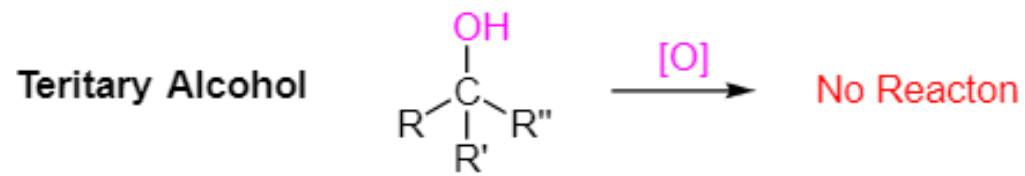
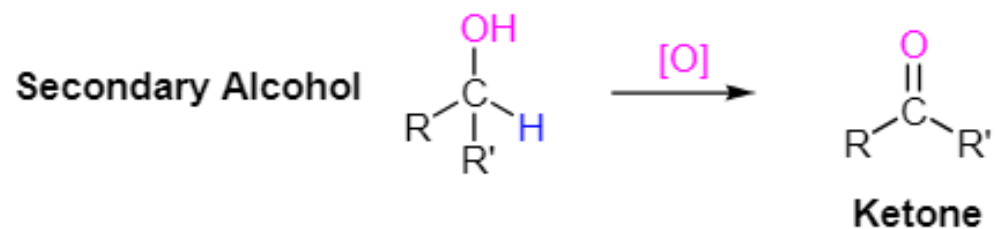
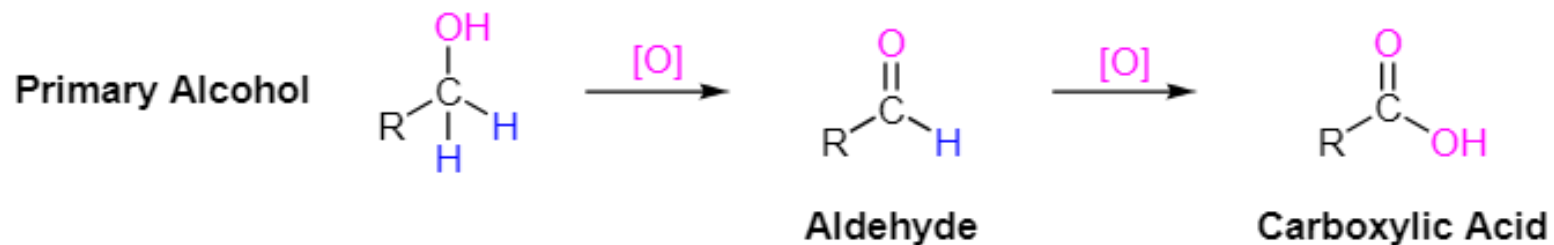


FCF-1012020 - Química Orgânica II

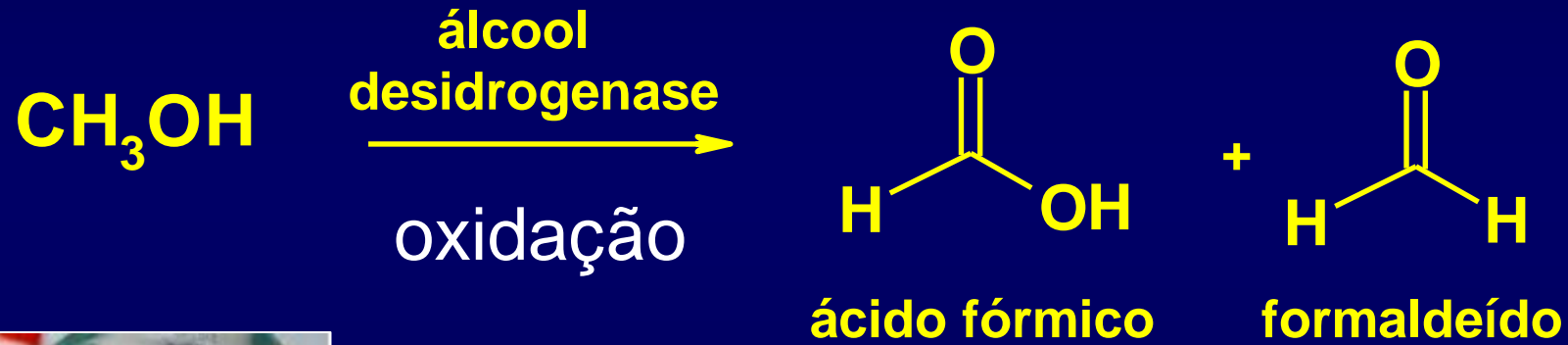
2024 (10 de maio)

Reações de oxidação



Metanol (álcool da madeira)

methy: intoxicar (Grego)

