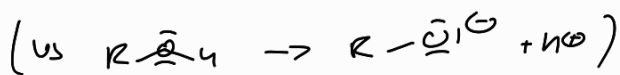
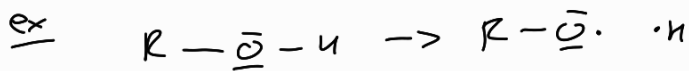
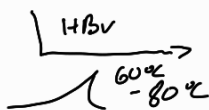


Radicals and carbenes (Ch. 37, 38)

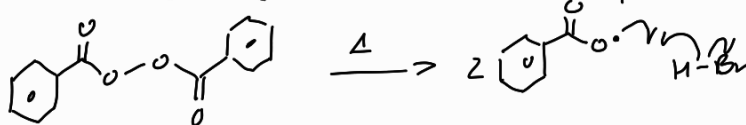
\Rightarrow Homolytic bond cleavage \Rightarrow unpaired e^-



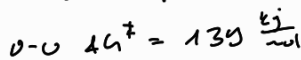
ex



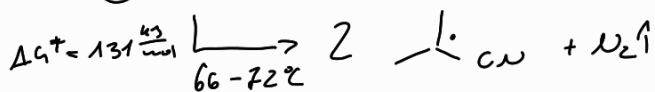
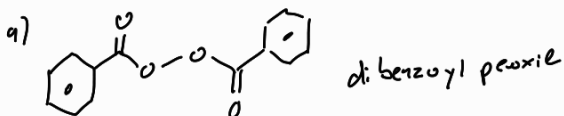
anti-Markovnikov addition



di-benzoyl peroxide



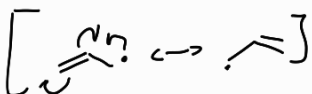
Radical initiators



c) $h\nu$

Radical stability

\Rightarrow Resonance stabilizer



Allyl groups stabilize Radicals just like carbocation

Reactions

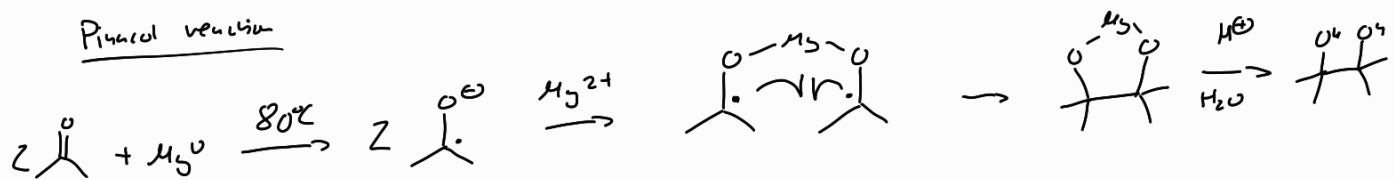
a) Coupling

b) Dehydrogenation

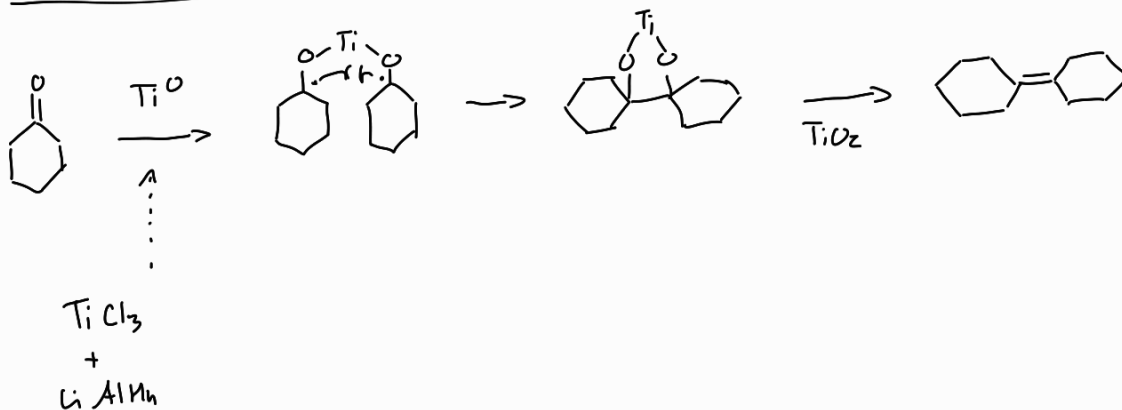
c) Cyclization

9) Cupryls (Single electron transfer SET)

