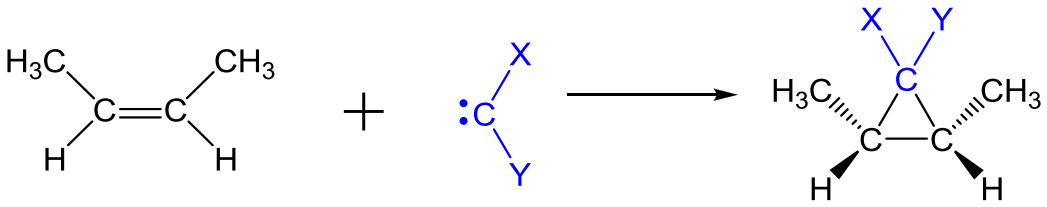
Recap Thursday: Carbenes

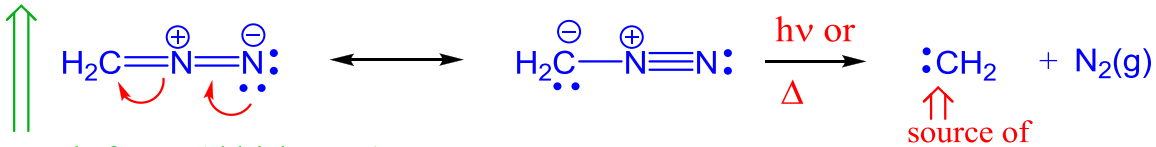


Singlet — concerted, stereo retained

Triplet — stepwise, stereo mixed (can rotate)

Best way to make carbenes: diazo compounds

e.g. diazomethane:

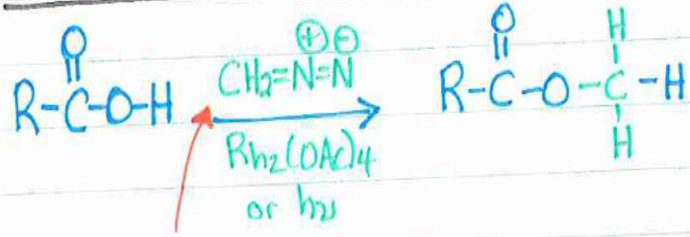


saw before... Aldrich story!

source of singlet carbene

Other reactions of carbenes/carbenoids

① Insertion into X-H bonds

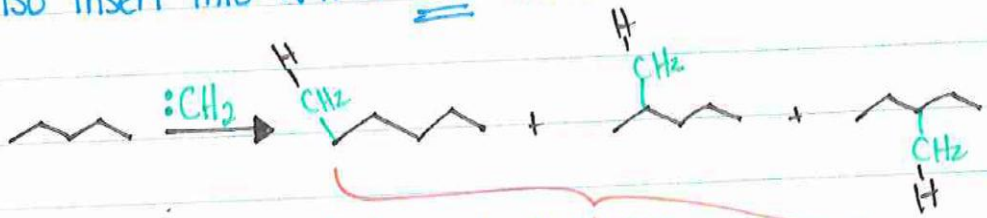


canary yellow

- used as "test" to detect RCO_2H (yellow colour fades) and as a way to make esters (aH. to $CH_3OH/H^+/\Delta$)

