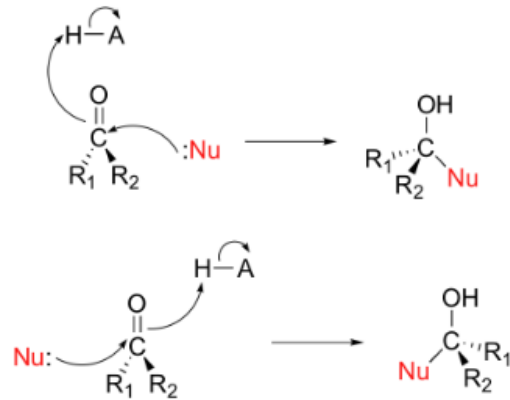
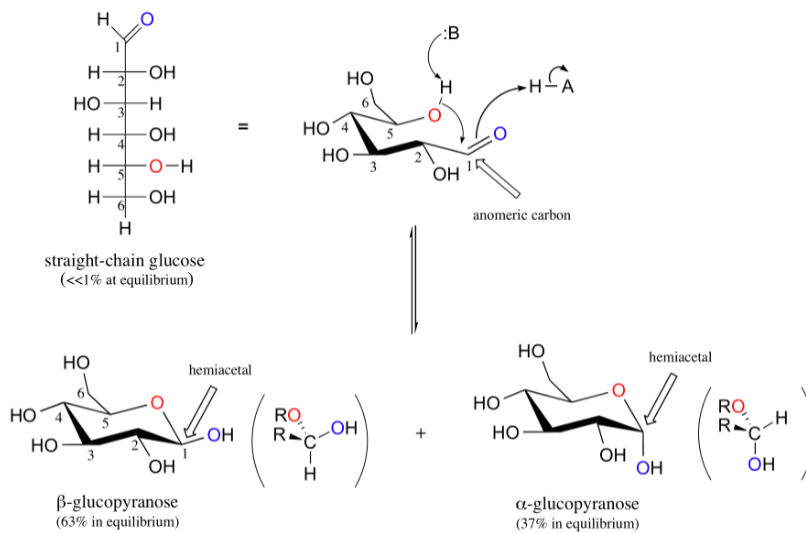




Faces re-si



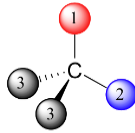
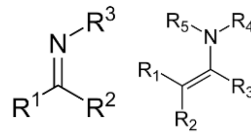
Faces re-si...



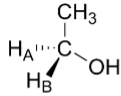
...doing
science
for better
health!



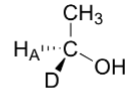
Carbonyl prochiral



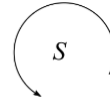
a prochiral carbon center



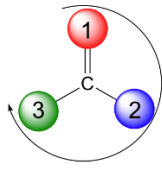
change H_B to D
stereocenter is now S.



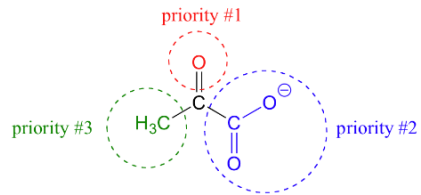
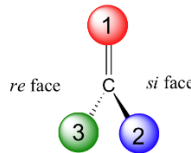
...so we refer to H_B as H_S



Faces re-si!



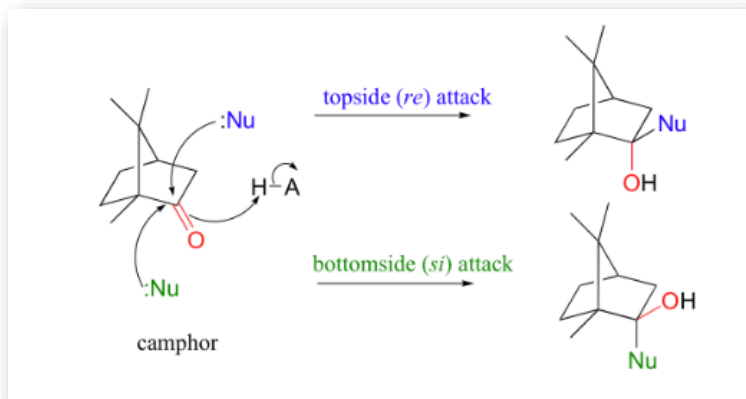
looking down on *re* face



...doing
science
for better
health!