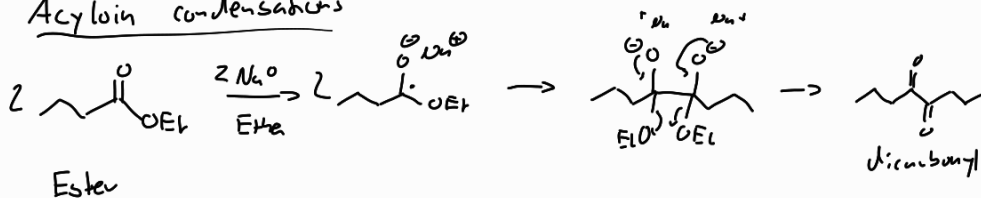
Pinacol reaction



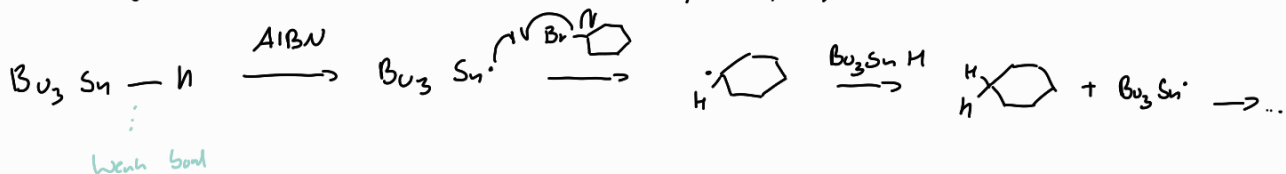
Mc Murry reaction



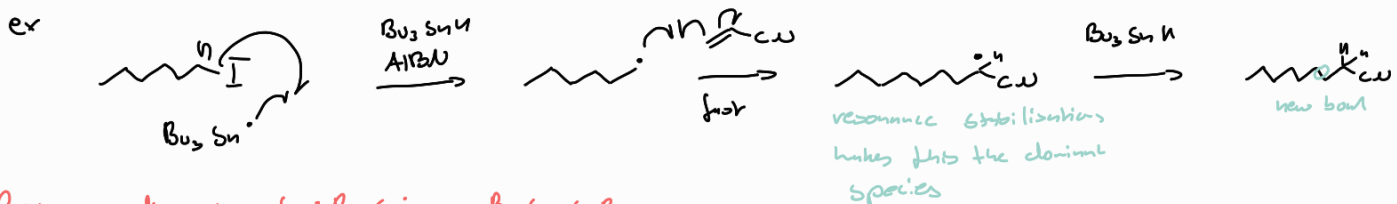
Acyloln condensations



b) De-Halogenations: red. with $\text{Bu}_3\text{Sn-H}$ (tributyl stannane)



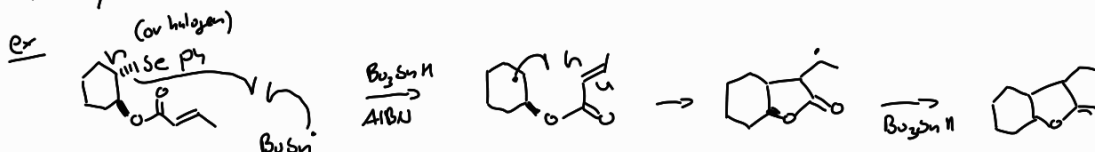
Dehalogenation \Rightarrow C-C bond with $\text{Bu}_3\text{Sn-H}$



