Sulphur Silicon and Phosphorous

C–P ≈ C–H not very strongly polarised

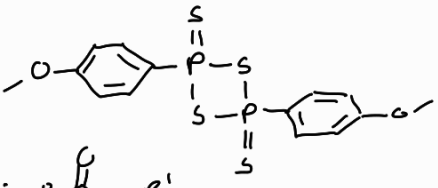
2.1 2.2

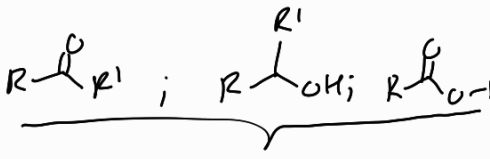
$C^{\delta+}-O^{\delta-}$ >> $C^{\delta+}-S^{\delta-}$ $C^{\delta-}-Si^{\delta+}$ other way around

3.5 2.5 1.8

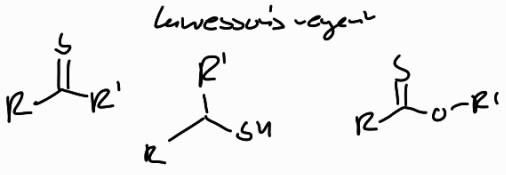
Synthesis

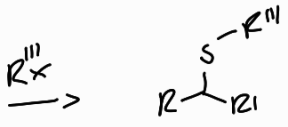
- Lawesson's reagent

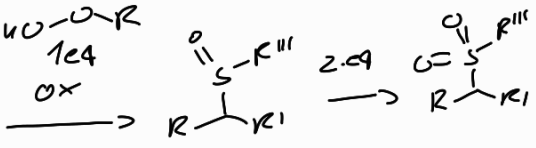




Lawesson's reagent

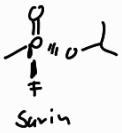




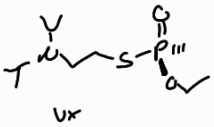


Phosphorous

ex



Sarin



Vx

=> Nerve gases

Silicon

R–O–SiR_3 R = Me; Bu; Ph....

TMS

= Protection group

⊕ Si–F extremely strong used to remove protection

Ylides – S

pka ~30–35

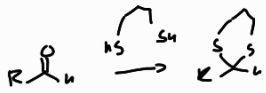
Why? – Not a big ΔEN => orbitals

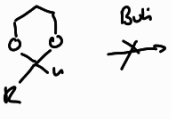
C–S can't overlap with neg. charge

=> Hyperconjugation

dithians

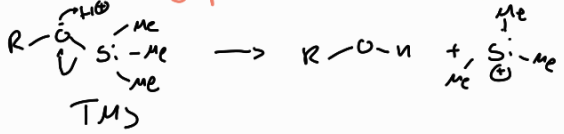
Umpolung:





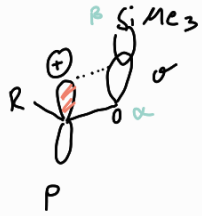
Why "ylide"? "Alkyl anion" + substitution a hetero atom

Silicon – a big proton with even bigger orbitals



TMS

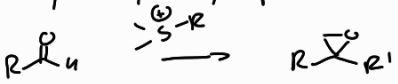
β-silicon effect

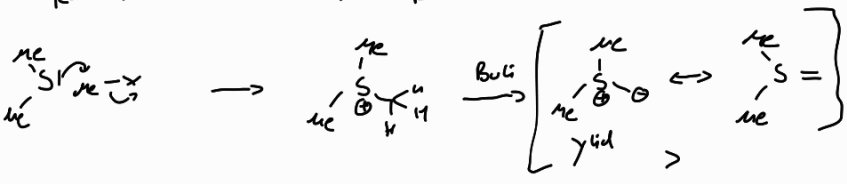


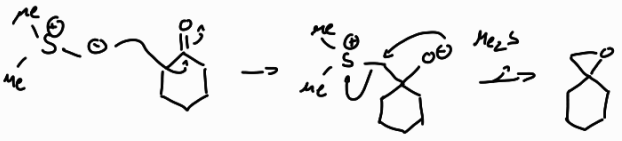
⇒ Delocalisation of C-Si σ into p-orbital with positive charge
→ stabilisation of pos. charge

⟹ S ; P stabilize Neg. charge, Si stabelises pos charge

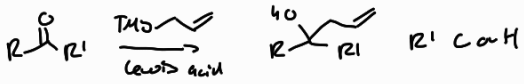
Corey-Chaykofsky epoxidation

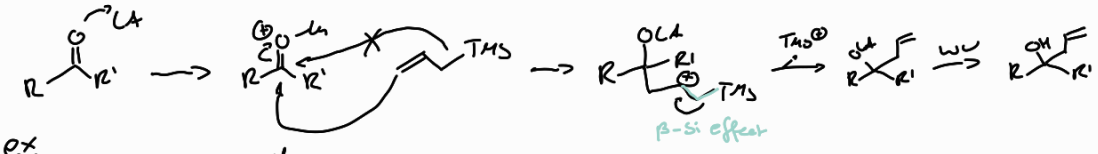




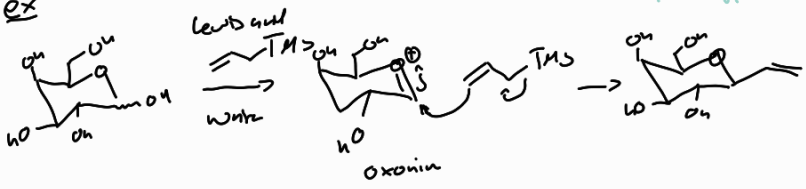


Sakurai alkylation

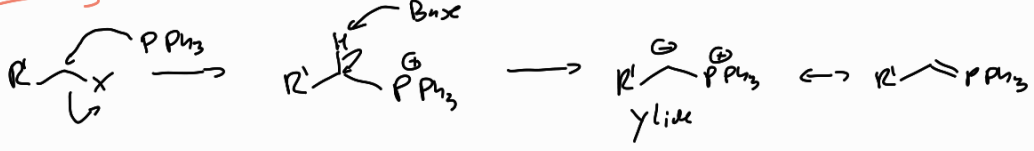




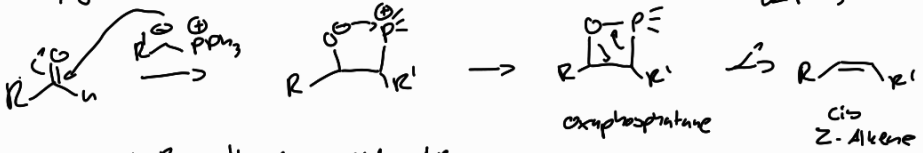
ex



Wittig

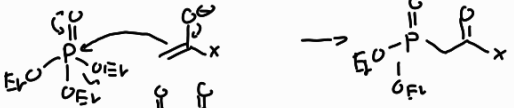


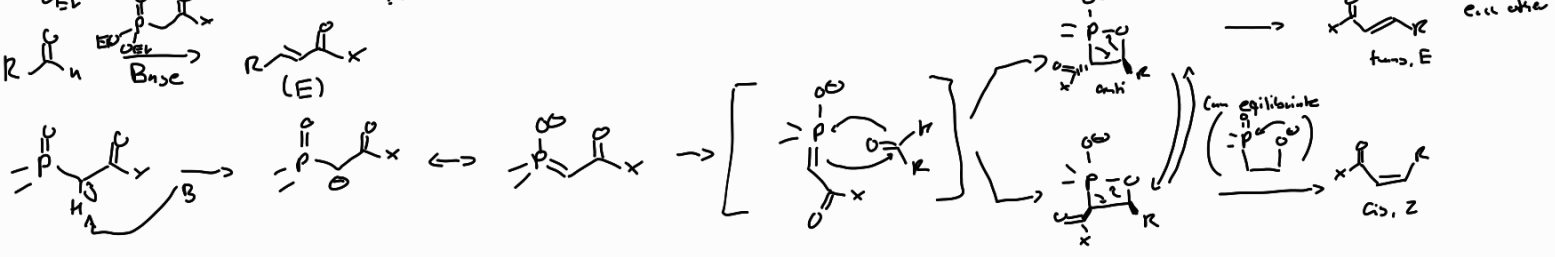
mostly good for aldehydes



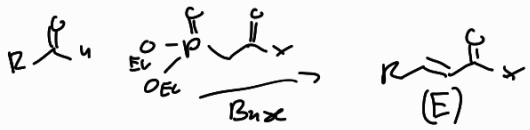
→ R' and R on the same side due to steric hindrance of P(Ph3)

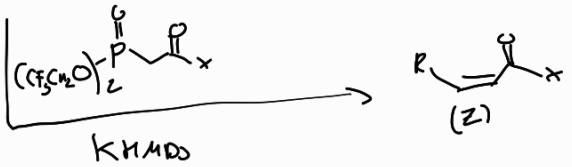
Horner Wadsworth Emmons HWE





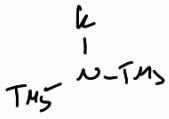
Horner - Wadsworth - Emmons - Still - Gennari





KHMDS

18 crown-6 (enters k inner sphere)



=> Fluorinated alkoxy oxaphosphonate → Stabilized ylid → faster decomposition of oxaphosphonate => Kinetic product