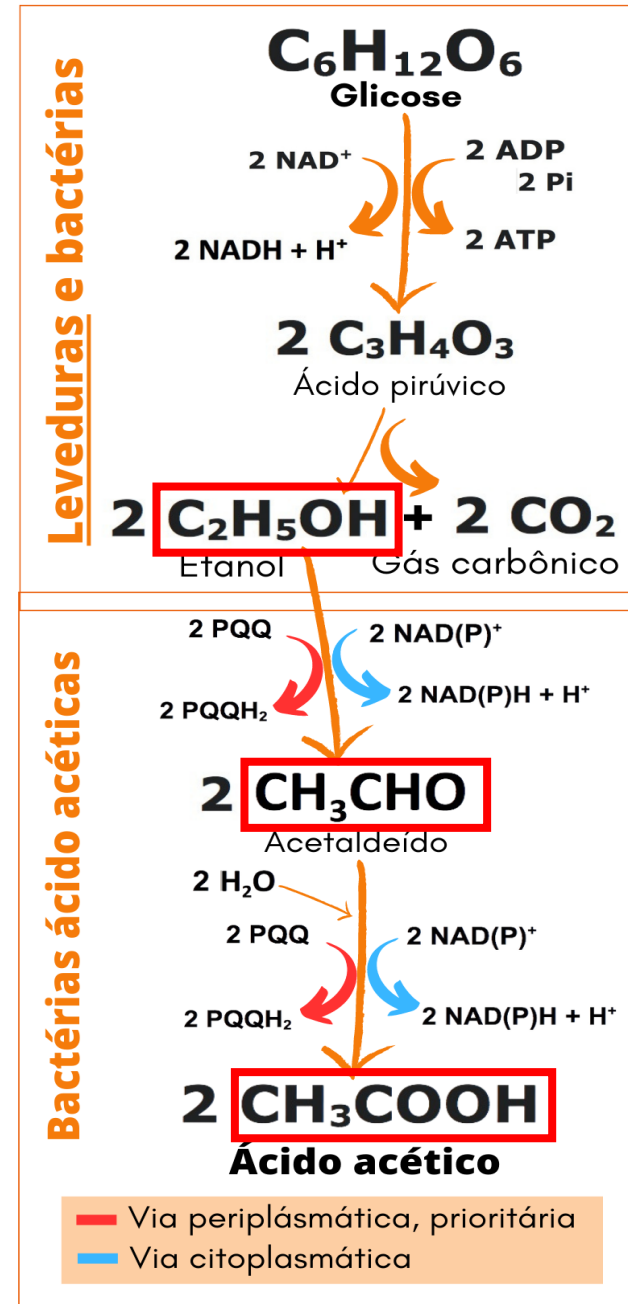


Ataca os gânglios da retina degenerando o nervo óptico

Oxidações biológicas

Fermentação do açúcar
Por leveduras e bactérias
com produção de etanol

Fermentação do etanol
bactérias acéticas com
produção de ácido acético



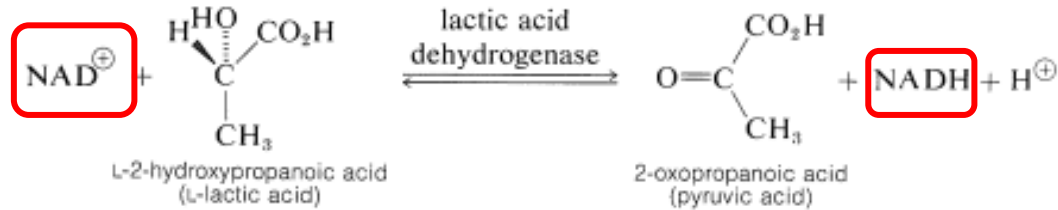
oxidação



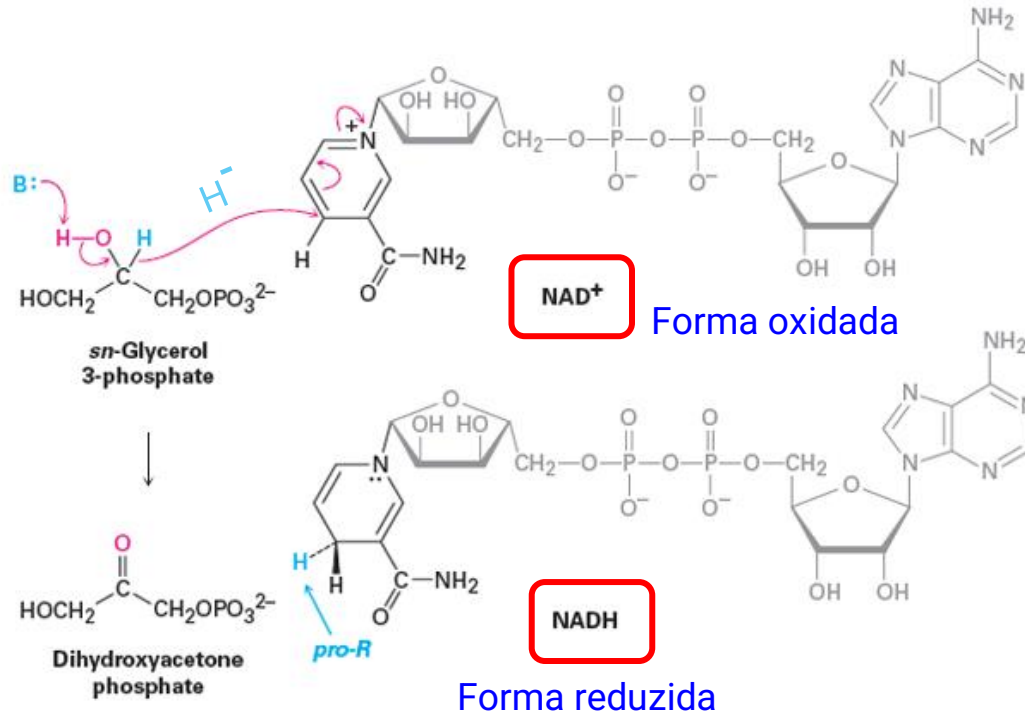
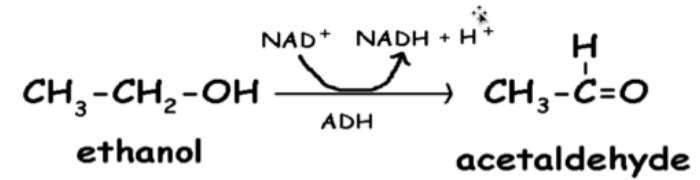
Oxidantes biológicos ($\text{NAD}^+ \rightarrow \text{NADH}$)

enzimas do tipo oxidoreduzases

Lactato desidrogenase



álcool desidrogenase



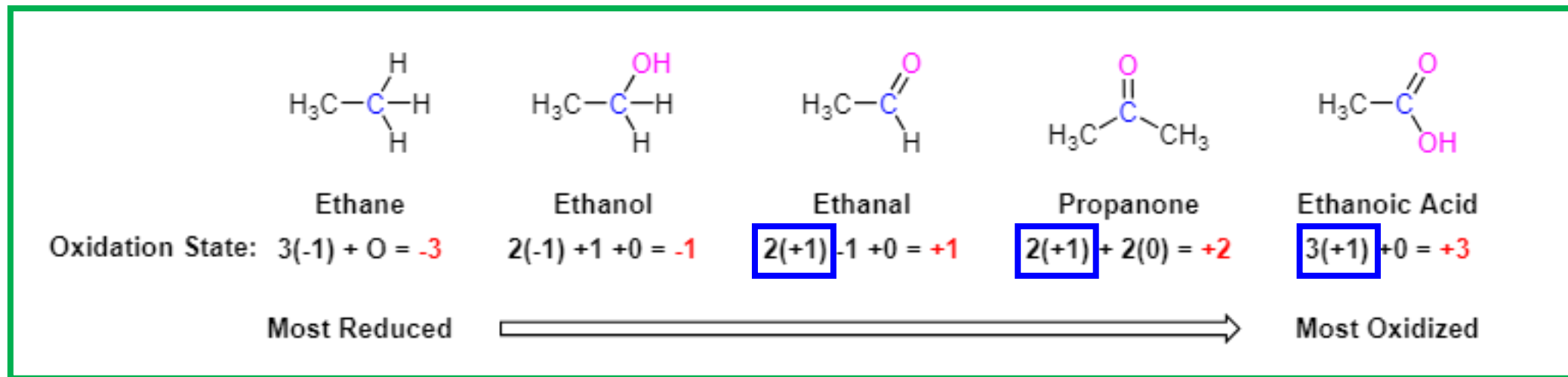
Estados de oxidação do carbono

Os estados de oxidação (não representam a carga real), estão associados ao número de elétrons (ganhos ou perdidos) por um átomo específico durante uma reação.

Regras para se calcular o estado de oxidação de um átomo de carbono:

Átomos ligado ao C	Adicione (ou subtraia)
C	0
H	-1
N, O, S ou halogênio	+1

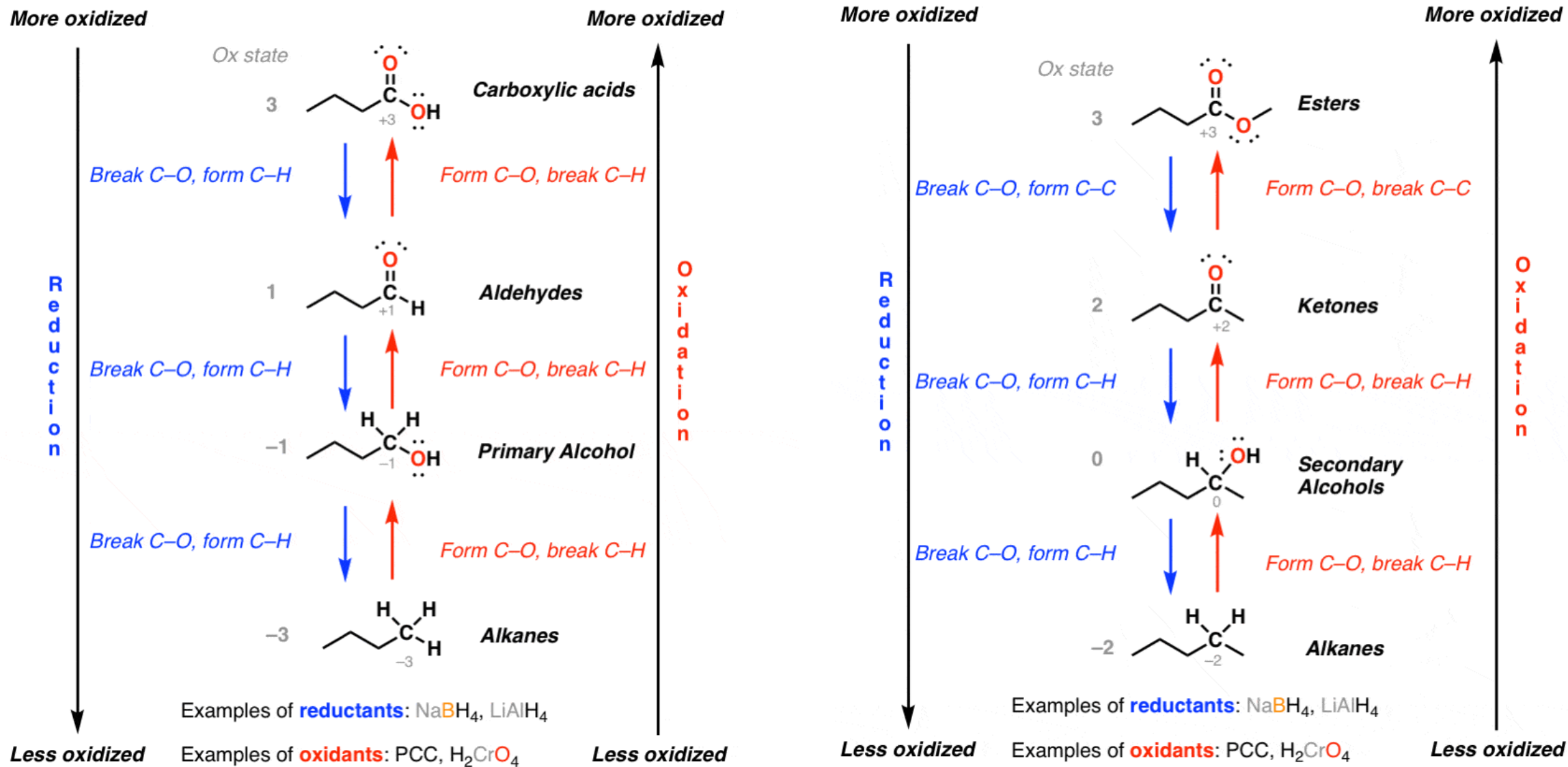
Exemplos:



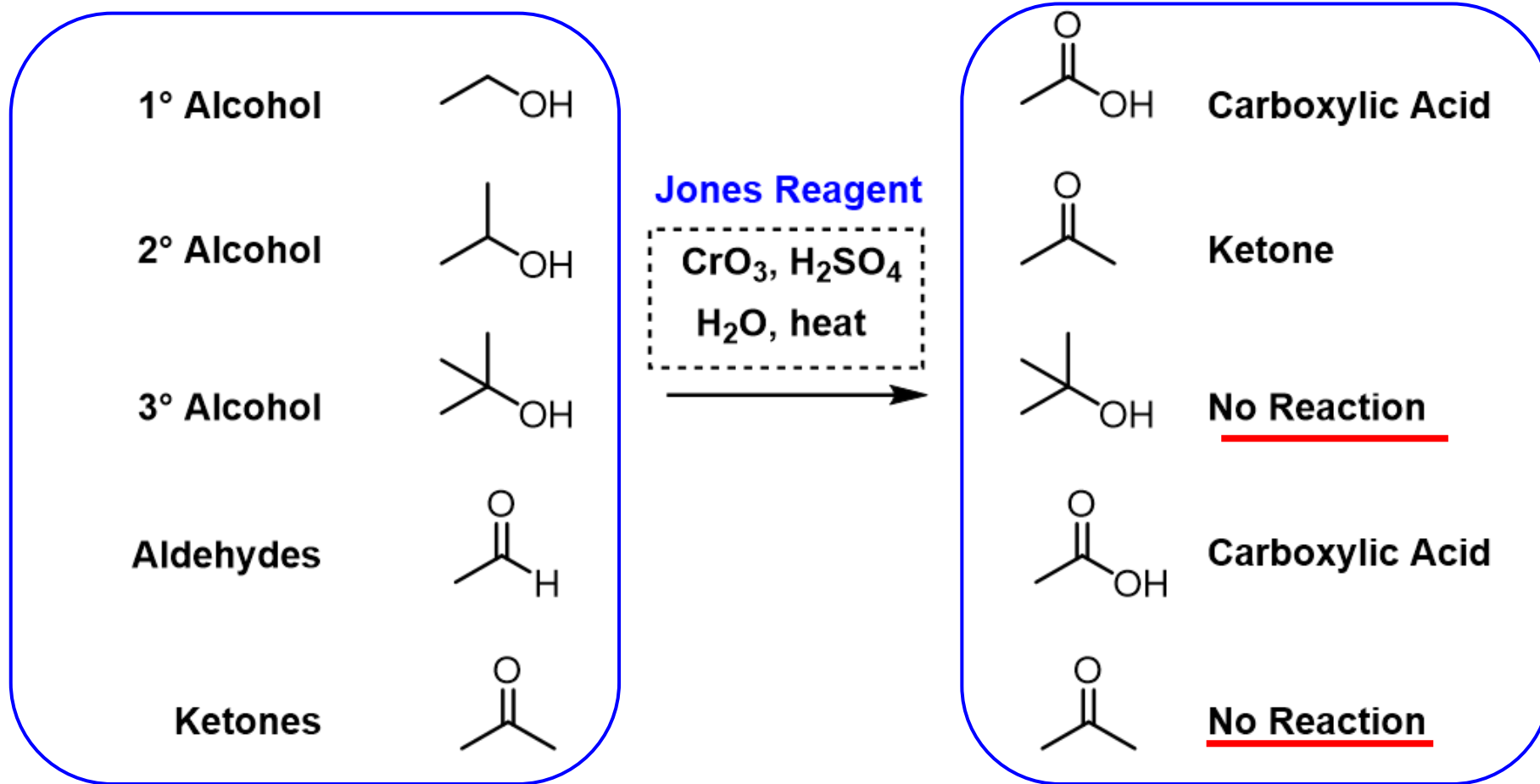
C=O (conta como 02 oxigênios)

03 oxigênios

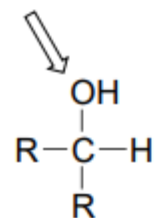
Estados de oxidação de compostos orgânicos



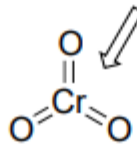
Oxidação de álcoois pelo reagente de Jones