Problem: dimerisation of $2 \text{ Bu}_3\text{Sn}^\cdot \rightarrow \text{Bu}_3\text{Sn-SnBu}_3$

\Rightarrow low concentrations e.g. Bu_3SnCl (0.1eq) + LiAlH_4 (1.2eq)

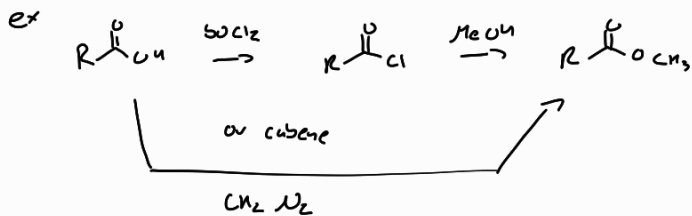
c) Cyclisations (intermolecular radical reactions)



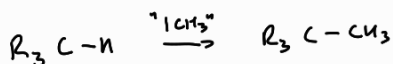
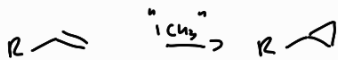
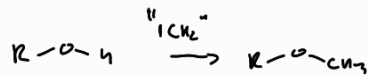
Carbenes

Neutral carbon with 6 valence e^-

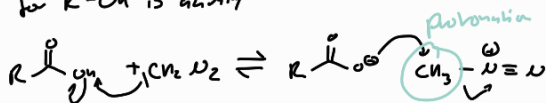
C^\cdot carbenes add or insert to give filled orbitals



Reactions typically happen on:

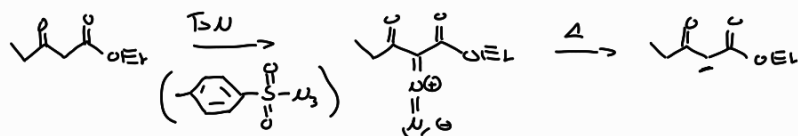
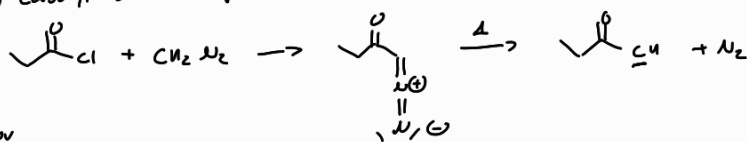


Requirement for R-CH is acidity

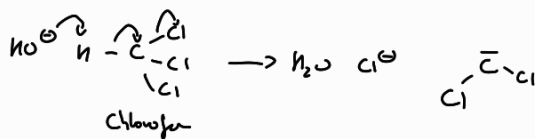


Diaz compounds:

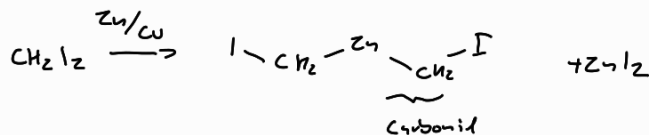
1) Carbonyl diazo compound



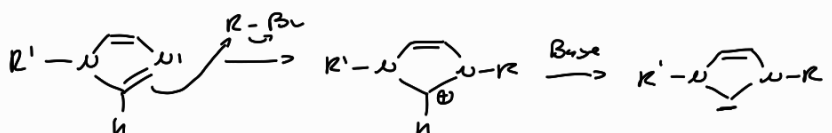
2) α -elimination of halo compounds



3) Zn-carbenoid: Simmons-Smith reagent



4) Deprotonation of heterocycles

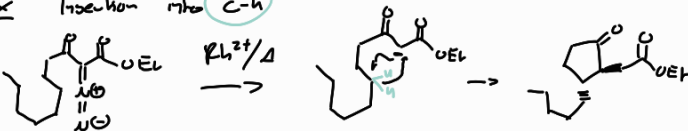


N-heterocyclic carbene
 \Rightarrow Used in metathesis reactions!

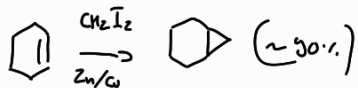
||

Reactions

ex Insertion into C-H



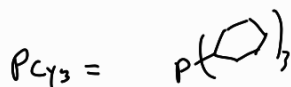
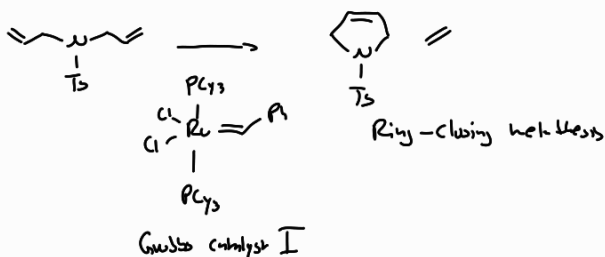
ex Insertion into alkene with Simons-Smith



A new important reaction

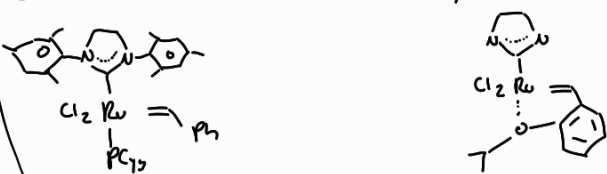
Alkene metathesis

ex

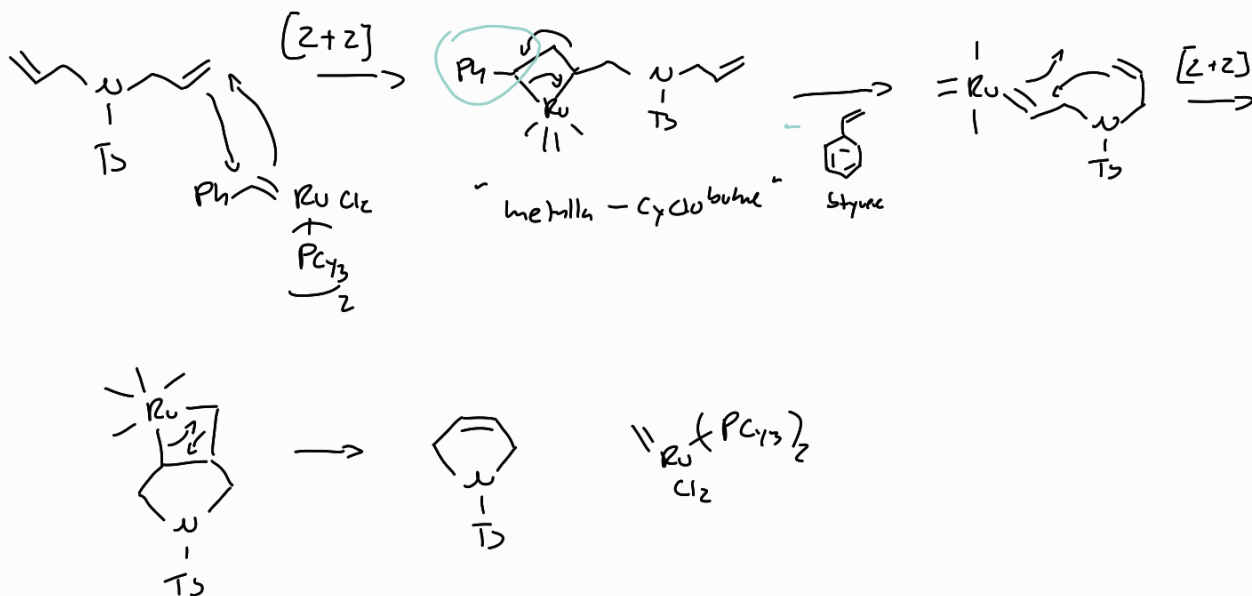


Other catalysts: Grubbs II

Hoveyda-Grubbs



RCM reaction:



also possible to do cross-metathesis:

