

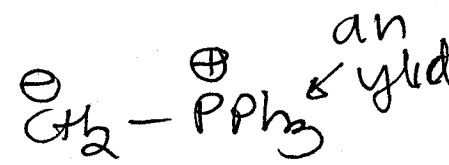
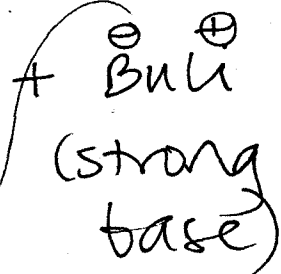
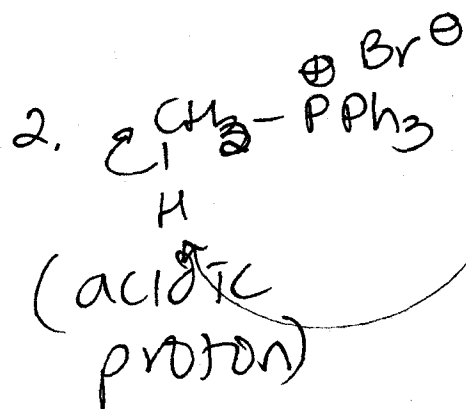
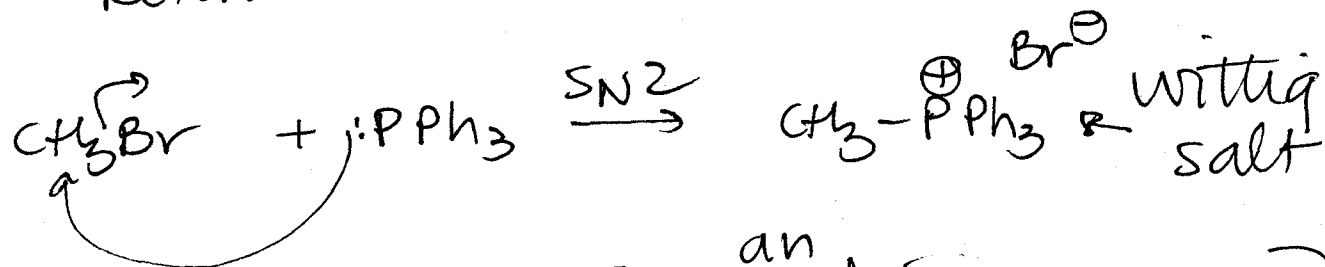
# Phosphorus Nucleophiles

\* Wittig Rxn

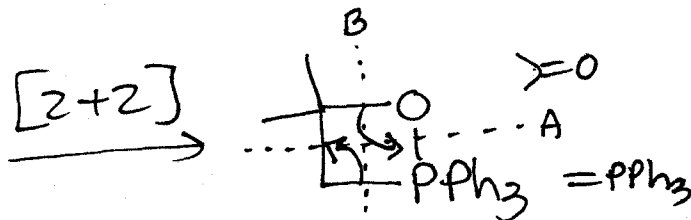
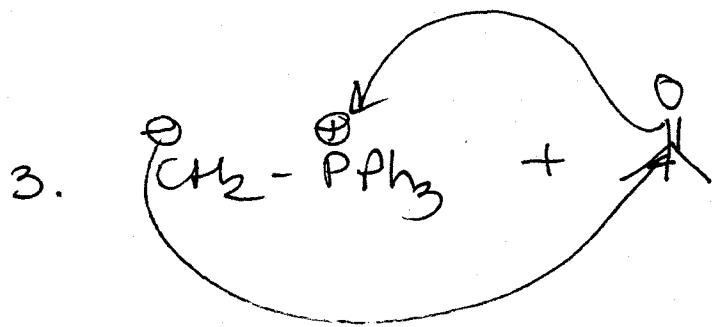
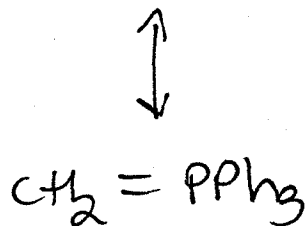
carbonyl + ylid  $\rightarrow$  alkene

$\uparrow$   
aldehydes  
ketones

1. 1°/2° RX

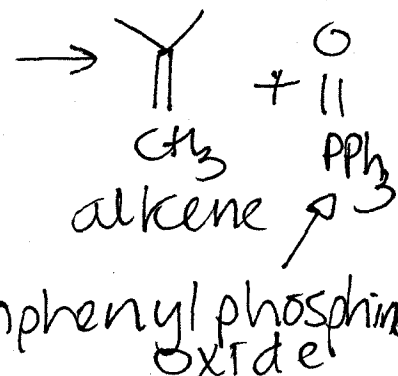


[ + butane  
+ LiBr  
from  
acid-base rxn ]



oxaphosphetane

decompose quickly  $\rightarrow$



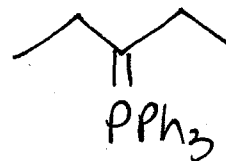
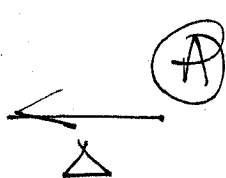
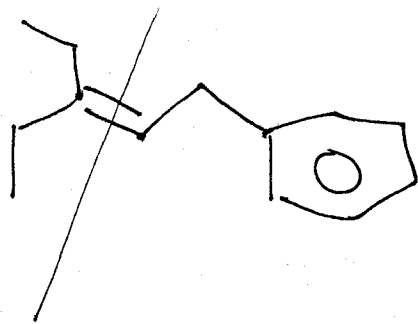
note: book says "stabilized" ylides  $\rightarrow$  E alkenes  
"unstabilized" ylides  $\rightarrow$  Z alkenes

Not always.