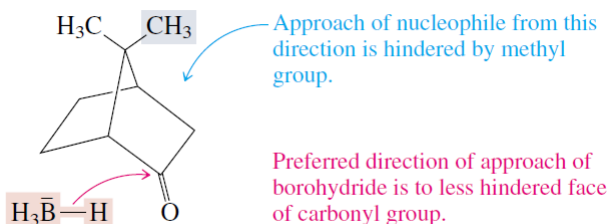
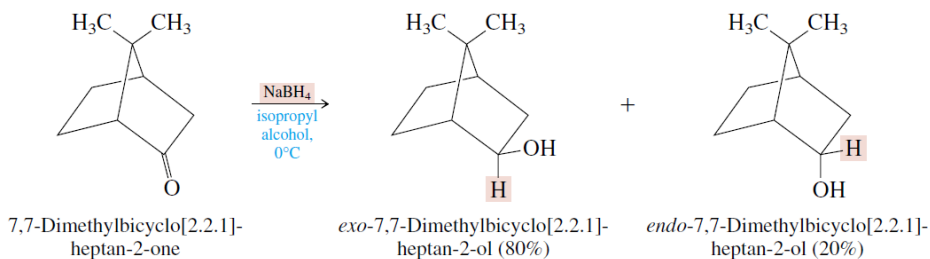


Faces re-si!

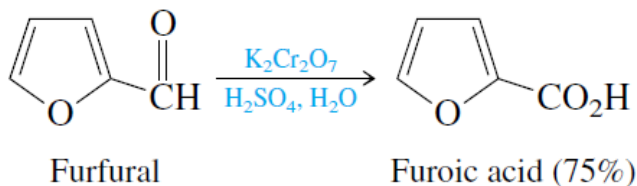
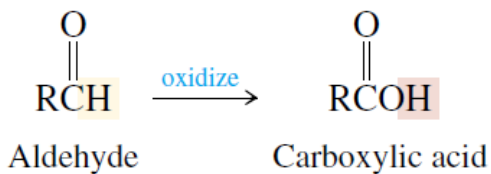




Adição Estereosseletiva...

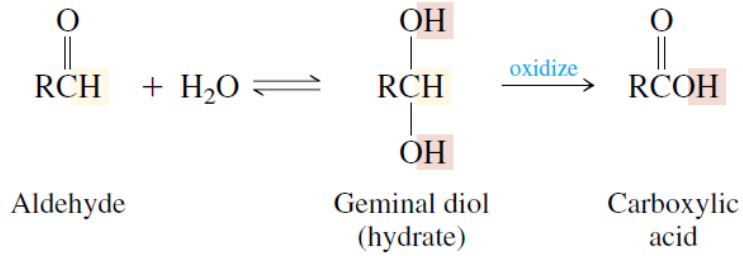


Oxidação de Aldeídos

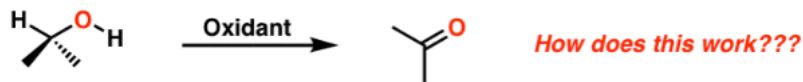




Provável mecanismo via hidratos

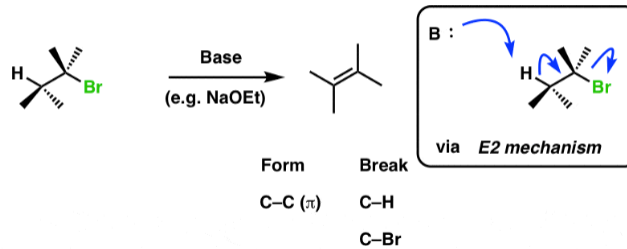


An unfamiliar mechanism: oxidation of alcohols



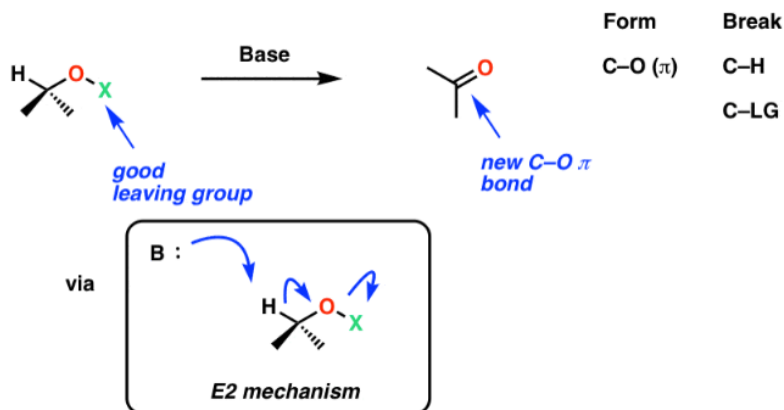
Common oxidants: PCC, H_2CrO_4 , Dess-Martin Periodinane, Swern

A familiar mechanism: elimination (E2) of alkyl halides to form alkenes





Imagine if we were to put a good leaving group on oxygen, and then add base. An E2 mechanism would give us a new C–O π bond



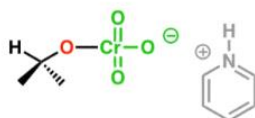
Most alcohol oxidations actually work this way!



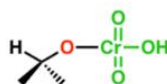
Here's what oxidants do:

- They coordinate to oxygen, and a proton transfer event breaks the O–H bond
- The atom coordinated to oxygen functions as a good leaving group
- A base then breaks C–H, forms C–O (π) and breaks the bond between O and the leaving group

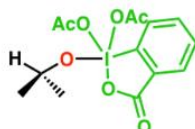
PCC



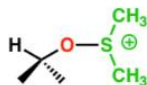
Chromic acid



Dess-Martin (DMP)



Swern

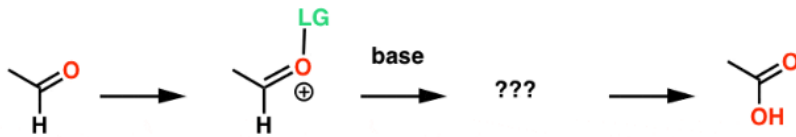


The group shown in green is the "leaving group" in an E2-type process



Oxidação de Aldeídos a Ácidos Carboxílicos

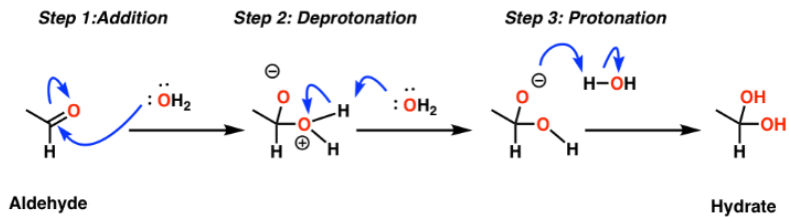
What about aldehydes going to carboxylic acids?



This isn't how it works !



The missing link: hydrate formation



The key step in aldehyde oxidation is elimination from a hydrate

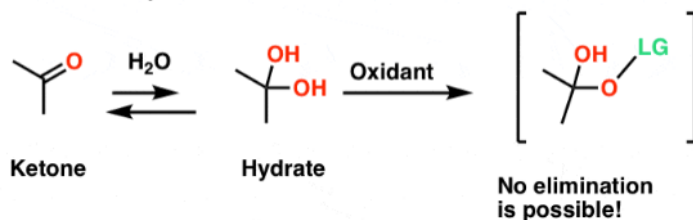




Por quê cetonas não são oxidadas?

So why don't ketones oxidize further?

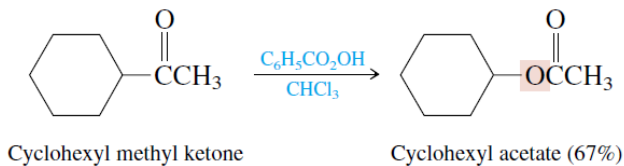
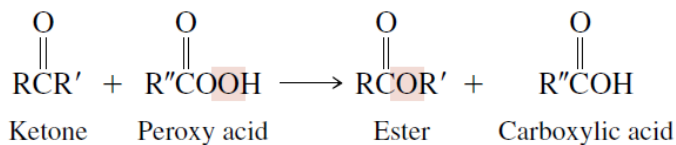
Because there's **no hydrogen that can be removed** to form a new pi bond on the ketone hydrate



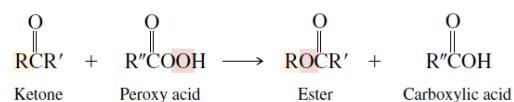
<https://www.masterorganicchemistry.com/>



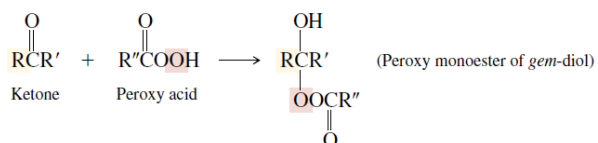
Oxidação de Cetonas via reação de Baeyer-Villiger



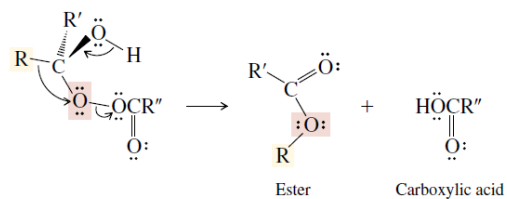
The overall reaction:



Step 1: The peroxy acid adds to the carbonyl group of the ketone. This step is a nucleophilic addition analogous to *gem*-diol and hemiacetal formation.



Step 2: The intermediate from step 1 undergoes rearrangement. Cleavage of the weak O—O bond of the peroxy ester is assisted by migration of one of the substituents from the carbonyl group to oxygen. The group R migrates with its pair of electrons in much the same way as alkyl groups migrate in carbocation rearrangements.



Mecanismo