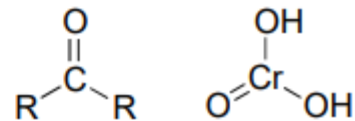
alcohol gets oxidized in the reaction



*oxidizing agent
(gets reduced in the reaction)*



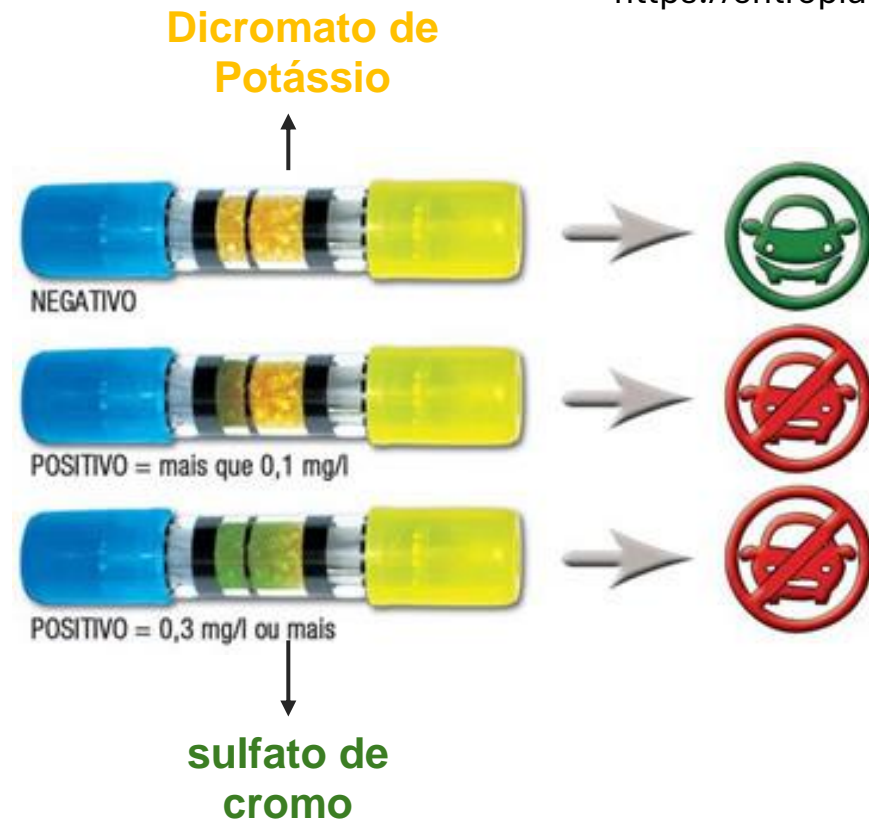
Cr lost a bond to oxygen



Teste do bafômetro



<https://entropialivre.blogspot.com/2011/11/como-funciona-o-bafometro.html>



Dicromato de Potássio

etanol

alaranjado

incolor



verde

incolor

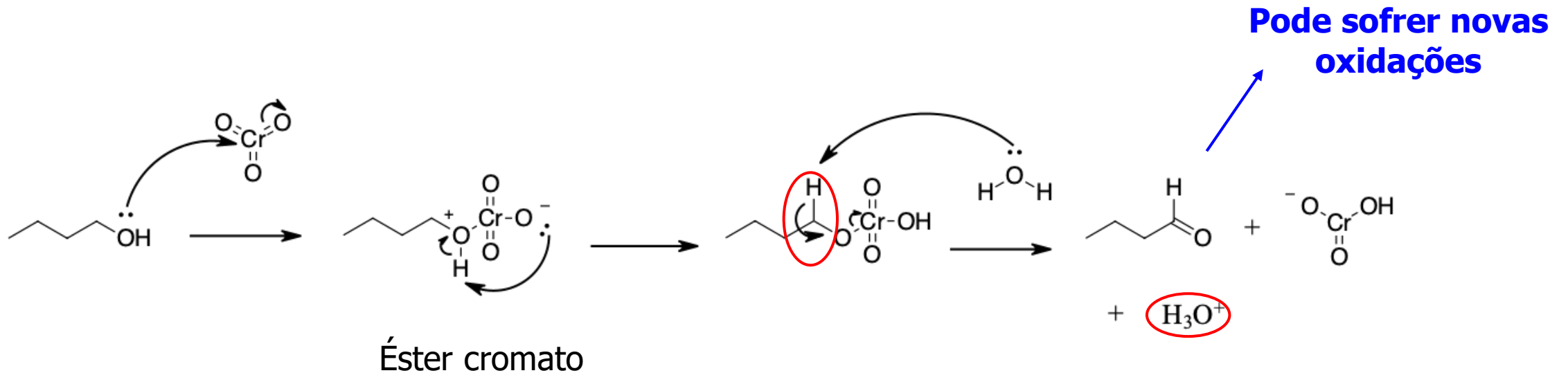


sulfato de cromo

acetaldeído

Mecanismo de oxidação do álcool

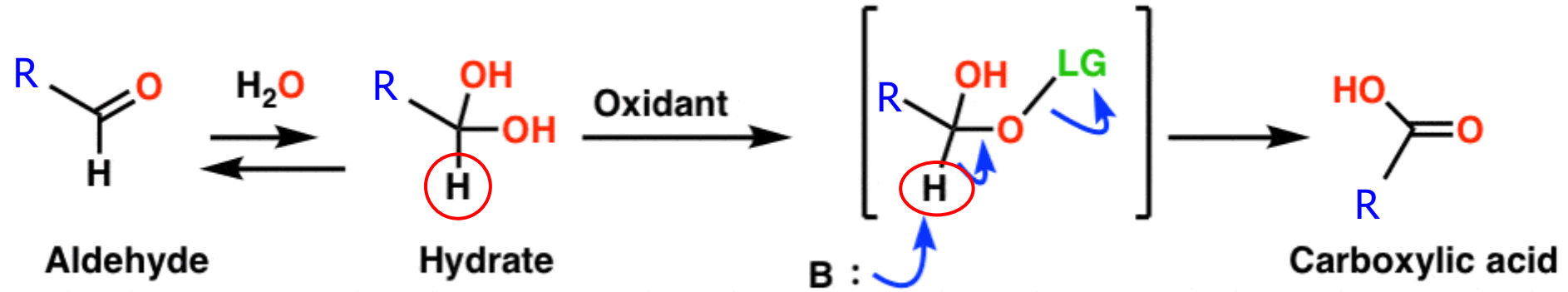
O cromo está sendo reduzido de Cr(VI) no CrO_3 para Cr(IV) no produto H_2CrO_3 .



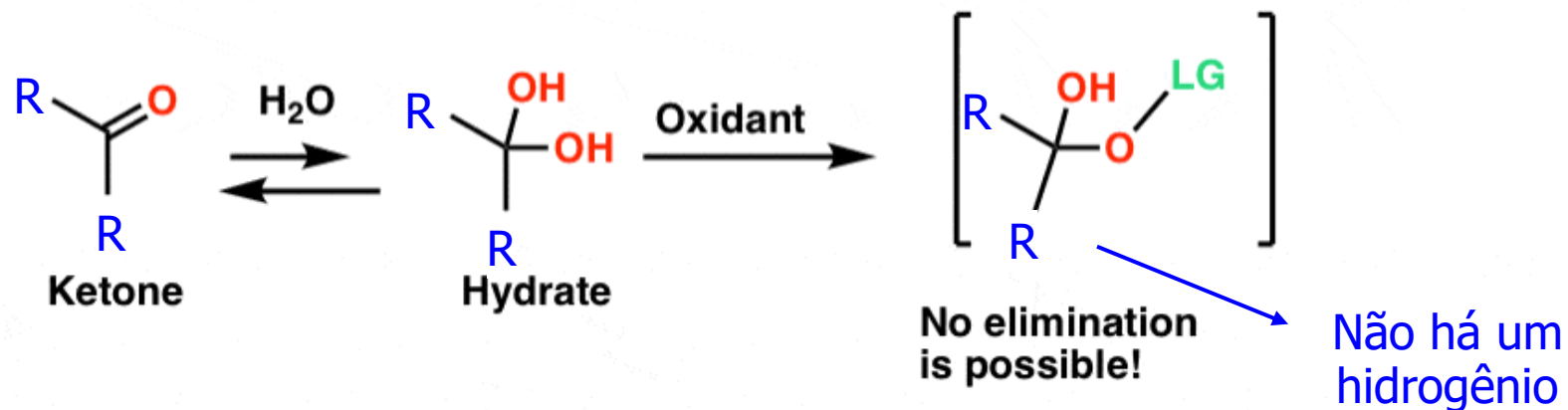
Éster cromato

A ligação $\text{C}=\text{O}$ é formada na terceira etapa por um mecanismo tipo E2

A **oxidação de aldeídos** requer a hidratação na primeira etapa e o mecanismo torna-se semelhante à oxidação de álcoois formando um éster de cromato