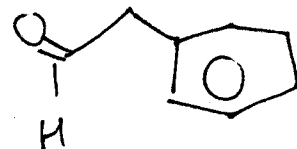
Also: section on "re" + "si" faces of carbonyls  
\*not on exam.

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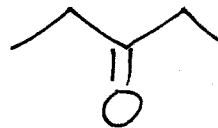
make:



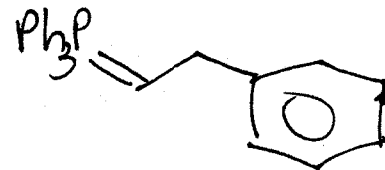
+



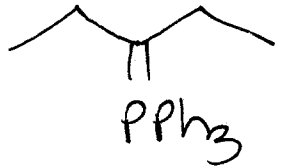
or



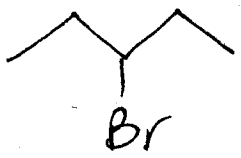
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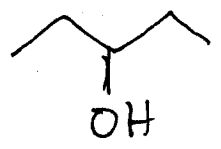
(A)



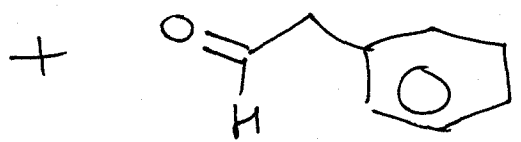
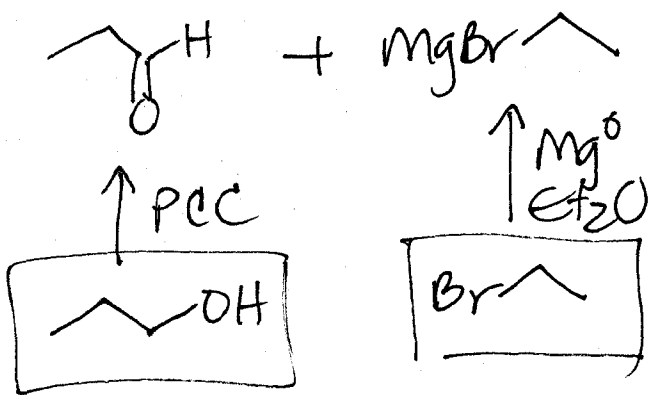
1) PPh<sub>3</sub>  
2) BuLi



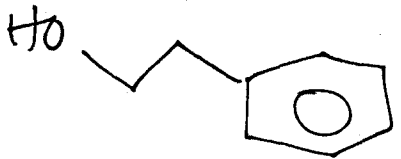
PBr<sub>3</sub>



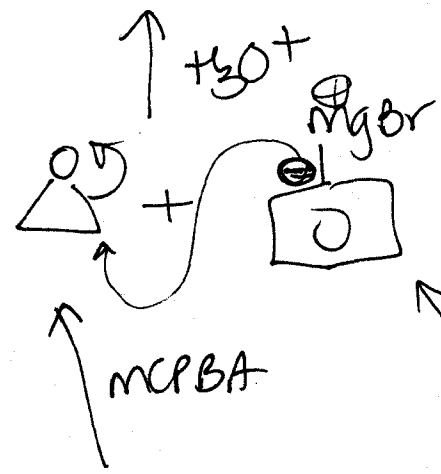
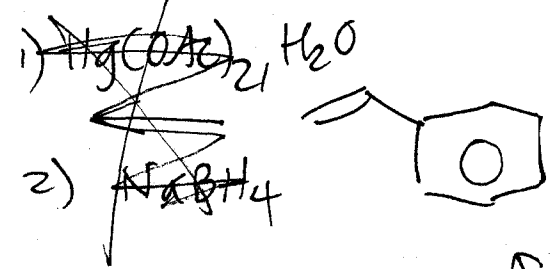
H<sub>3</sub>O<sup>+</sup>



PCC

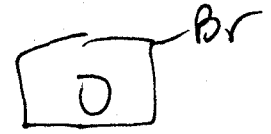
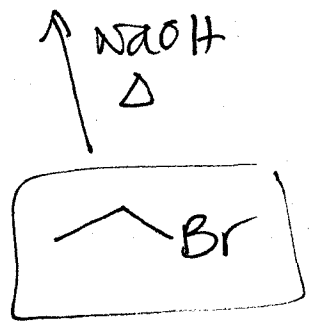


