OC2

Radicals & Polymerisation

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Radical Polymerisation and other Radical Reactions

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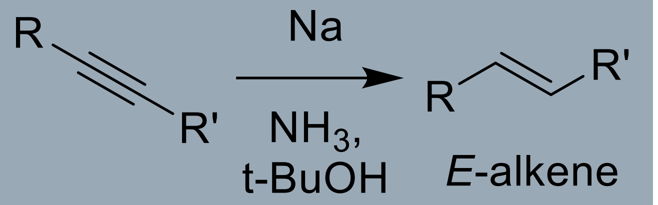
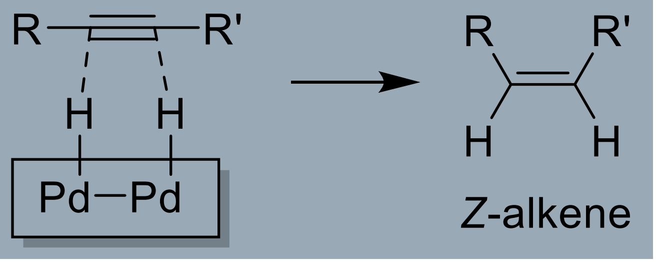
Reduction of Alkynes to *E*-alkenes

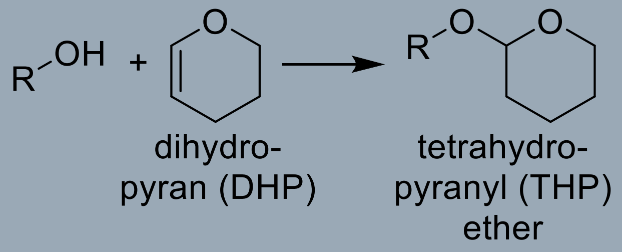
Single Electron Transfer (SET)
e.g. from Na

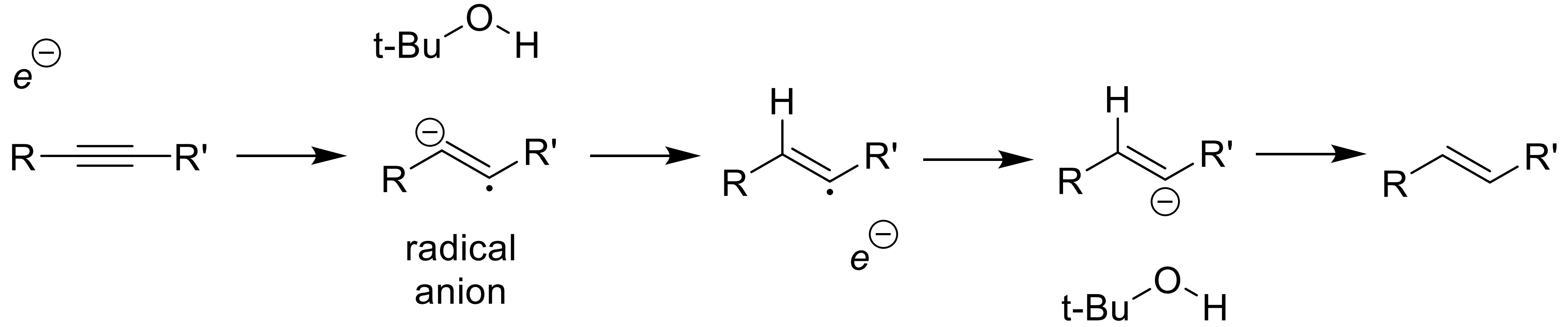


Compare: heterogeneous Pd(0) catalysis (Lindlar cat.; e.g. 5 wt% Pd(0), $CaCO_3$, $PdAc_2$, quionoline)

