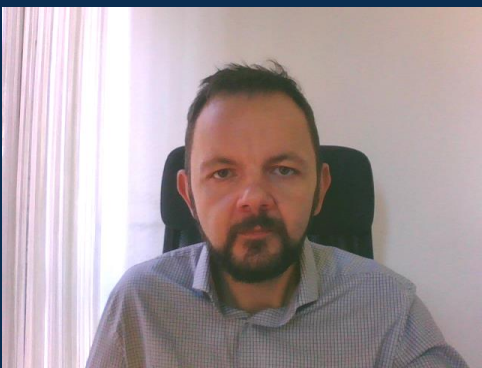
OC2

Radicals & Polymerisation
–
Radical Stability, Selectivity and Radical Chain Reactions

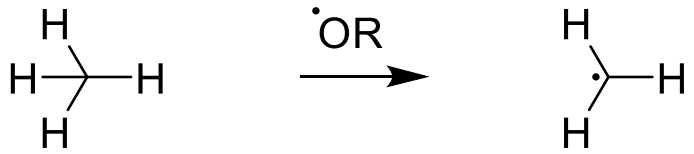
Dr. Michael J. Bojdys

michael.bojdys@kcl.ac.uk
http://bojdyslab.org
@mjbojdys



Radical Stability

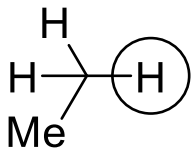
Simple rule: any substituent stabilises a radical!



ΔG C–H (kJ mol^{-1})	**ΔG O–H (kJ mol^{-1})**
439	**498**

C-centred radicals are trigonal (sp^2)

Primary, secondary and tertiary radicals



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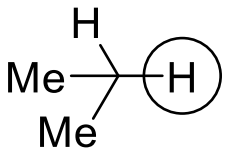

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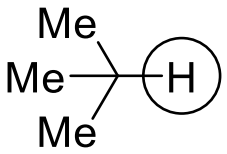
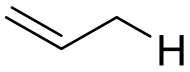


397

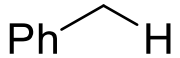
Radicals stabilised by conjugation

allyl



364

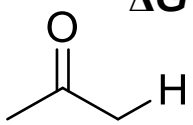
benzyl



372

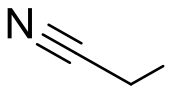
Radical Stability

Radicals stabilised by electron-withdrawing groups



ΔG C–H (kJ mol^{-1})

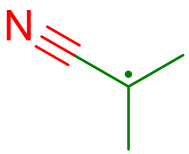
385



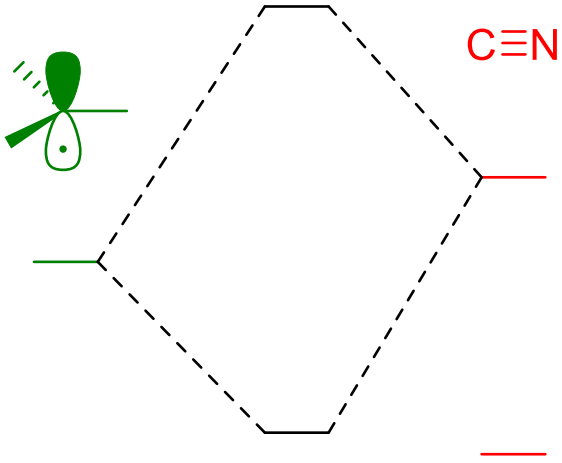
ΔG C–H (kJ mol^{-1})

360

C-centred radicals are trigonal (sp^2)



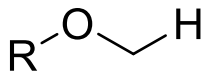
odd electron in SOMO (Singly Occupied Molecular Orbital)



Radical Stability

Radicals stabilised by electron-donating groups

ΔG C–H (kJ mol^{-1})