1) BH<sub>3</sub>·THF 2) H<sub>2</sub>O<sub>2</sub>

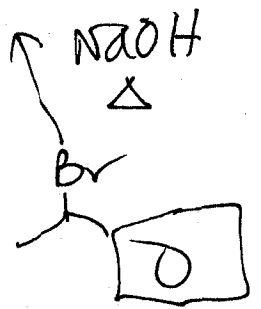


mCPBA

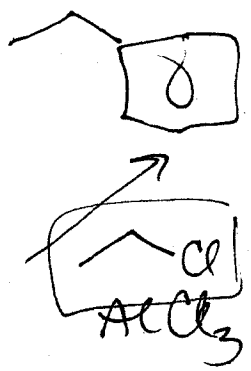
=



Mg<sup>0</sup>, Et<sub>2</sub>O



Br<sub>2</sub> hν



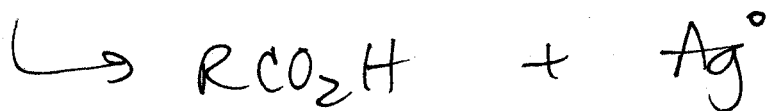
## Other oxidations of aldehydes

1. aldehyde  $\rightarrow$  carboxylic acid -  
any of the  $\text{Cr}^{\text{VI}}$

2. Silver reagents

a.  $\text{Ag}_2\text{O}/\text{NaOH}$  then  $\text{H}_3\text{O}^+$   $\rightarrow \text{RCO}_2\text{H}$

b.  $\text{Ag}(\text{NH}_3)_2^+/\text{H}_2\text{O}$  Tollen's reagent



\*functional group test  
specific for aldehydes

# Baeyer-Villiger oxidation

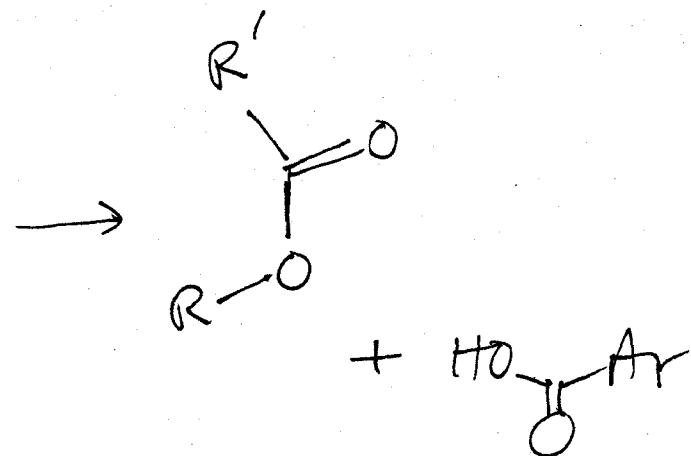
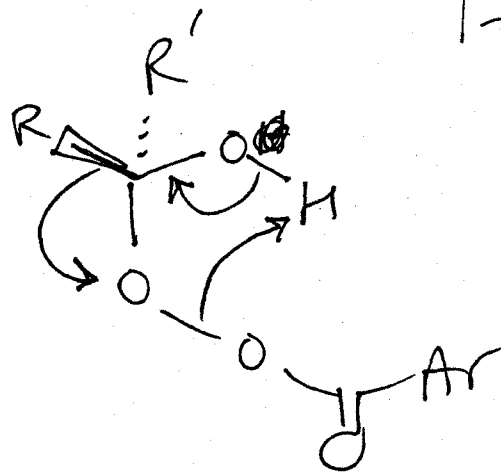
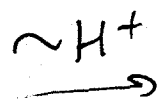
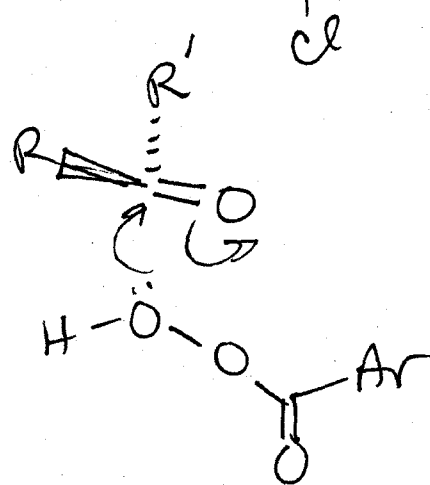
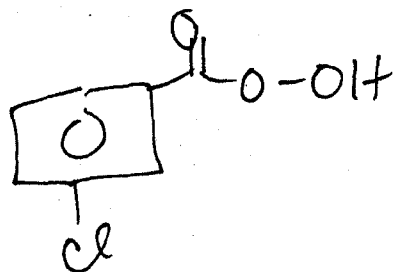
aldehyde + peracid  $\rightarrow$  carboxylic acid

ketone + peracid  $\rightarrow$  ester

A peracid is  $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{OH}$

most common: MCPBA

metachloroperbenzoicacid



(Recall: peroxide  
is  $\text{HO}-\text{OH}$ )

migratory Aptitudes  
of R group:

