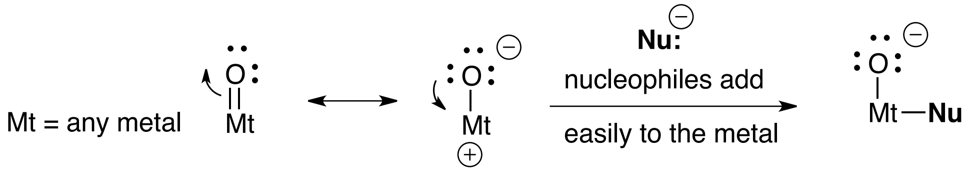
CHEM 203

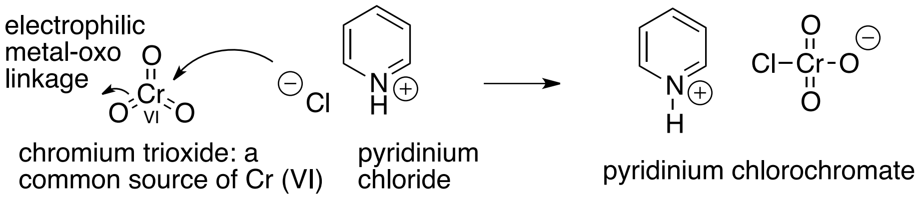
Topics Discussed on Nov. 25

Toxic and carcinogenic properties of Cr(VI) compounds – including CrO_3

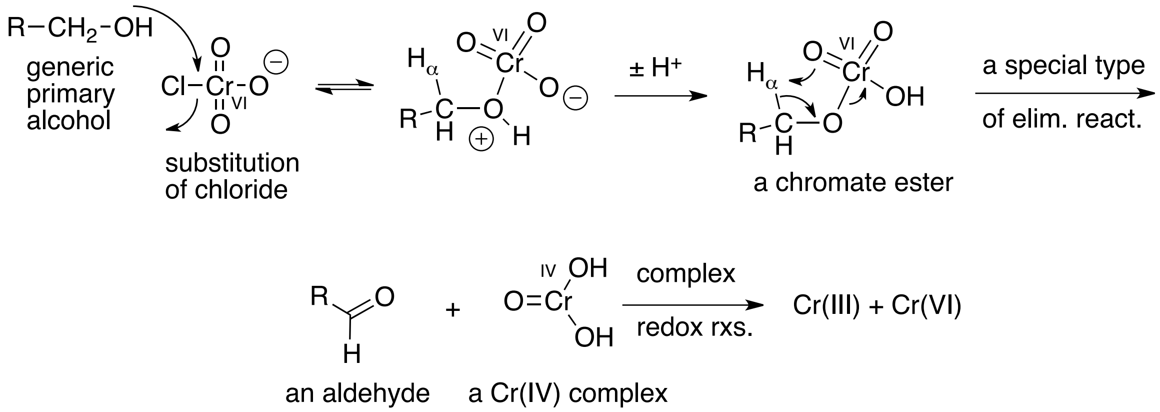
Electrophilic reactivity of metal-oxo linkages, Mt=O:



Pyridinium chlorochromate (PCC):

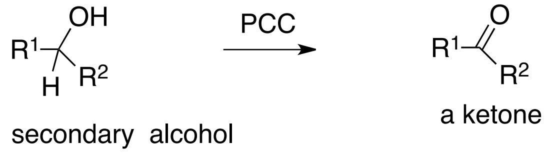


PCC oxidation of primary alcohols to aldehydes & secondary alcohols to ketones

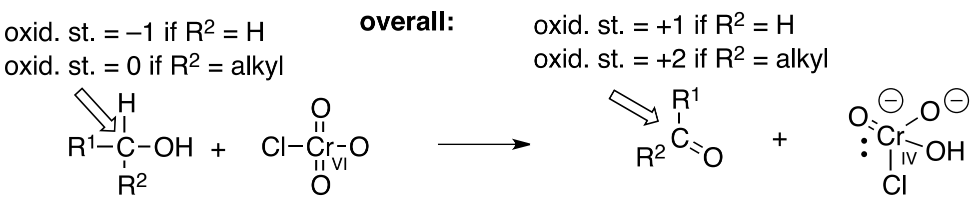


fine details of the mechanism of PCC oxidation remain unclear. The mechanism shown above is one of a number of plausible mechanism that differ for the precise sequence of events leading to the Cr(VI) complex that ultimately decomposes to give the carbonyl product.