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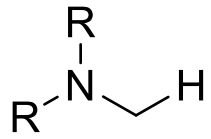
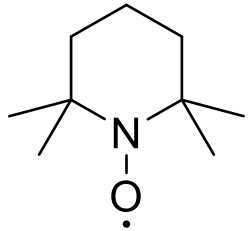
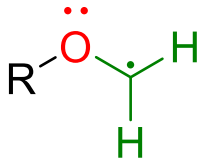
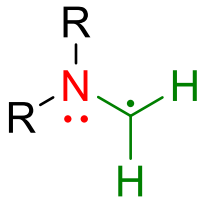


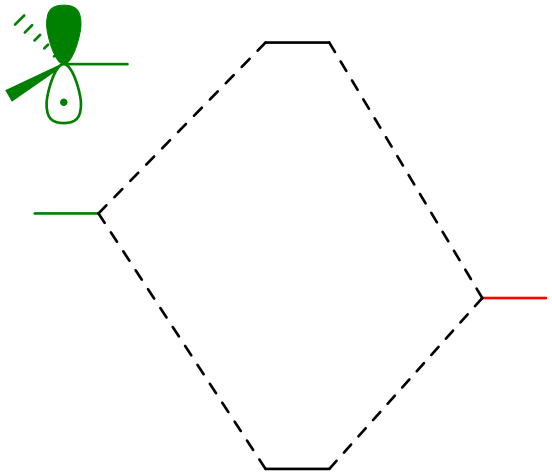
TEMPO
a stable radical







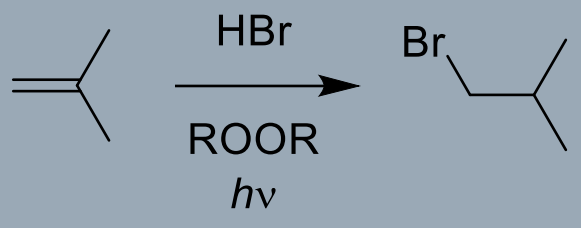
SOMO



lone pair

Radical Chain Reactions

Consider the radical reaction of isobutene with hydrogen bromide



(1) Initiation

(a) **Homolysis** of dialkyl peroxide to alkoxy radicals

(b) **Abstraction** of H from HBr (radical substitution) to give Br•

(2) Propagation

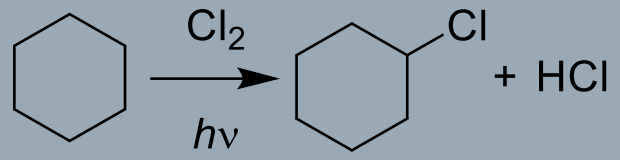
(a) Br• adds to isobutene to give carbon-centred (more stable) radical

(b) carbon-centred radical abstracts H from HBr to yield product and regenerate Br•

