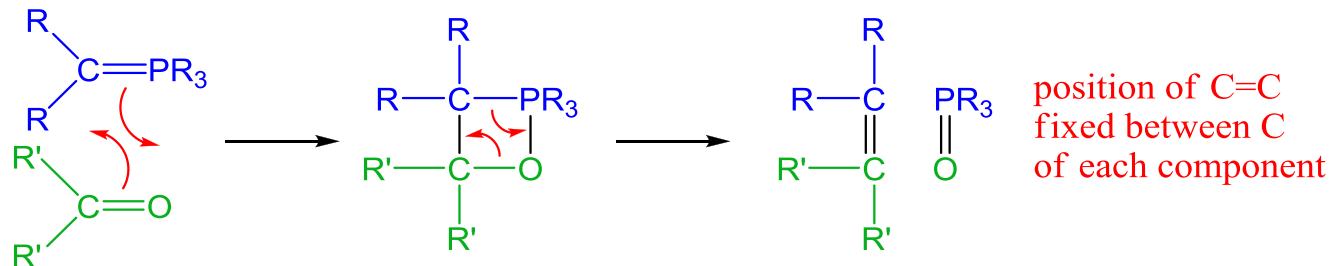


## Overheads: - Today's Outline

## Recap Tuesday: Wittig Reaction

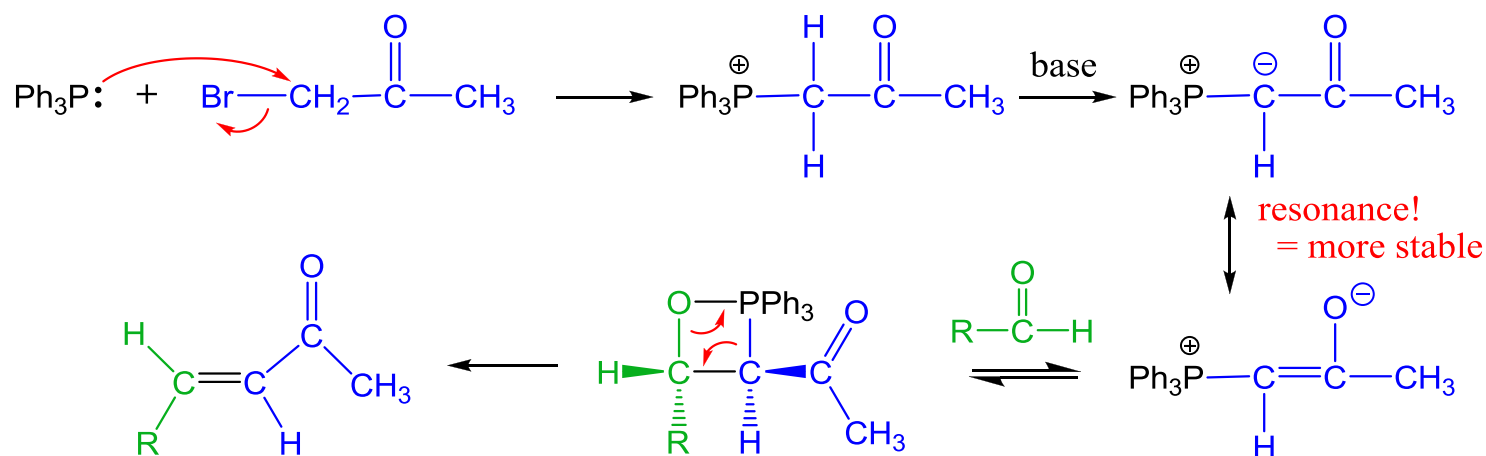


## Stereochemistry of alkene:

- Bulky R's = more Z / cis

But – if ylide has electron-withdrawing group (like C=O) get mostly trans/E

- Called a stabilized ylide



another way to make α,β-unsaturated ketone!

because of stability of C<sup>-</sup> can equilibrate, so get more stable, trans product.  
(thermodynamic product!)

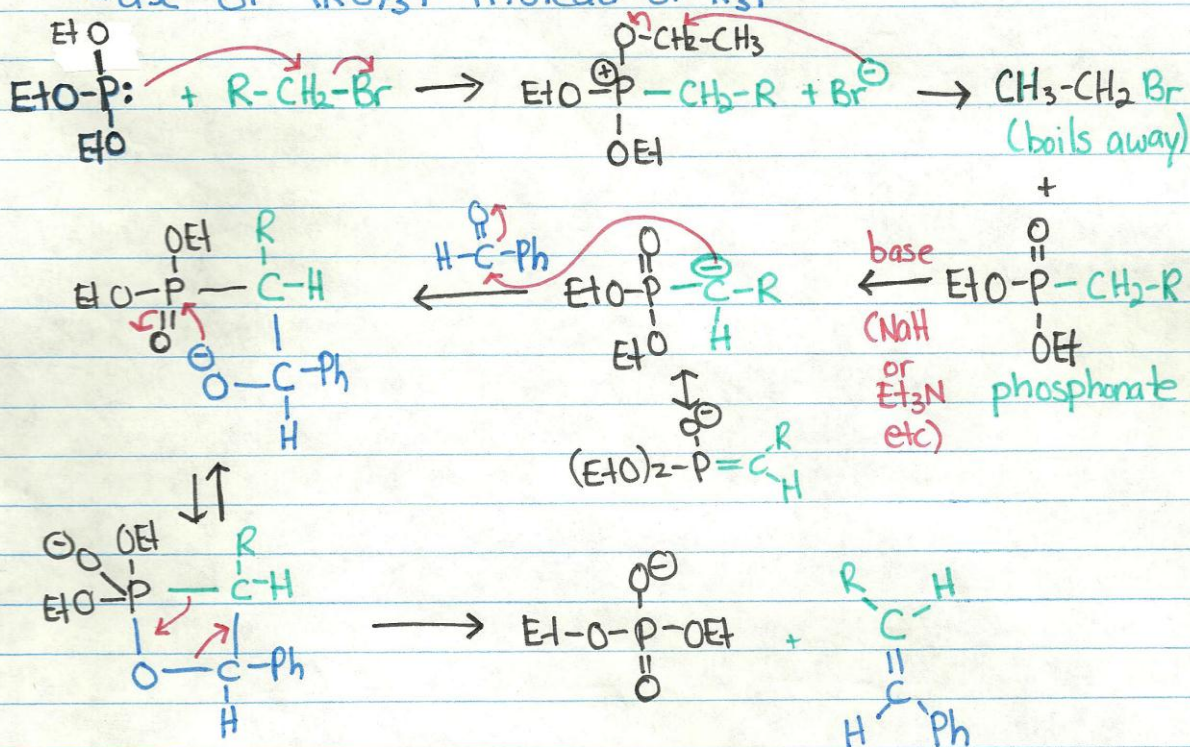
## Summary

- stabilized ylide  $\rightarrow$  trans / E
- unstabilized ylide  $\rightarrow$  cis / Z - especially if bulky  $R_3P$

Note: also affected by base used (Li salt vs others etc)  
 $\rightarrow$  even more complicated!

## Horner-Emmons modification of Wittig

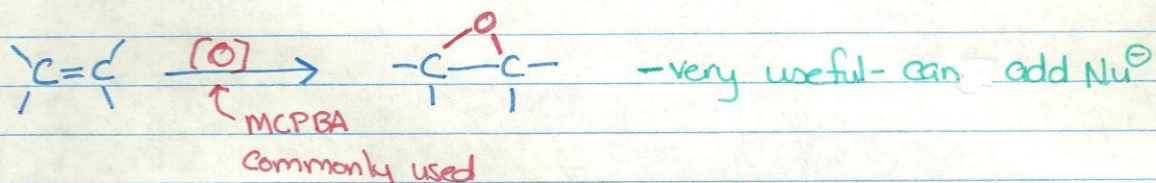
- use of  $(RO)_3P$  instead of  $R_3P$



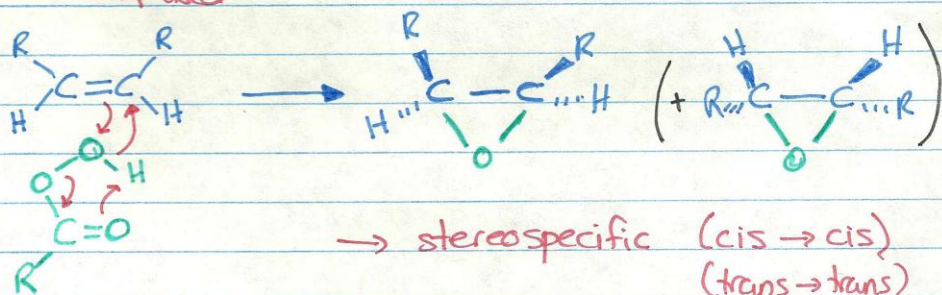
- Advantages
- ①  $(RO)_2P(=O)O^-$  water soluble  $\therefore$  can wash away
  - ②  $(RO)_3P$  cheaper than  $R_3P$
  - ③ Better trans selectivity

## Making Epoxides:

More common way to make epoxides  
-oxidation of alkenes



Mechanism:



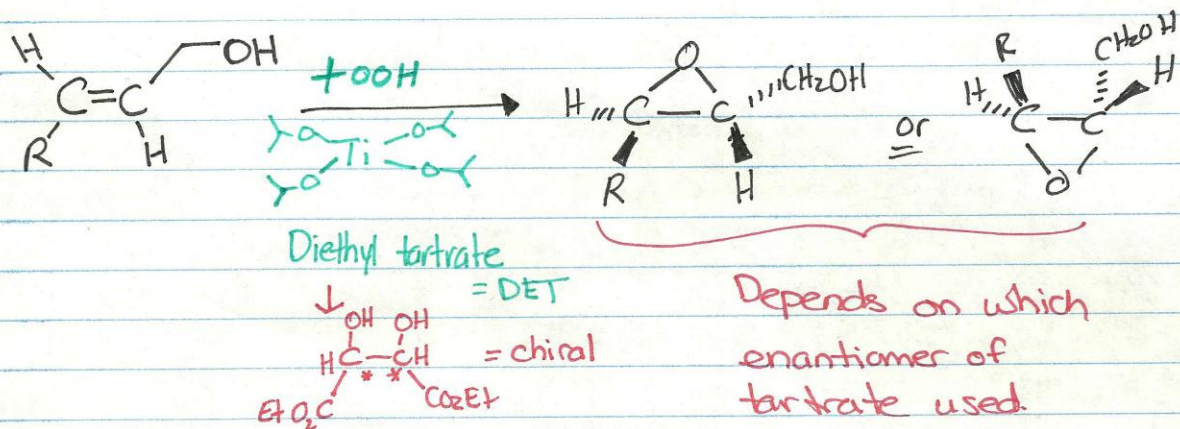
BUT not enantioselective  
(get racemic RS/SR or RR/SS)

→ would be great to get only one enantiomer!



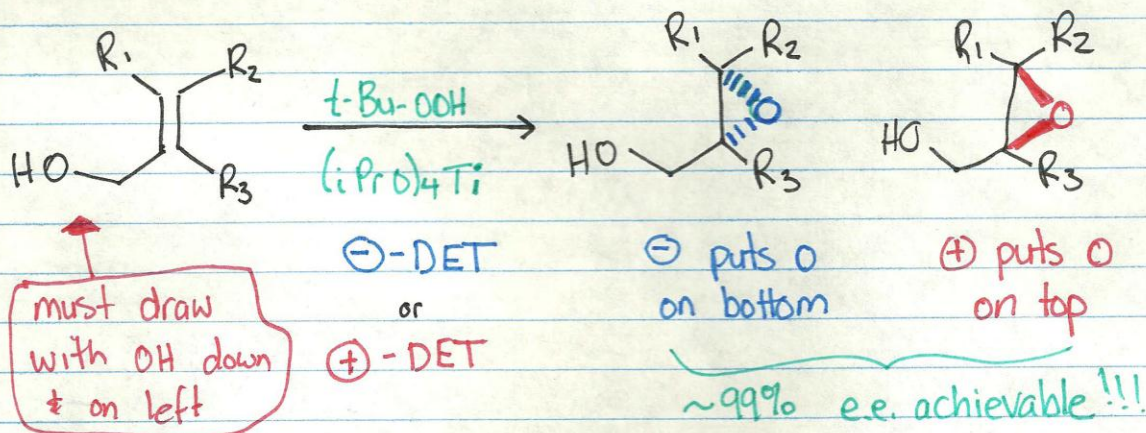
# Sharpless Epoxidation (Barry Sharpless)

- gives chiral epoxides
- works only for allylic alcohols  $\text{CH}_2=\text{CH}-\text{OH}$



$\rightarrow$  Ti coordinates DET ( $\therefore$  chiral) and allylic alcohol  
 $\therefore$  controls which side R-O-O-H adds to.

Key to determining chirality of product: (empirical tool)

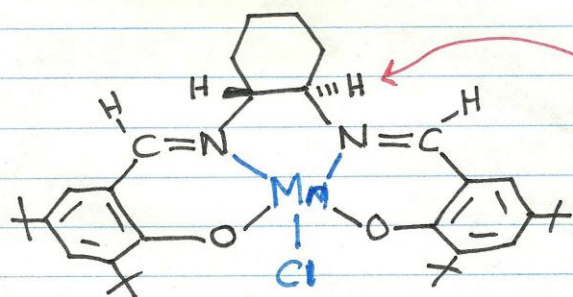


Note:  $\ominus$ -DET = S,S-enantiomer

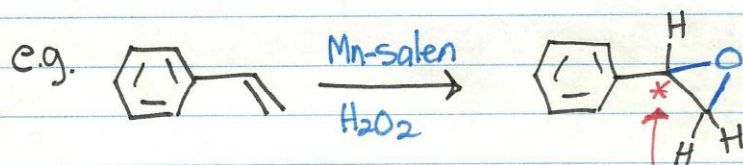
$\oplus$ -DET = R,R-enantiomer



Jacobsen's Catalyst - uses Mn-salen complex



chiral  
- can buy (+) or (-) catalyst



R/S controlled by  
which catalyst  
used (+) or (-)

\* does not need OH on  $\approx$ OH to coordinate

\* works best for conjugated C=C

\* not as easy to predict R or S (just have to try one)

Seen: - add "CH<sub>2</sub>" to C=O  
- add "O" to C=C }  $\rightarrow$

$\rightarrow$  add "CH<sub>2</sub>" to C=O  $\rightarrow$  = cyclopropane!

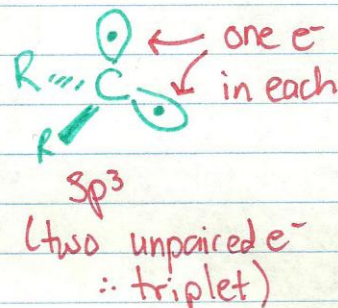
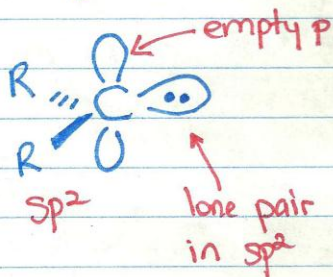
Carbene:  $\left\{ \begin{array}{l} \text{C has only 6e- (like C+)} \\ \text{- 2 non-bonded e- (like C-)} \end{array} \right\}$  but no charge!

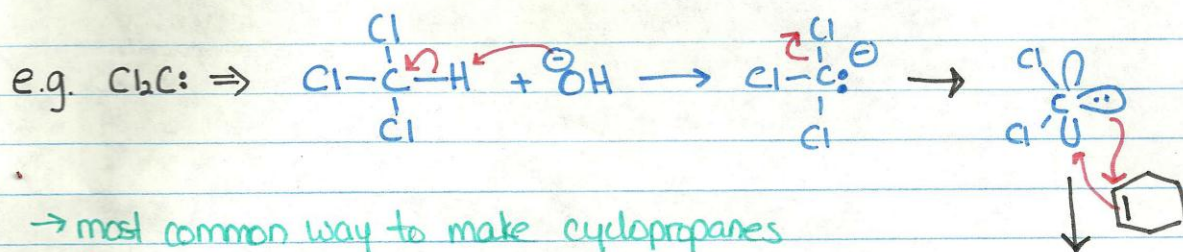
Structure:

singlet carbene

vs

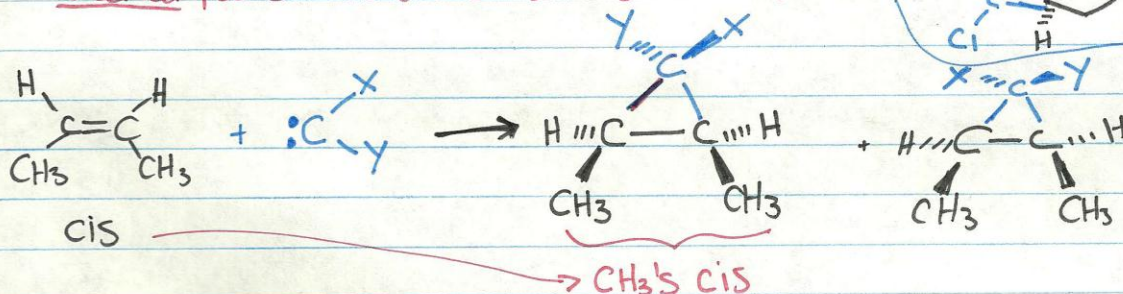
triplet carbene





→ most common way to make cyclopropanes

→ for singlet carbenes, the reaction is concerted, so stereochem. of alkene retained.



- for triplet carbenes - one bond formed at a time, so can rotate in between.