Likewise:



The conversion of an alcohol into a carbonyl compound as an oxidation reaction



oxid. st. = –1 if R^2 = H
oxid. st. = 0 if R^2 = alkyl

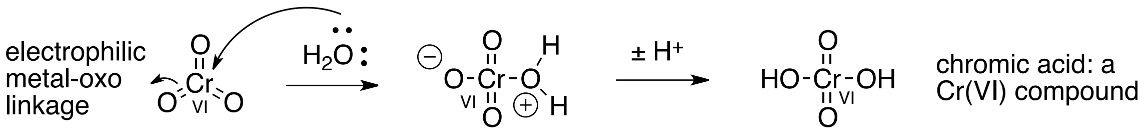
overall:

oxid. st. = +1 if R^2 = H
oxid. st. = +2 if R^2 = alkyl

the OH-bearing C atom advances from the oxidation state of –1 or 0 to that of +1 or +2:
it undergoes a two-electron oxidation.
the Cr atom recedes from the oxidation state of +6 to that of +4:
it undergoes a two-electron reduction.

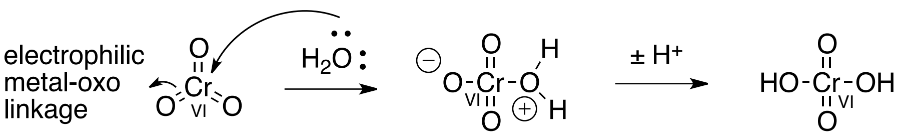
Inability of tertiary alcohols to undergo oxidation, due to the absence of α-H's

Conversion of chromium trioxide into chromic acid, H_2CrO_4 (the Cr analog of H_2SO_4)



chromic acid: a Cr(VI) compound

The Jones reagent: a solution of chromic acid, H_2CrO_4, in aqueous H_2SO_4:



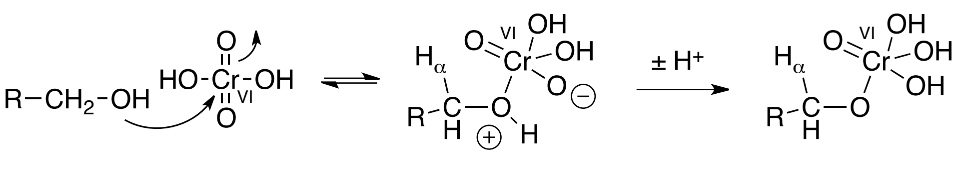
chromic acid: a Cr(VI) compound

the Jones reagent is prepared by adding CrO_3 to aq. H_2SO_4

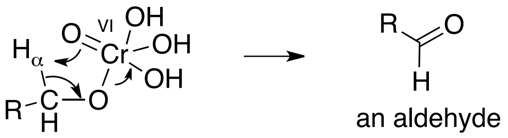
IMPORTANT: PCC is used ONLY in anhydrous (=water-free) media, while Jones rgt. is an aqueous solution. This seemingly minor difference has a major influence on the course of the reaction of primary alcohols with the two reagents.

The Jones reagent: oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones in aqueous medium

Reaction of the Jones reagent with primary alcohols: initial formation of a chromate ester:

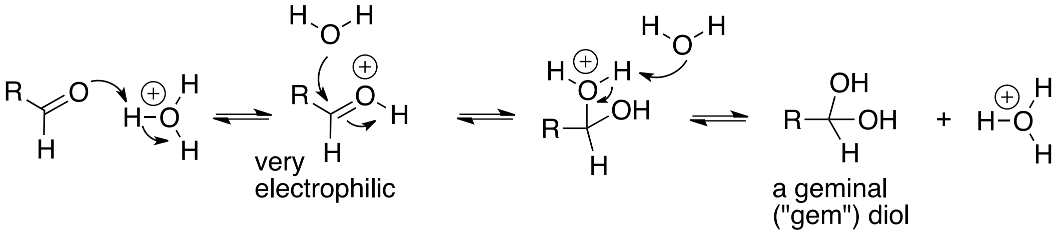


Reaction of the Jones reagent with primary alcohols: decomposition of the chromate ester to give an aldehyde:

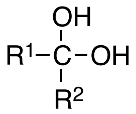


but the aldehyde is not the final product of the reaction (the carboxylic acid is): evidently, something must happen to the aldehyde that causes it to become a carboxylic acid…

Acid-promoted equilibration of the aldehyde with a geminal diol in aqueous acid:

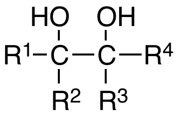


note: geminal diols (obtained by the reversible hydration of carbonyl functions) display a pair of OH groups connected to the same carbon atom. Vicinal diols (obtained by OsO_4 oxidation of alkenes) have their OH groups connected to adjacent carbon atoms:



$$R^1-\overset{\overset{OH}{|}}{\underset{\underset{R^2}{|}}{C}}-OH$$

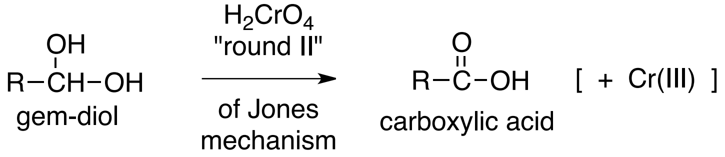
a geminal diol: both OH groups are attached to the same C atom



$$R^1-\overset{\overset{HO}{|}}{\underset{\underset{R^2}{|}}{C}}-\overset{\overset{OH}{|}}{\underset{\underset{R^3}{|}}{C}}-R^4$$

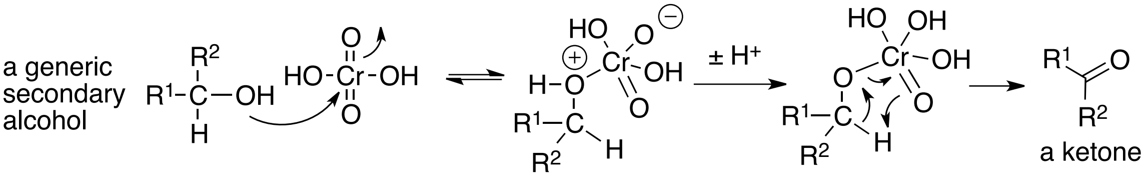
a vicinal diol: the OH groups are attached to adjacent C atoms

(iii) further oxidation of the *gem*-diol to an acid by Cr(VI) through a second round of the mechanism shown earlier:



$$\underset{\text{gem-diol}}{R-\overset{\overset{OH}{|}}{C}H-OH} \xrightarrow[\text{of Jones mechanism}]{H_2CrO_4 \text{ "round II"}} \underset{\text{carboxylic acid}}{R-\overset{\overset{O}{\|}}{C}-OH} \quad [\ +\ Cr(III)\ ]$$

Oxidation of secondary alcohols to ketones with the Jones reagent; e.g.:

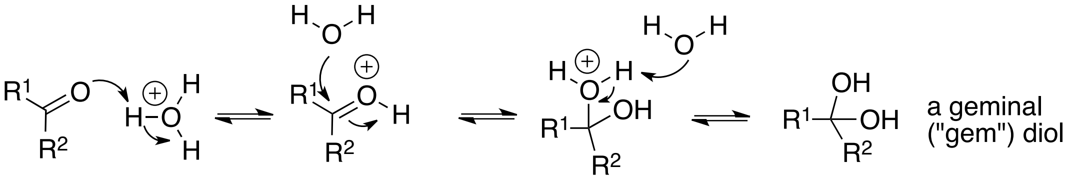


note: ketones can — and do — form geminal diols by reaction with H_3O^+, but the geminal diol of a ketone cannot undergo further oxidation because it has no α-H's

Summary of the above oxidation reactions:

R–CH_2–OH to R–CHO	possible only in a water-free medium: requires PCC
R–CH_2–OH to R–COOH	possible only in an aqueous medium: requires Jones reagent
R^1R^2CH–OH to R^1R^2C=O	may be achieved with either PCC or Jones reagent

Principle: *any* carbonyl compound will equilibrate with the corresponding geminal (gem-) diol in an aqueous acidic medium. However, gem-diols are thermodynamically disfavored relative to carbonyls, and this primarily on entropic grounds. Therefore, any attempt to isolate gem-diols will actually return the corresponding carbonyl compounds (at least as far as the carbonyl compounds seen in CHEM 203 are concerned)



Overall ΔG slightly positive