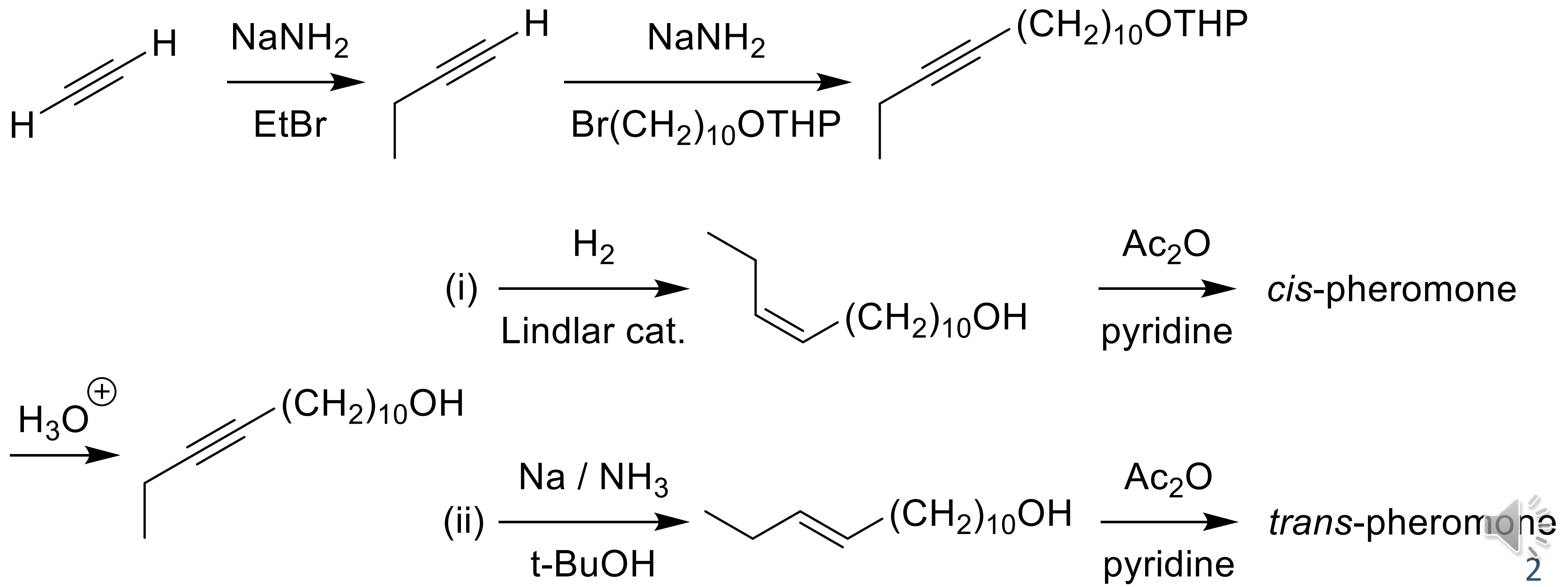


Protection of alcohol as THP ether





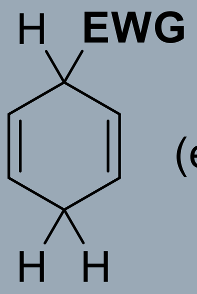
Example: European corn borer moth sex pheromone $CH_3CH_2CH{=}CH(CH_2)_{10}OAc$; geometry of double bond depends on moth race



Birch Reduction

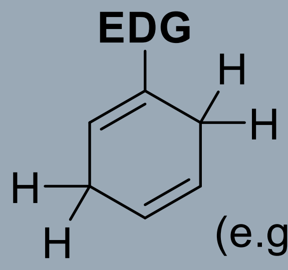
Birch's empirical rules:

For electron withdrawing groups (**EWG**s) → double-bond of the product avoids substituents

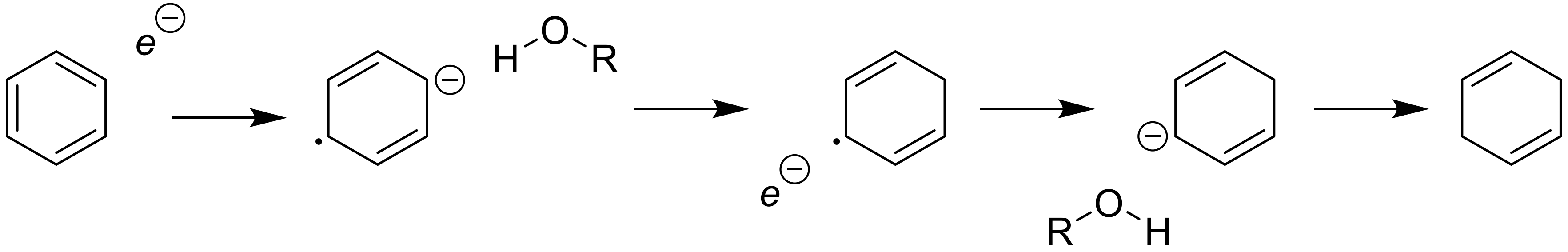


(e.g. $-CO_2R$)