(3) Termination

Selectivity in Radical Chain Reactions

Radical halogenation of cyclohexane

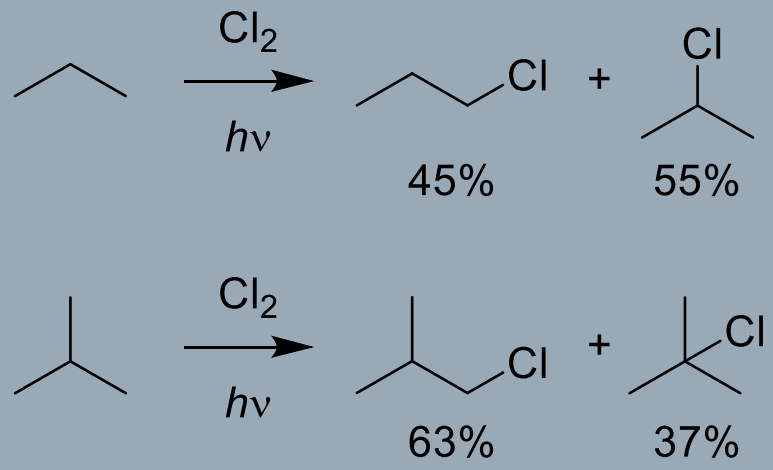


(1) Initiation

(2) Propagation

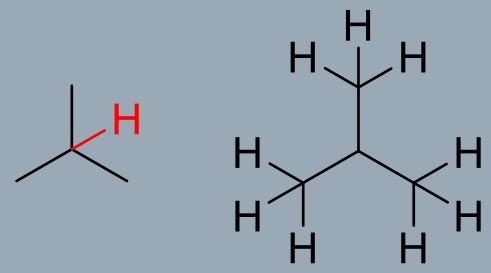
(3) Termination

Radical halogenation of other alkenes



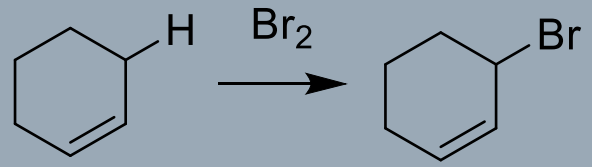
Stability

Probability

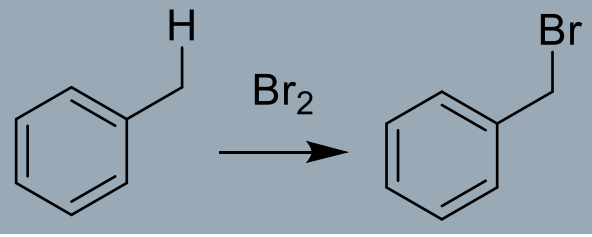


Radical Bromination

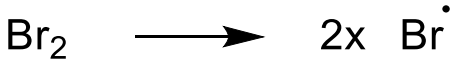
(i) Allylic Bromination



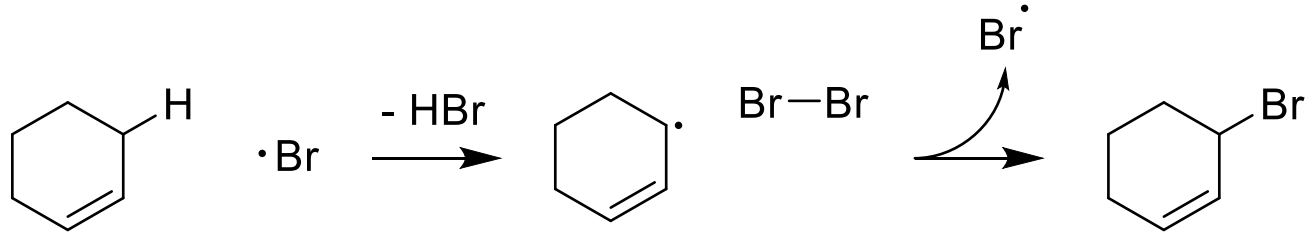
(ii) Benzylic Bromination



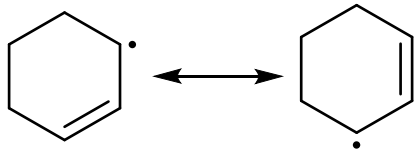
Initiation



Reaction at the α-carbon: (i) allylic bromination

