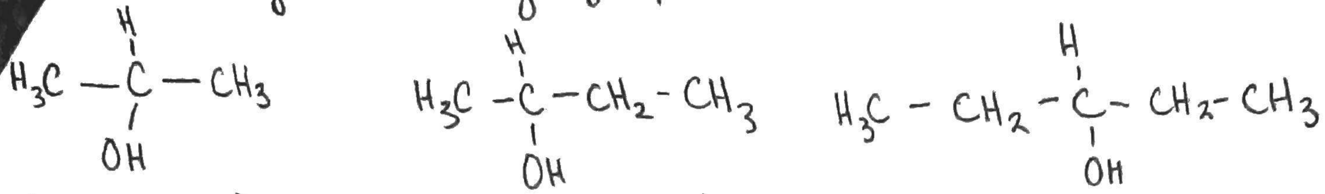


(2-methylpropan-1-ol)

↳ Note: methanol is the exception to this rule (it is classified as a primary alcohol despite not having alkyl groups)

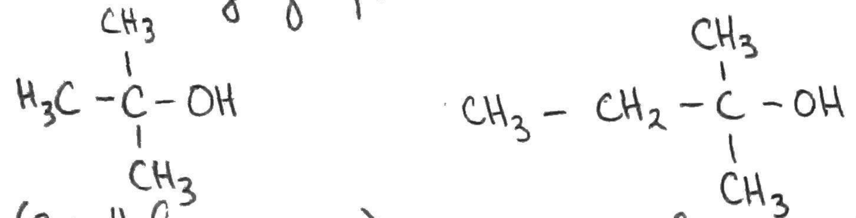
H_3C-OH

- 2° (Secondary) Alcohols: the carbon atom with the OH group attached is ...ined directly to two alkyl groups



(propan-2-ol) (butan-2-ol) (pent-3-ol)

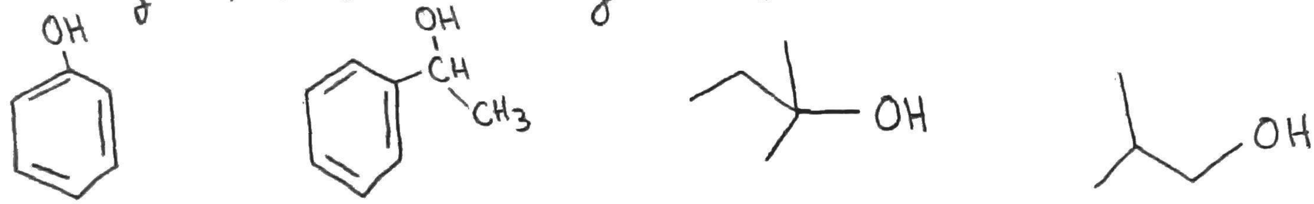
- 3° (tertiary) alcohols: the carbon atom holding the OH group is attached to three alkyl groups



(2-methylpropan-2-ol) (2-methylbutan-2-ol)

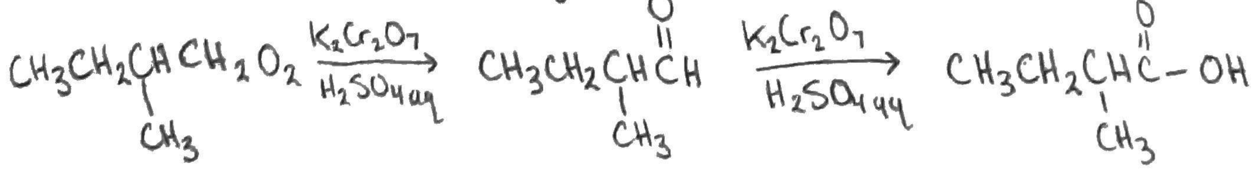
↳ conj. acid of tert-butyl oxide!

Ex. Classify (1°, 2°, 3°) the following alcohols



2° 2° 3° 1°

- Reactions of Primary Alcohols (KMnO4 w/ base or H_2CrO_4 are also plausible)
  - When $K_2Cr_2O_7$, $Na_2Cr_2O_7$, or CrO_3 is used in aqueous env. (w/ acid), a primary alcohol is oxidized first to an aldehyde (which can't be isolated) and then to a carboxylic acid. The oxidation can't be stopped at the aldehyde stage in an aqueous medium, since an aldehyde is in equilibrium with a hydrate that can undergo further oxidation.



- Water promotes the transformation of aldehydes into COOH because, in water, aldehydes are in equilibrium w/ hydrates formed by the addition of water across the C=O bond

$$R-\overset{O}{\overset{\|}{C}}H + H_2O \rightleftharpoons R-\overset{OH}{\overset{|}{C}}H-OH \xrightarrow{Cr(VI)} R-\overset{O}{\overset{\|}{C}}-OH$$

(aldehyde) (aldehyde hydrate) (COOH)

- Aldehyde hydrates are really alcohols & therefore can be oxidized like secondary alcohols. Because of the absence of water in anhydrous reagents like PCC, a hydrate doesn't form & reaction stops at the aldehyde.

- When we treat a primary alcohol with PCC (pyridinium chlorochromate), we oxidize it to the aldehyde. ↳ You may also see DMP used
  - PCC: an <u>anhydrous</u> Cr(VI) complex with pyridine & HCl

CrO_3() HCl

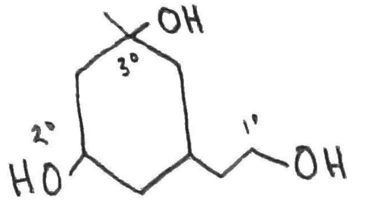
$$CH_3(CH_2)_8CH_2OH \xrightarrow[CH_2Cl_2\,(solv.)]{PCC} CH_3(CH_2)_8\overset{O}{\overset{\|}{C}}-H$$

- Reactions of Secondary Alcohols: Secondary alcohols are oxidized to a ketone in either $K_2Cr_2O_7$ (or other Cr(VI) reagents) in aqueous acid or PCC

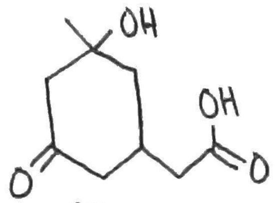
- Reactions of Tertiary Alcohols: tertiary alcohols can't be oxidized under these normal conditions because they lack the α C-H bonds that must be broken in the mechanisms

↳ Note: We can break alcohol oxidants into "weak" and "strong" categories. Weak oxidants will only oxidize primary alcohols to aldehydes. Strong oxidants will oxidize primary alcohols to carboxylic acids (secondary alcohols oxidized to ketones regardless with tertiary alcohols not oxidized at all)

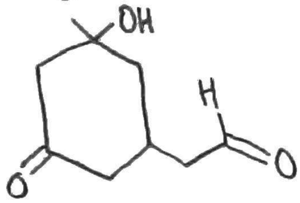
Treat the compound shown below with the following reagents.



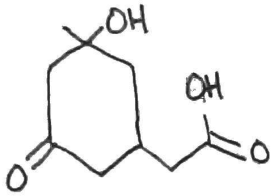
1. 1. $KMnO_4$, NaOH, rt → 2. H_3O^+



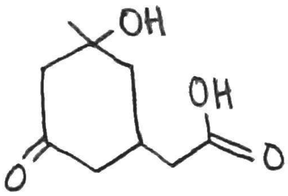
2. DMP, → CH_2Cl_2 (solv.)



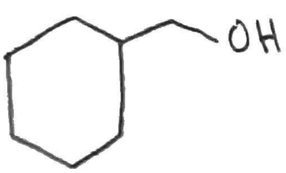
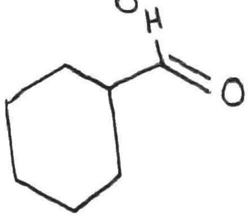
3. CrO_3 → H_3O^+/H_2O

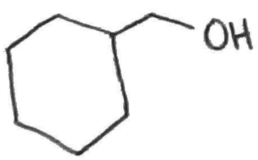
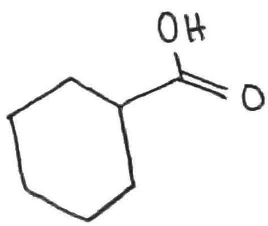


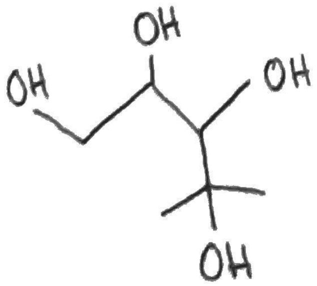
4. $Na_2Cr_2O_7$ → H_2SO_4



Ex. Find the product of the following rxns.

 PCC → CH_2Cl_2 (solv.) 

 CrO_3 → H_3O^+/H_2O 

 PCC → CH_2Cl_2 (solv)