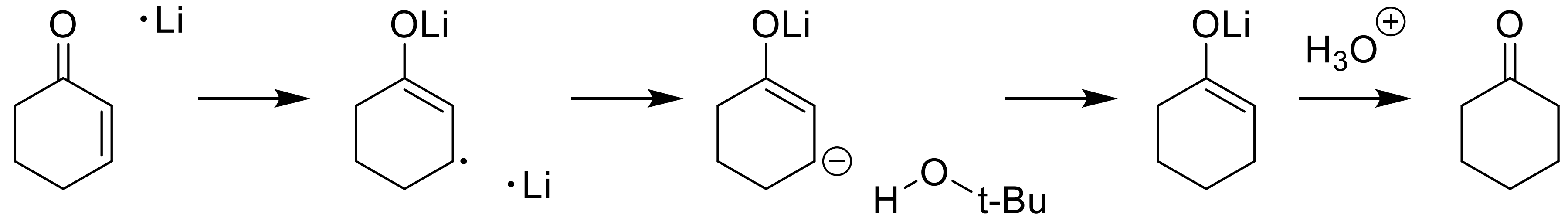
For electron donating groups (**EDG**s) → the product has the maximum number of substituents on the double-bond



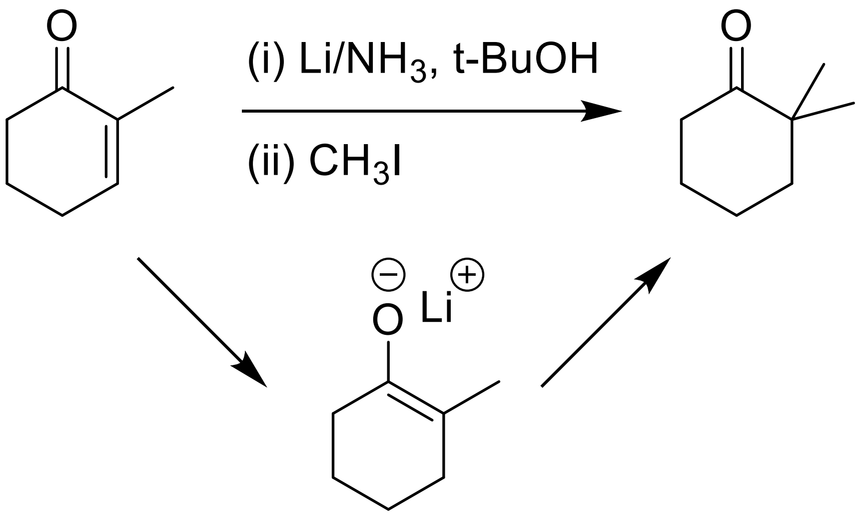
(e.g. -OMe, -OH)