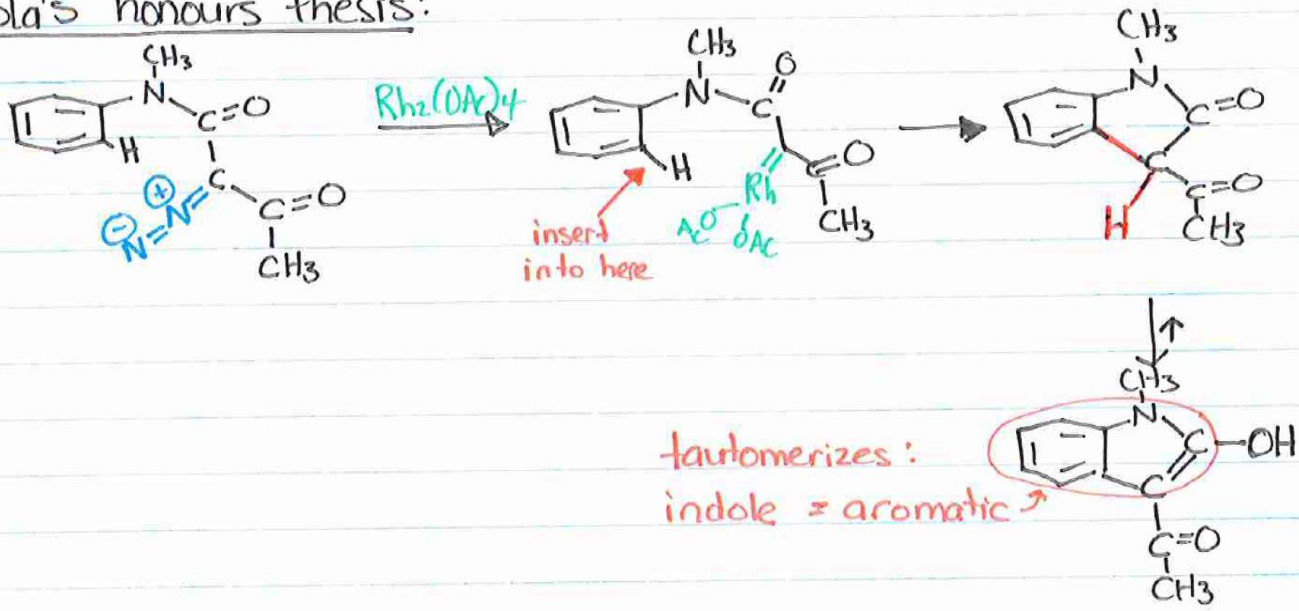
But - CH_2N_2 = toxic/explosive

- also insert into N-H or C-H bonds.

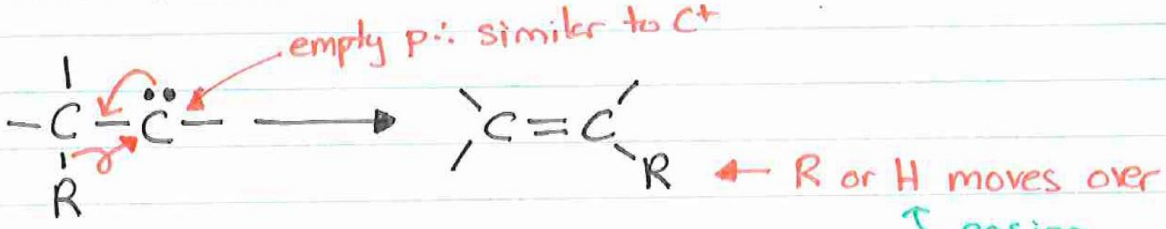
e.g. 

unselective - get all three

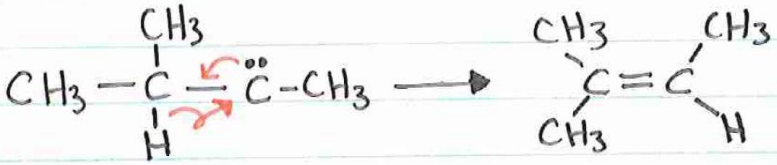
Nola's honours thesis!

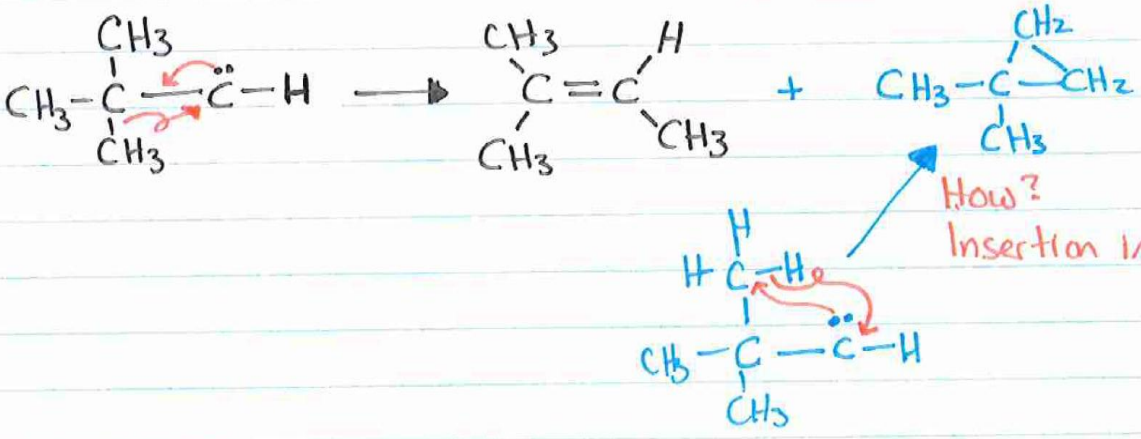


② Rearrangement of carbenes



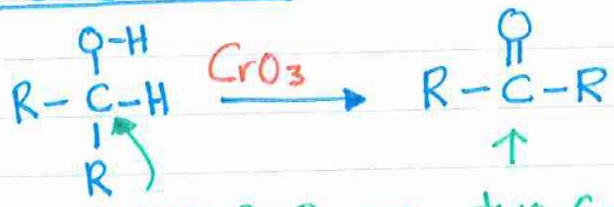
e.g.