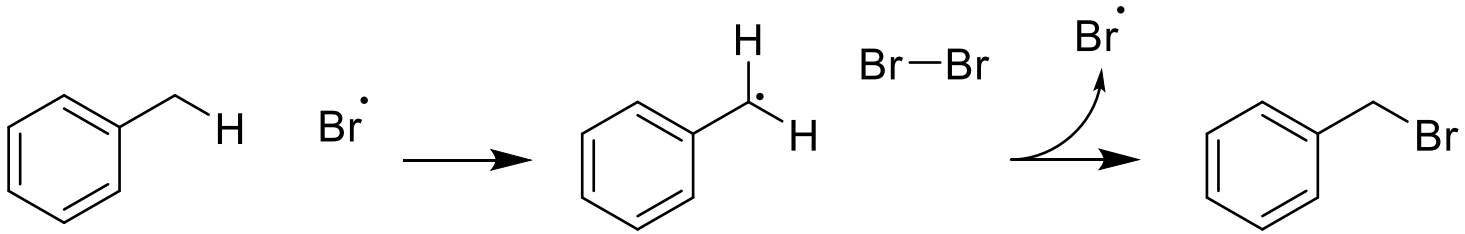


allylic bromide



allylic radical

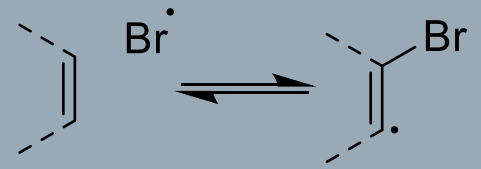
(ii) benzylic bromination

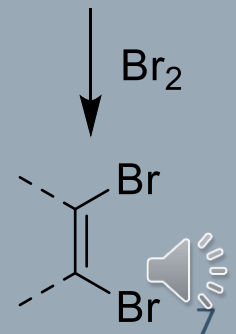


benzyl radical

benzyl bromide

Competing addition reaction

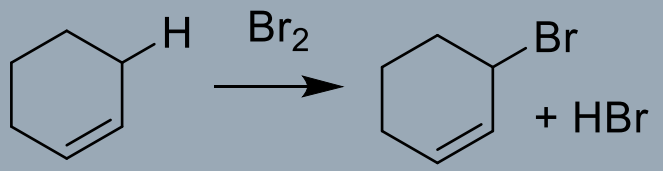




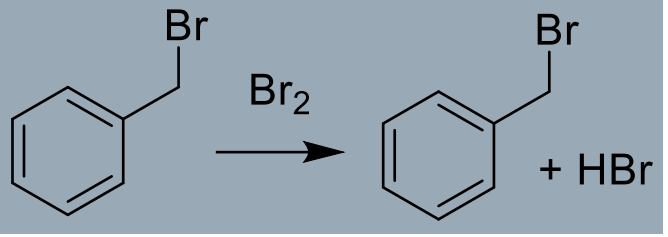
can be prevented if $[Br_2]$ conc. is kept low

Selective Radical Bromination by NBS (*N*-Bromo Succinimide)

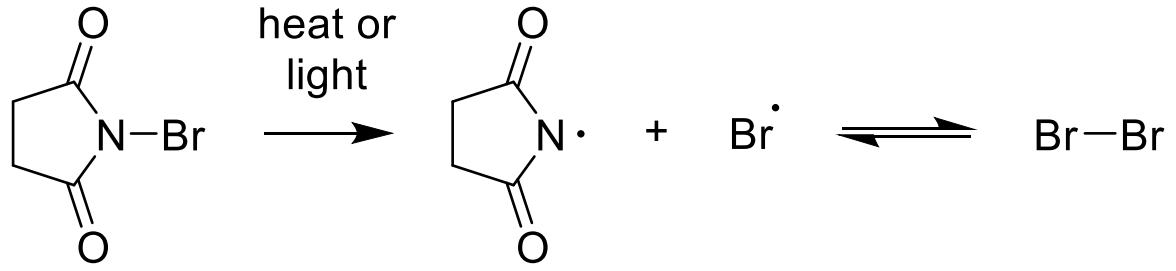
Allylic Bromination



Benzylic Bromination



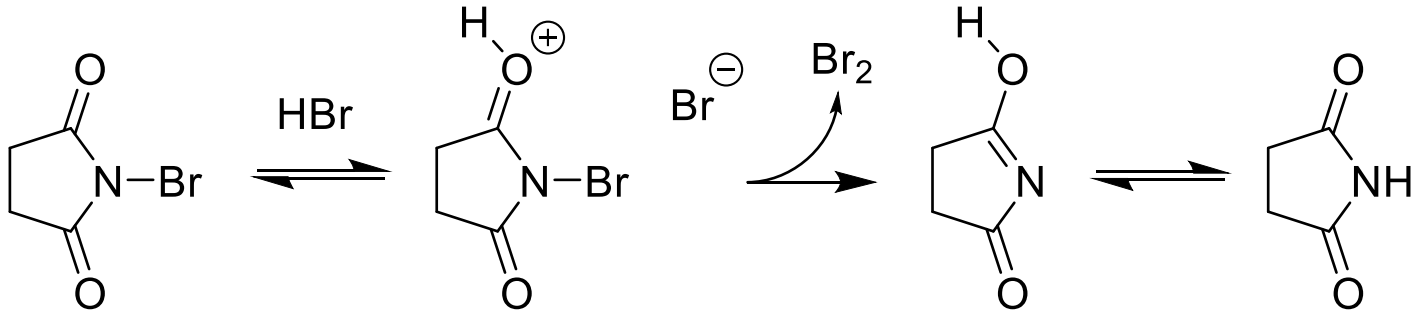
Initiation by NBS (*N*-Bromo Succinimide)