Reduction of α-, β-unsaturated Ketones

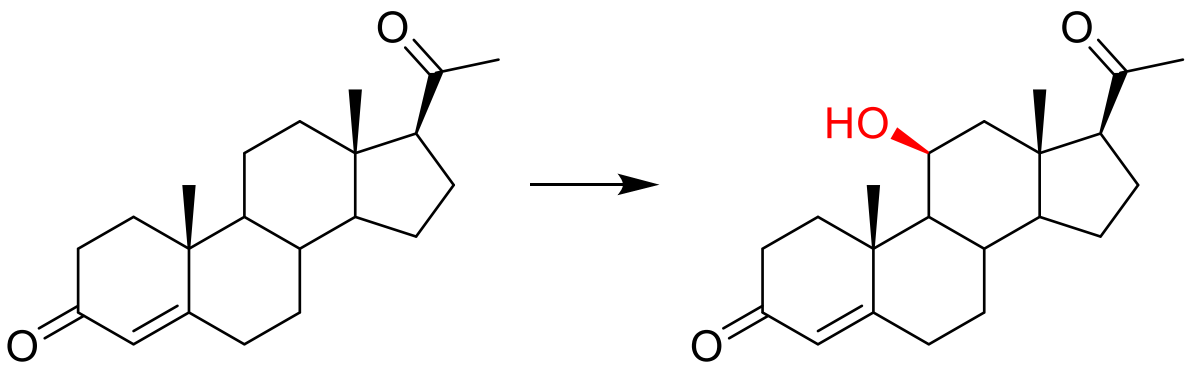


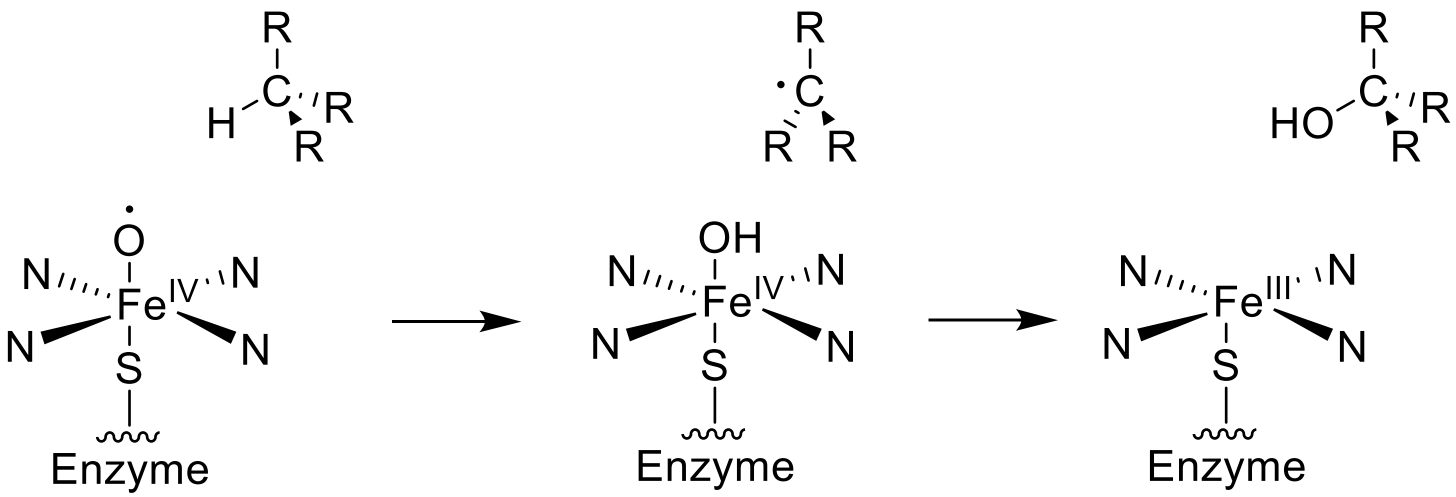
Reaction on trapped enolate



Hydroxylation of Alkanes

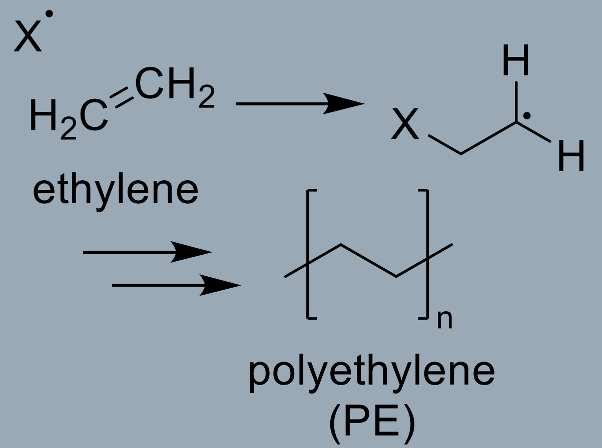
Occurs in Phase I metabolism as well as e.g. biosynthesis of cortisol