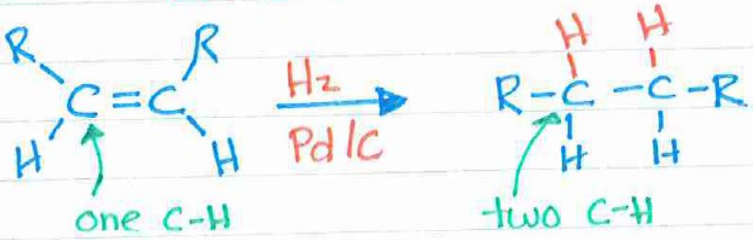


Oxidation + Reduction Reactions in Organic Synthesis

Seen some before:

e.g. 

one C-O → two C-O ∴ oxidation
one C-H (increase in C-O bonds)



one C-H → two C-H ∴ reduction
(increase in C-H bonds)

Important Aspects

① Chemoselectivity - ability to reduce or oxidize only one group in a molecule that has several groups

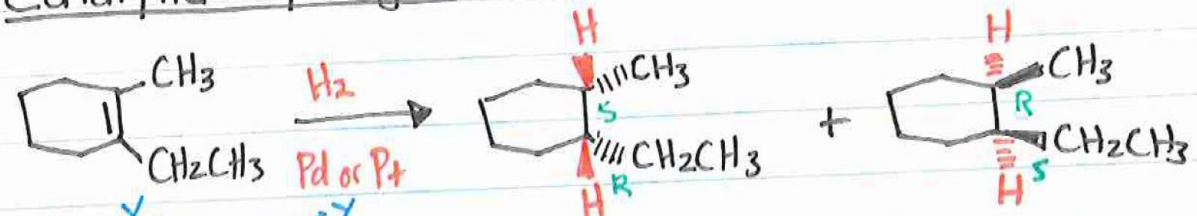
② Stereoselectivity - ability to preferentially get one stereoisomer over another
= "asymmetric" reduction or oxidation

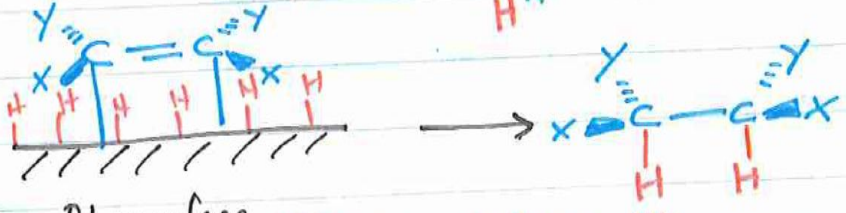
Reduction - 3 common methods → increase C-H bonds

① addition of $H_2(g)$ - catalytic hydrogenation
② addition of "H^-" (hydride) - $NaBH_4$, $LiAlH_4$ etc
③ addition of electrons - reducing agents such as Zn, Na

* Have seen examples of all three in Chem 241/242!

① Catalytic Hydrogenation



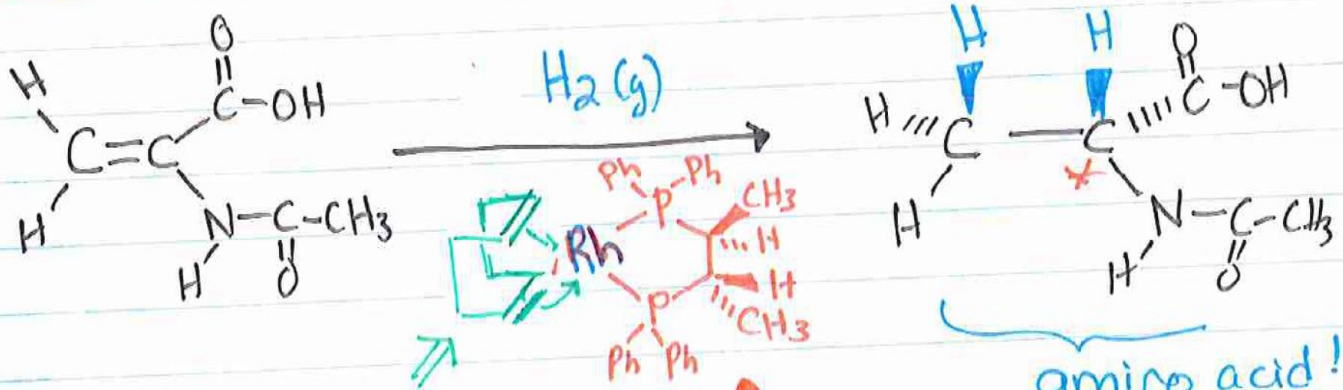


delivers H's to same side

But - can add H's to top or bottom ∴ racemic

∴ RS/SR (but no RR/SS)

Chiral Catalyst - can give more of one enantiomer



"COD" = cycloctadiene

S,S-chiraphos

* mostly "R" 90% ee

[R,R-chirophos → 90% ee S]

What does 90% ee mean?

R major ∴ %R − %S = 90%

95% R − 5% S