weak
N-Br bond

stable delocalised
radical

NOTE: Bromine radicals for propagation steps still come from bromine (Br_2)!

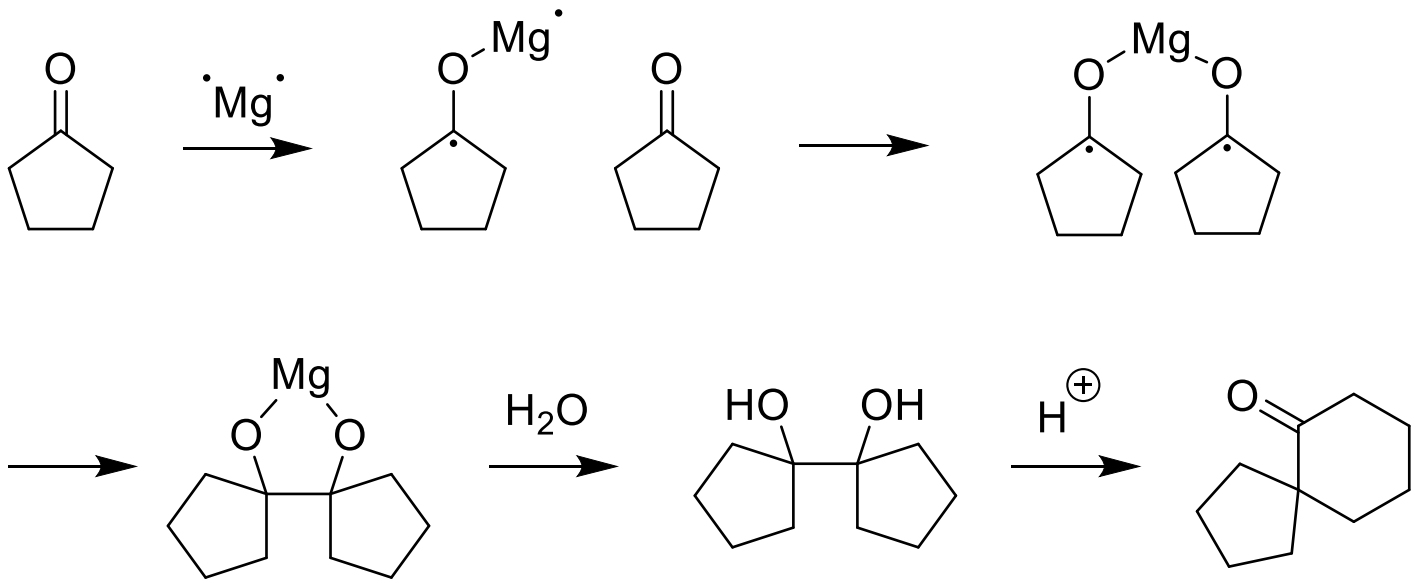


With NBS: Only enough bromine is formed to react with the (allylic or benzylic) radical

Other reactions with bromine are avoided

‘Pinacol’ Dimerisation of Ketones

Mg ideal as two-electron donating metal forming strong Mg–O bonds



Pinacol rearrangement converts 1,2-diol to a carbonyl compound

What’s next?

Radical Polymerisations and other Radical Reactions