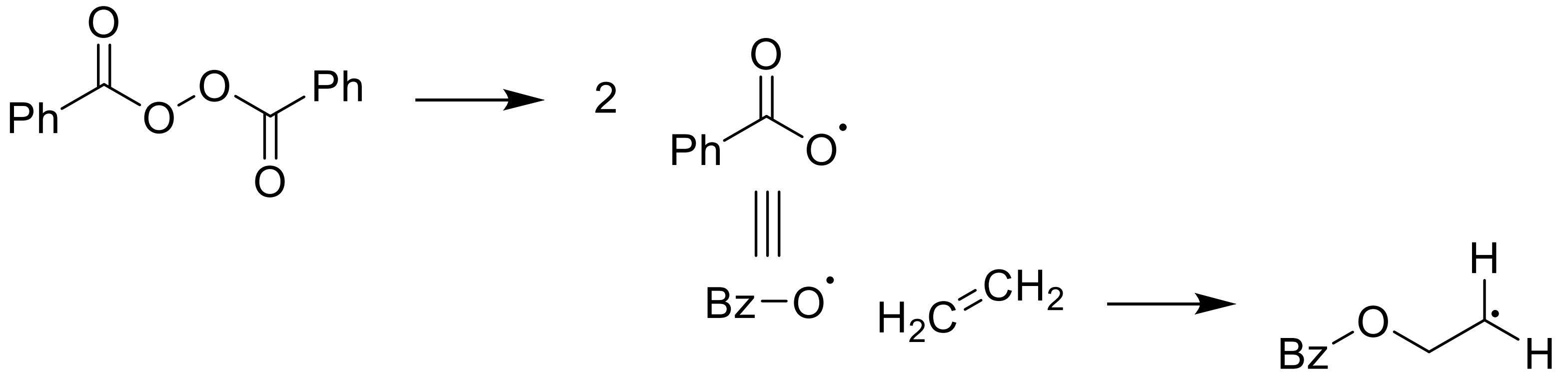
Radical Polymerisation

Polyethylene (PE)

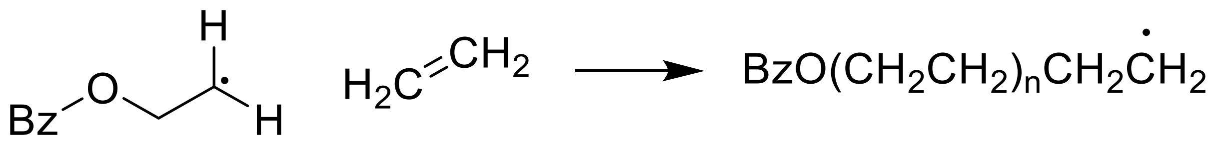


annual production of >100 M t; accounts for 1/3 of the total plastic market

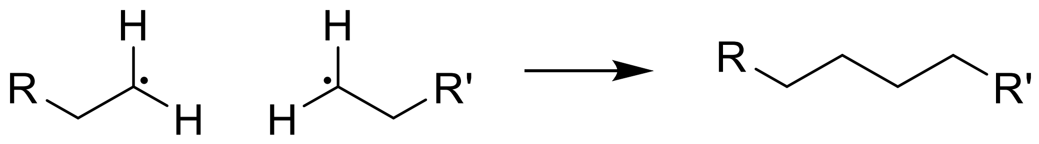
(1) Initiation



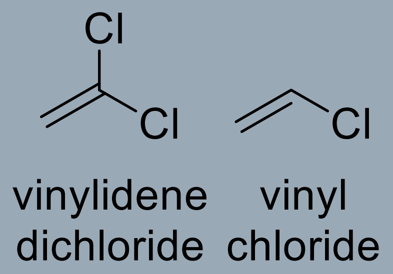
(2) Propagation



(3) Termination

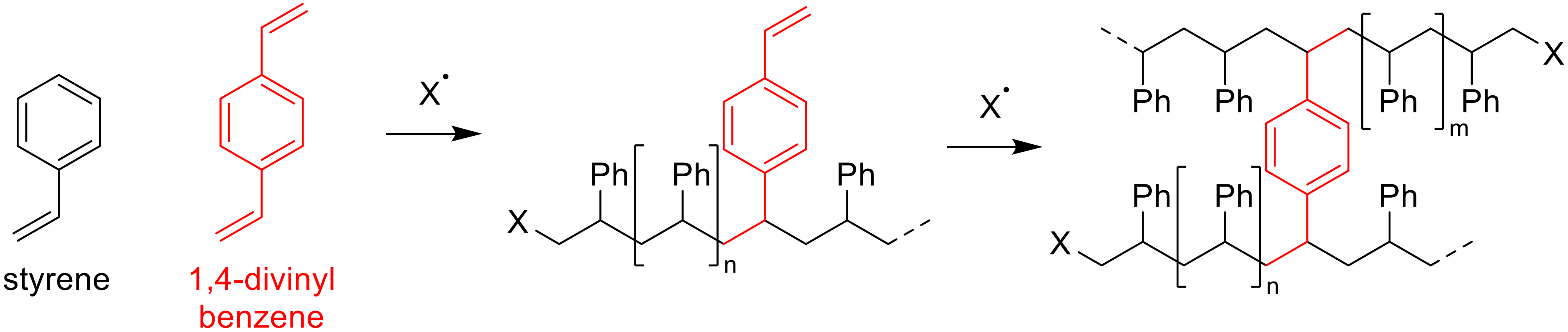


Polyvinylchloride (PVC) from



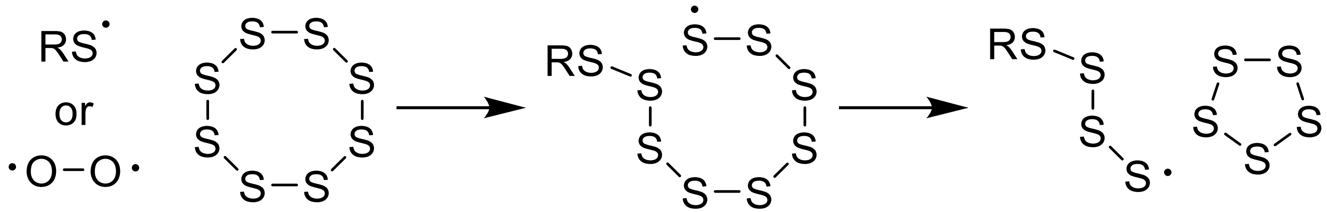
Cross-linked Polymers

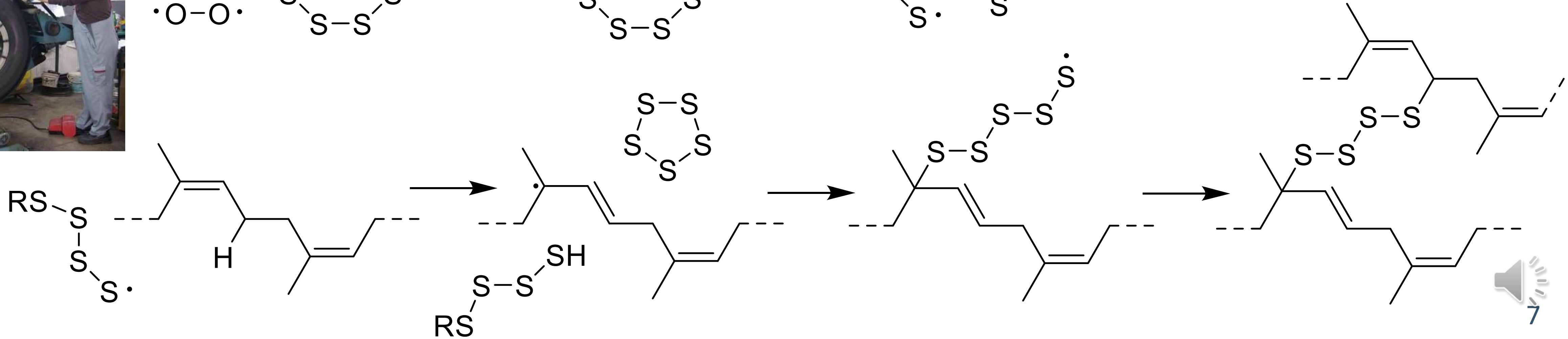
(1) Ab initio: polymers are stiffened and strengthened by (small amounts of) **cross-linkers**



(2) Cross-linking of pre-formed polymers (e.g. vulcanisation of rubber)

NOTE: vulcanised rubber contains many *E*-alkenes, unvulcanised rubber is all *Z*-alkenes → abstraction of allylic H by S-radical !

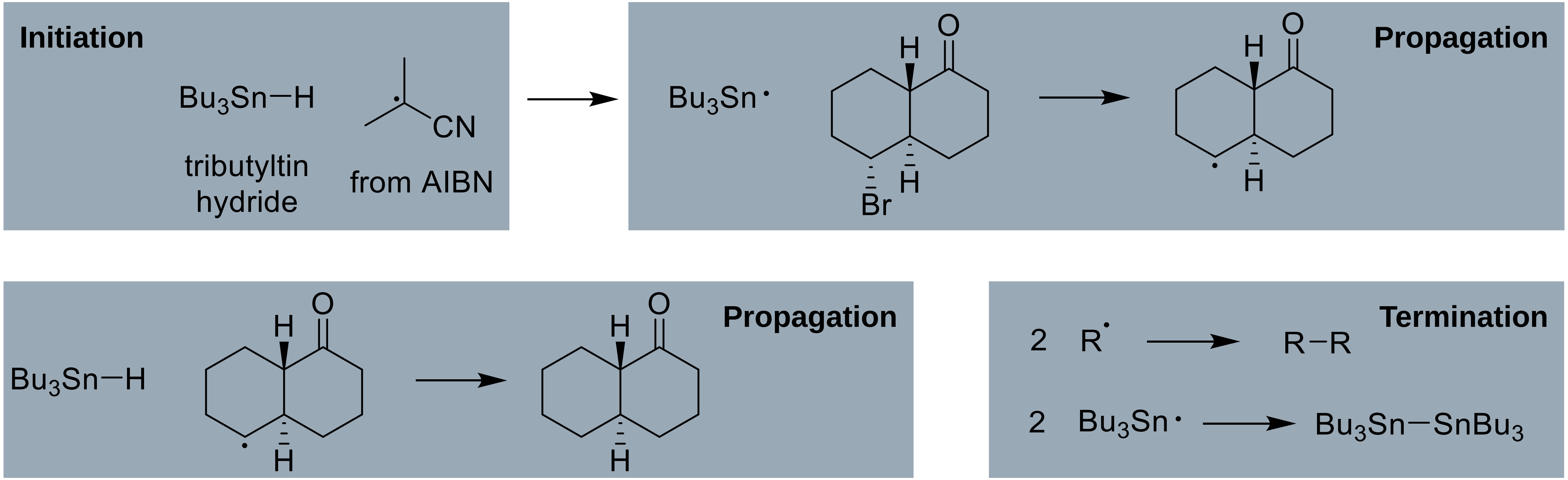




Some well-known Polymers

Monomer	Formula	Polymer	Applications
Ethylene	$H_2C{=}CH_2$	Polyethylene	Packaging, bottles
Propene (propylene)	$H_2C{=}CHCH_3$	Polypropylene	Mouldings, carpets
Chloroethylene (vinyl chloride)	$H_2C{=}CHCl$	Poly(vinyl chloride) (PVC), Tedlar	Insulations, pipes, records
Styrene	$H_2C{=}CHPh$	Polystyrene	Foam, mouldings
Tetrafluoroethylene	$F_2C{=}CF_2$	Teflon	Gaskets, non-sticky coatings
Acrylonitrile	$H_2C{=}CHCN$	Orlon, Acrilan	Fibres
Methyl methacrylate	$H_2C{=}C(CH_3)CO_2CH_3$	Plexiglas, Lucite	Paint, sheets, mouldings
Vinyl acetate	$H_2C{=}CHOC(O)CH_3$	Poly(vinyl acetate)	

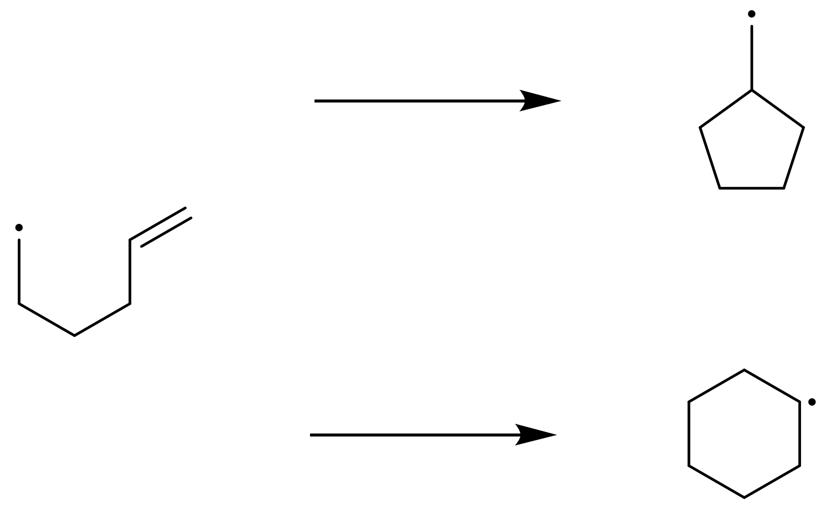
Radical Dehalogenation with Tributyltin hydride (Bu_3SNH)



ΔG C–H ($kJ\ mol^{-1}$)	ΔG Sn–H ($kJ\ mol^{-1}$)	ΔG C–Hal ($kJ\ mol^{-1}$)	ΔG Sn–Hal ($kJ\ mol^{-1}$)	
~400	**~300**	**~280**	**~500**	**applies to Br, I**

Radical Cyclisation

NOTE: *exo*-product (5-ring with 1° radical) formed two orders of magnitude faster than *endo*-product (6-ring with 2° radical)



Bond strengths and kinetics generally more important than radical stability!

What's next?

Synthesis