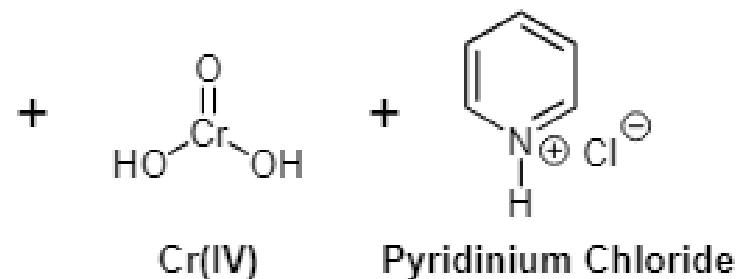
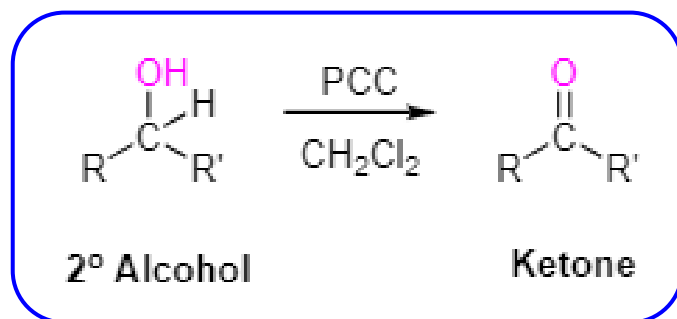
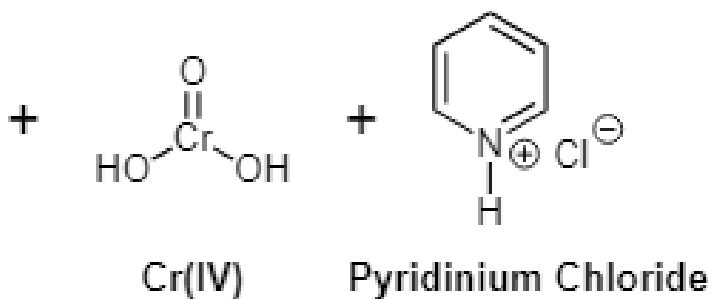
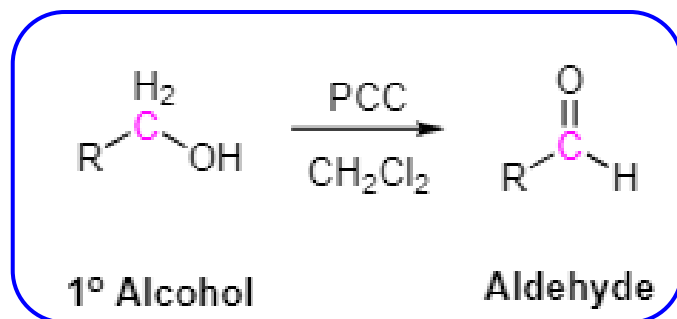


A oxidação de cetonas não progride devido à ausência de um hidrogênio que possa ser removido como em aldeídos



Reações de oxidações de álcoois com PCC (clorocromato de piridina) à aldeídos

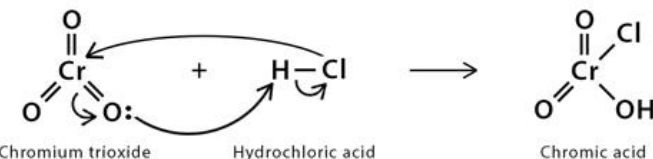
O PCC oxida álcoois primários para aldeídos
(mas não até ácidos carboxílicos).



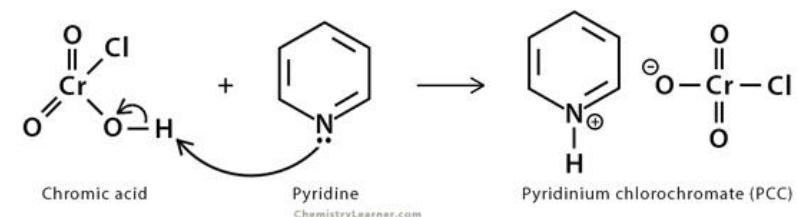
Álcoois secundários são oxidados
para cetonas.

Preparation of PCC Reagent

Step 1: Chromium trioxide dissolves in hydrochloric acid to form chlorochromic acid

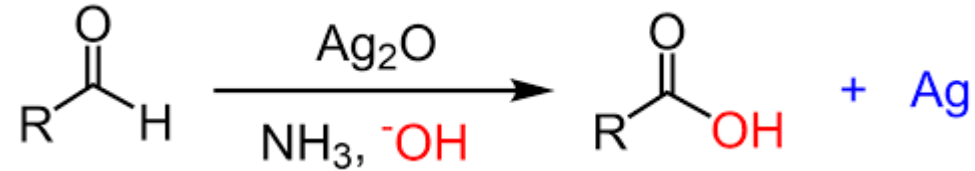


Step 2: Addition of pyridine to chlorochromic acid gives PCC reagent



Reações de oxidações de aldeídos com nitrato de prata amoniacal (teste de Tollens#: diferencia aldeídos de cetonas)

<https://theedge.com.hk/blog/the-silver-mirror-test/>



A prata metálica se deposita no frasco reacional.

Teste de Tollens para aldeídos e açúcares redutores.
O depósito de prata forma um revestimento espelhado no interior do frasco reacional.



A giant silver mirror (<https://www.youtube.com/watch?v=y-4qqcCx6g>)

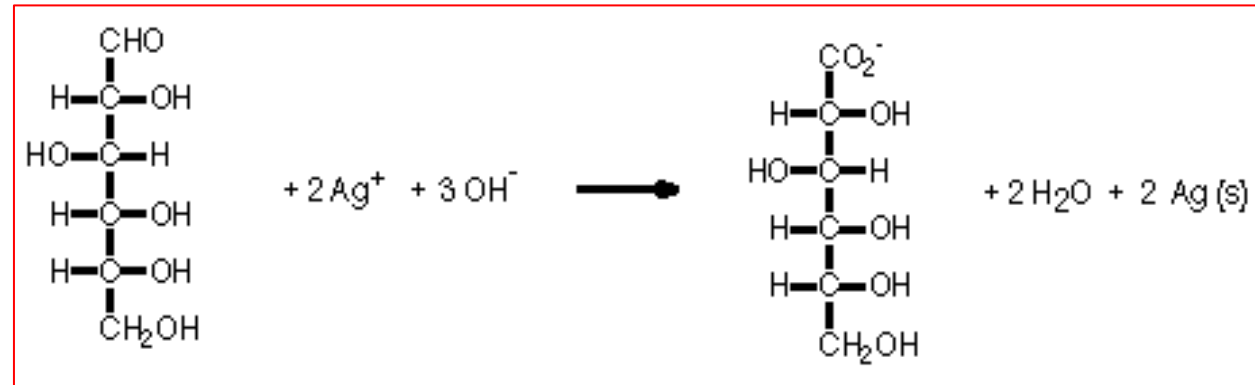
Royal Society of Chemistry



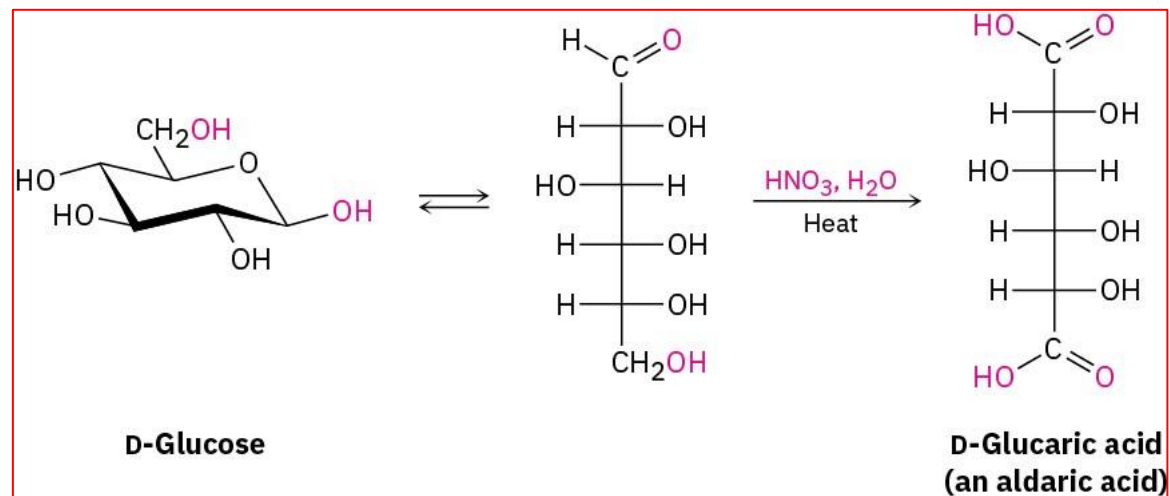
Bernhard Tollens
(1841-1918)

Açúcares redutores podem ser oxidados para ácidos

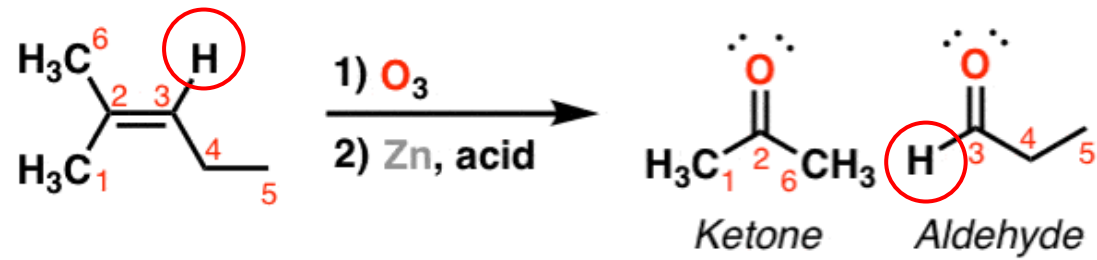
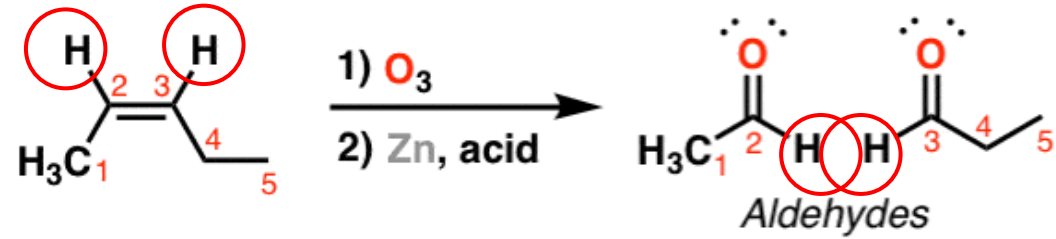
Teste de Tollens em açúcares redutores



Oxidações de açúcares com ácido nítrico

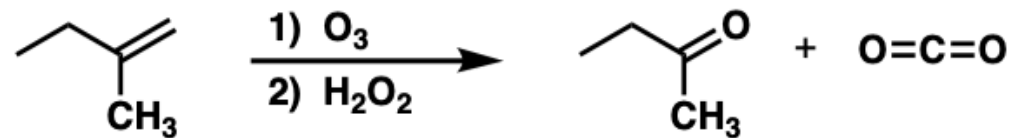
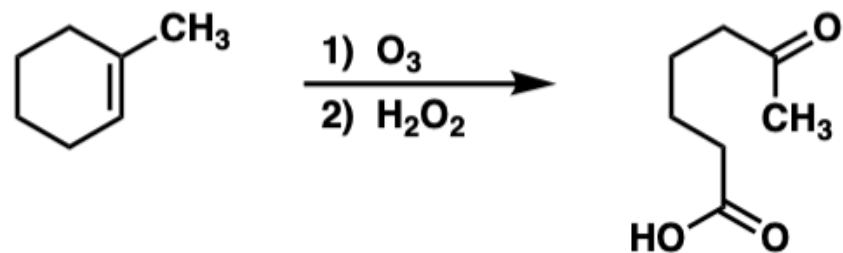
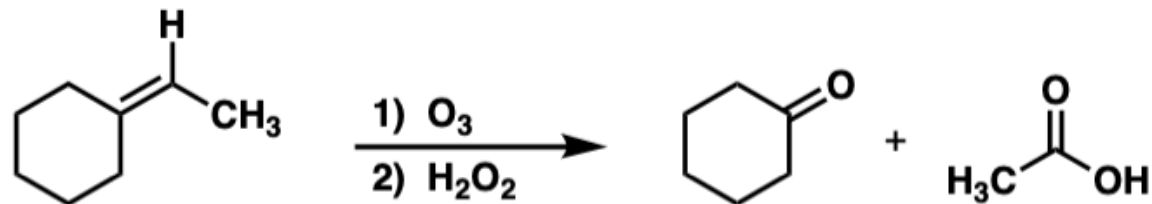
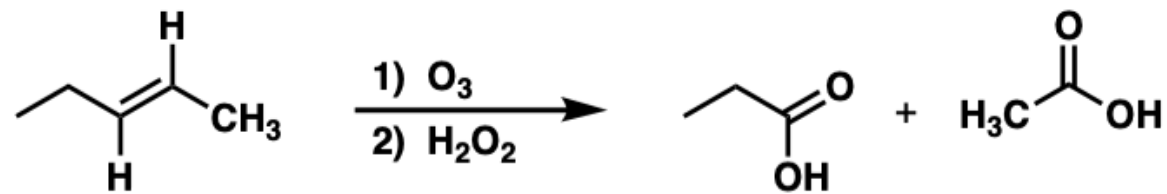


Reações de clivagens oxidativas de olefinas e acetilenos com ozônio (com Zn, a reação é branda e oxida até aldeído)



Reações de clivagens oxidativas de olefinas com ozônio

Com H_2O_2 , a reação leva até cetonas ou ácidos (se H ligado à dupla ligação)

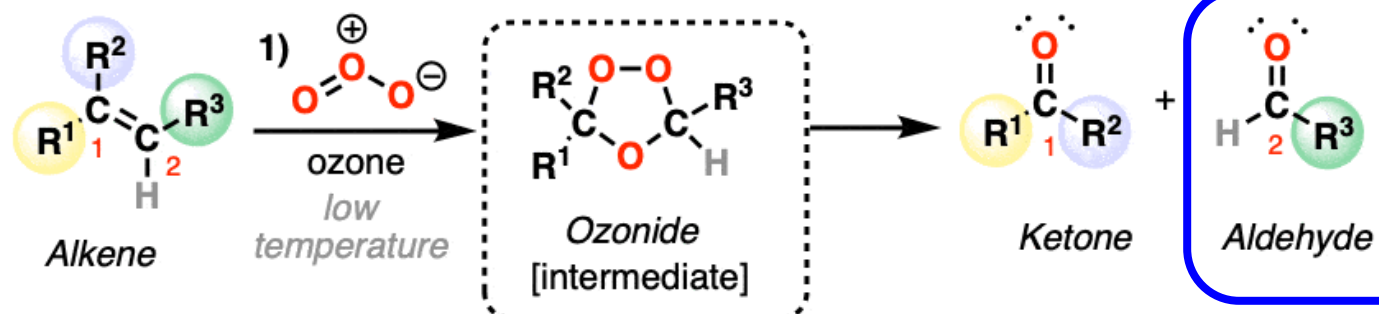


Reações de hidrólise do ozonídeo

Summary - Ozonolysis of Alkenes (and Alkynes)

- Ozonolysis is a useful reaction for the oxidative cleavage of alkenes to carbonyl compounds.
- When a C-H bond is present on the alkene, choice of workup will affect the final product(s). Reductive workup leaves C-H bonds alone. Oxidative workup gives COOH

Step 1: Ozonolysis



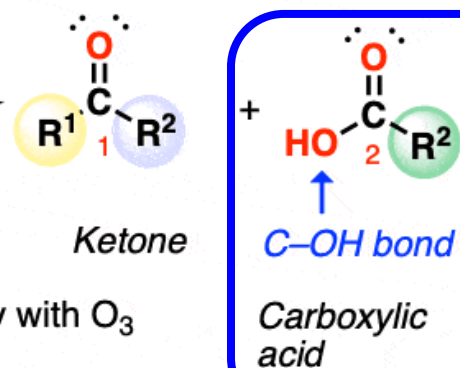
Reductive workup (most common)

- Dimethyl sulfide (DMS, $(\text{CH}_3)_2\text{S}$)
- or
- Zinc (Zn) + acid

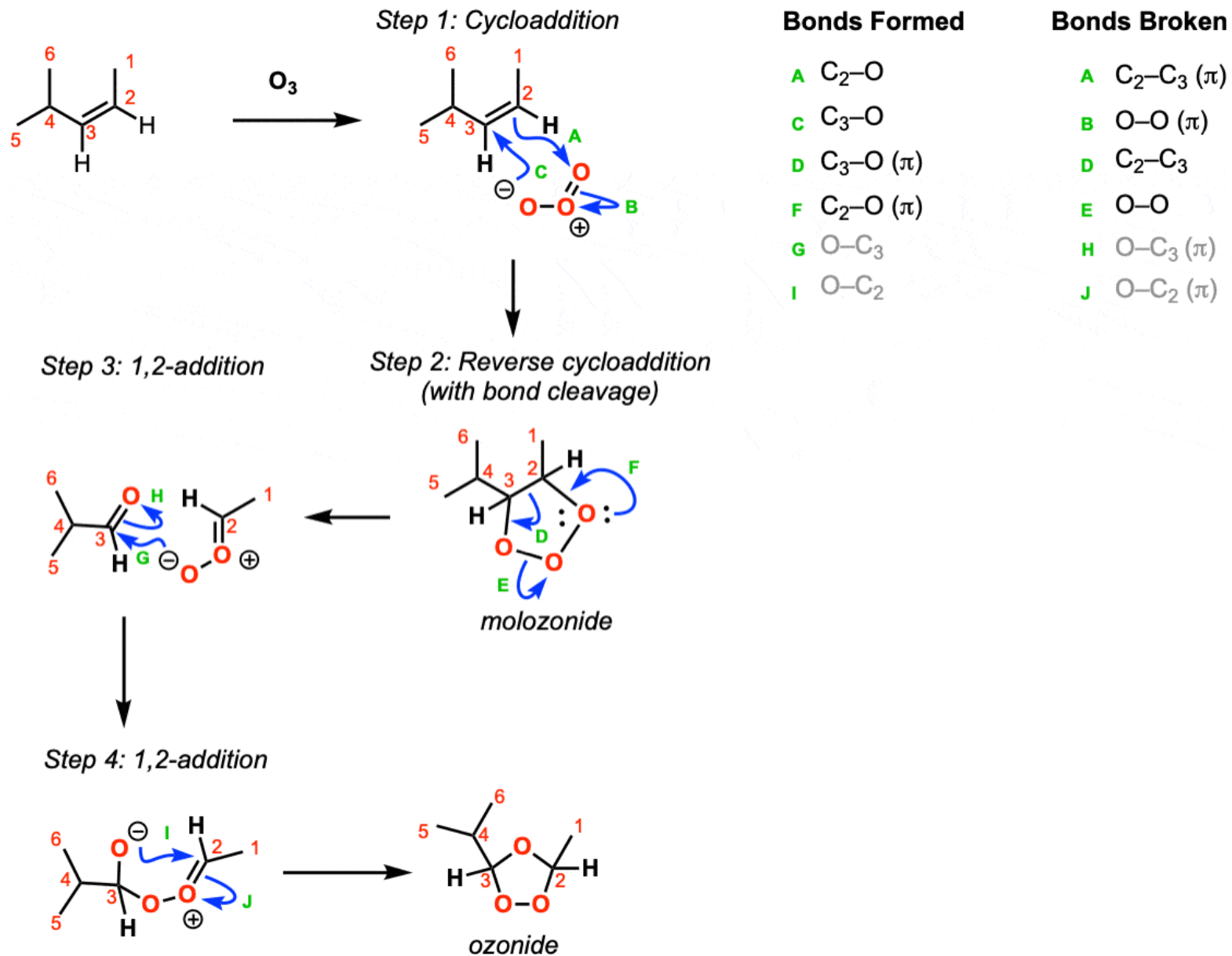
Oxidative workup

- Hydrogen peroxide (H_2O_2)

- Generally, more electron-rich alkenes react preferentially with O_3
- Ozonolysis of compounds with multiple alkenes gives fragments
- Ozonolysis of alkynes gives carboxylic acids

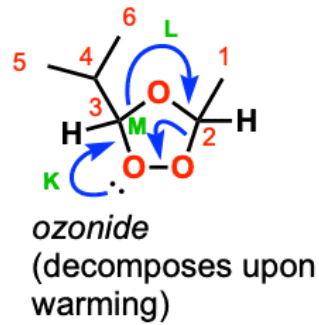


Mecanismo de clivagens oxidativas de olefinas com ozônio

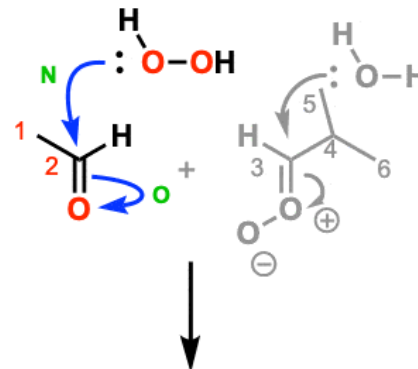


Mecanismo de clivagens oxidativas de olefinas com ozônio

Step 5: Breakdown of ozonide



Step 6: 1,2-addition (of HOOH)



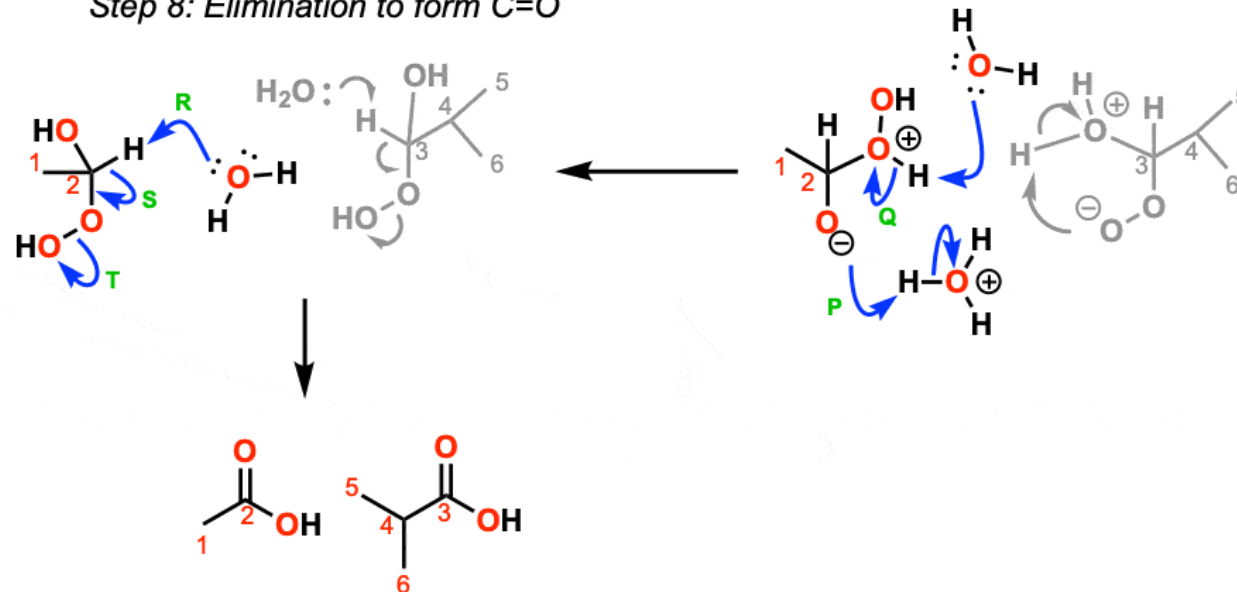
Bonds Formed

- K C₃-O (π)
- L C₂-O (π)
- N O-C₂
- P O-H
- R O-H
- S O-C₂ (π)

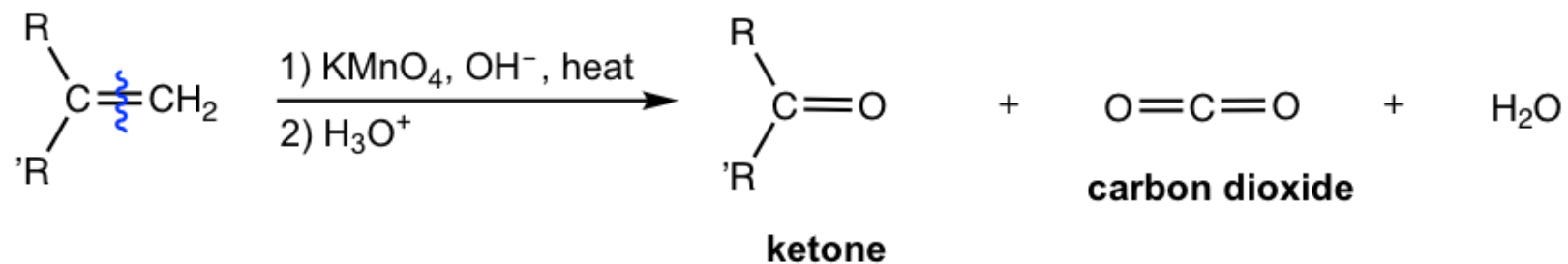
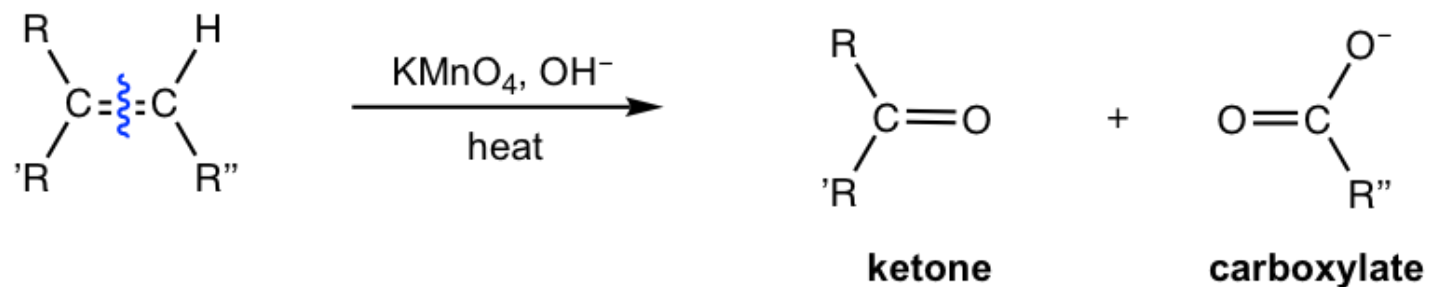
Bonds Broken

- L C₃-O
- M C₂-O
- O O-C₂ (π)
- Q O-H
- S C₂-H
- T O-OH

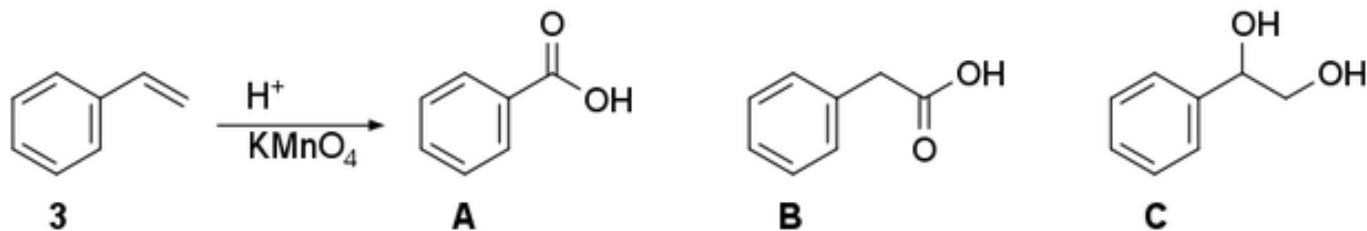
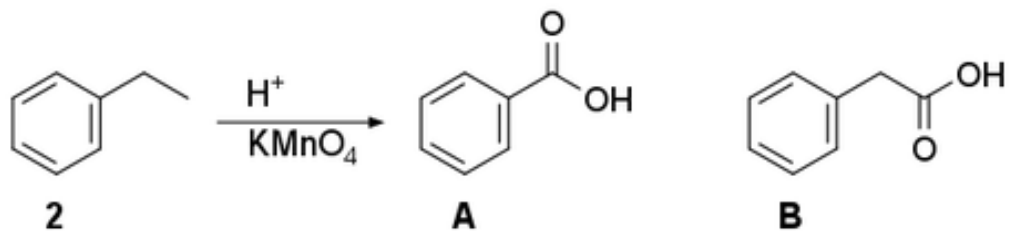
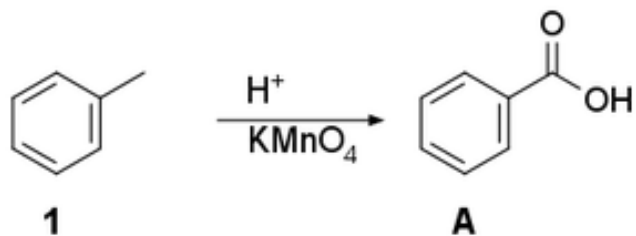
Step 7: Proton transfer



Reações de clivagens oxidativas com KMnO_4



Reações de oxidações de alquil benzenos com KMnO_4



Reações de clivagens oxidativas com OsO₄ seguido de NaIO₄

Reações com OsO₄ geram os correspondentes diois que, por sua vez, podem ser clivados por NaIO₄

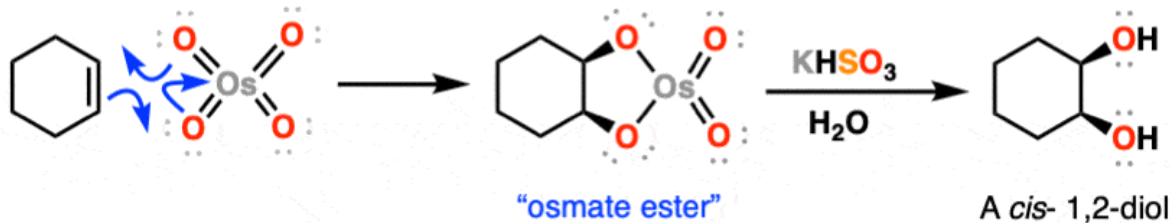
How it works: Dihydroxylation of alkenes

The dihydroxylation reaction with OsO₄ proceeds as a concerted **cycloaddition** between the alkene pi-bond and two Os=O bonds

In the first step:

- two C–O bonds form → This forms an “osmate ester”
- a C–C pi bond breaks

In the second step, the osmate ester is hydrolyzed to the diol (e.g. with KHSO₃)

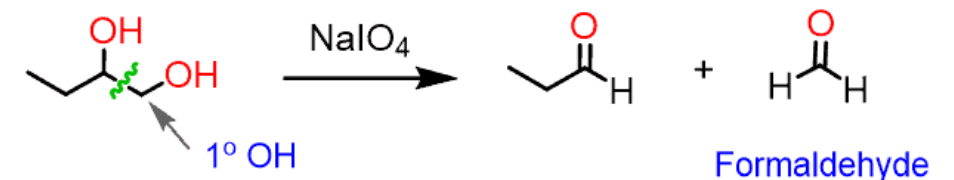
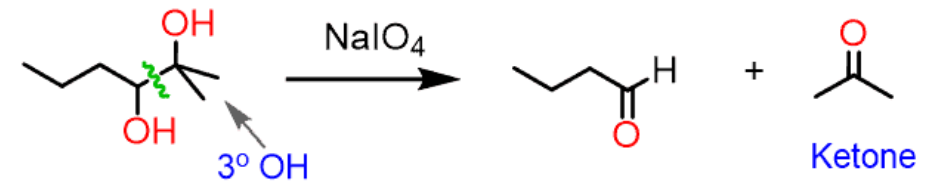
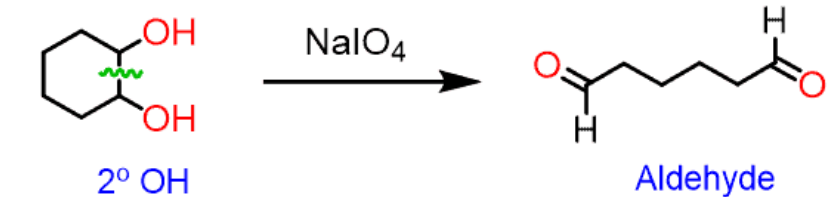


This addition occurs **exclusively** on **one** face of the alkene

An example of “**syn**” addition

Note that the oxidation state of Os has gone from +8 to +6

The purpose of KHSO₃ or NaHSO₃ (bisulfite) is to break down this cyclic osmium compound into the diol and an osmium salt



Reações de oxidações de alquil benzenos com KMnO_4

