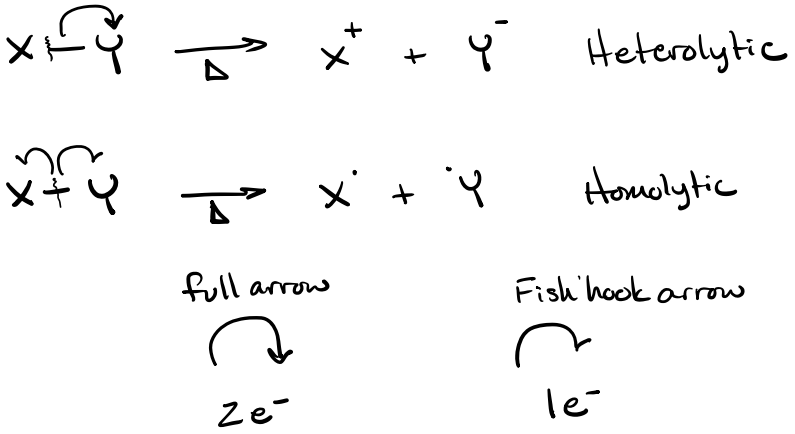
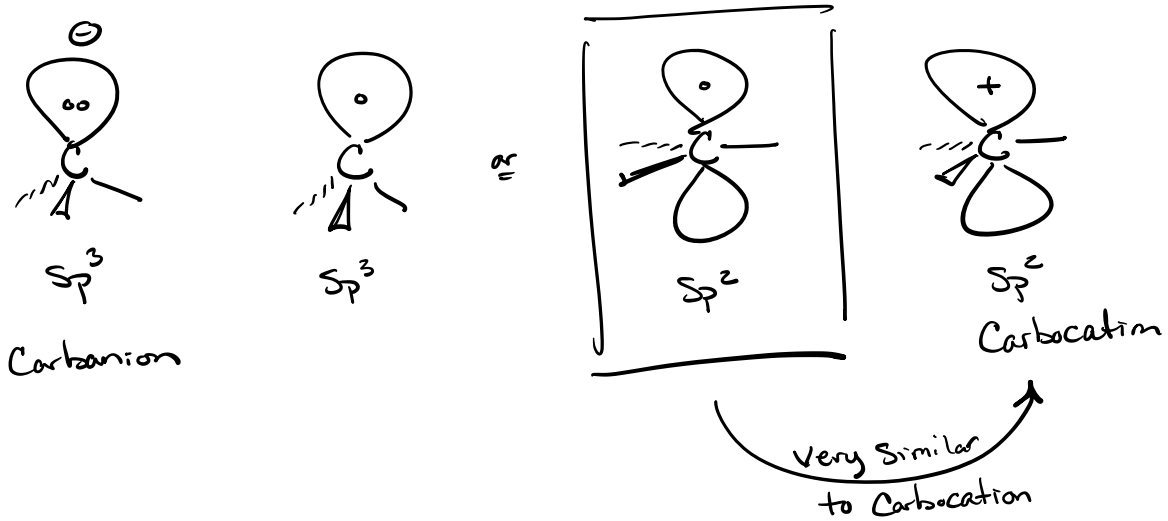
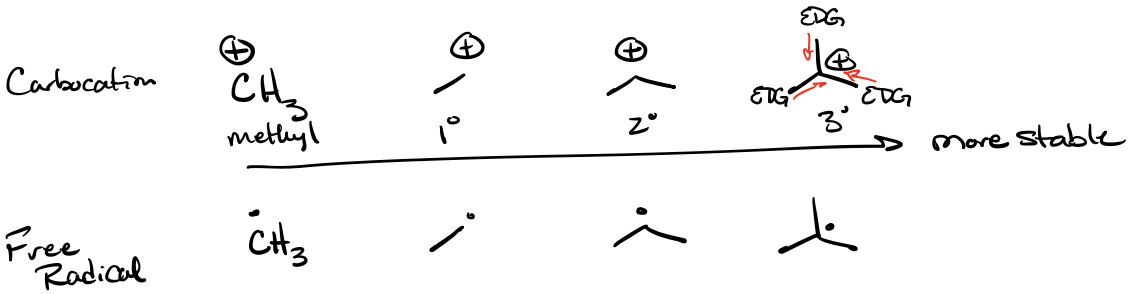
Free Radicals



Structure



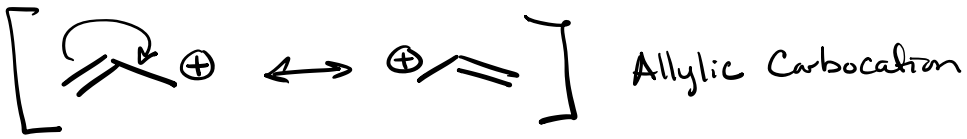
Free radical are Similar in structure to Carbocations & Stabilized by many of the Same factors.



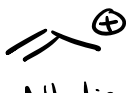
Free radical are e⁻ defficient Similar to Carbocations.

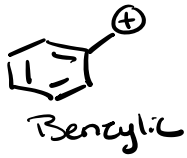
EDG Stabilize Free radicals

also Resonance ! Resonance > Induction

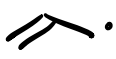


Very Stable C⊕





Very Stable C•



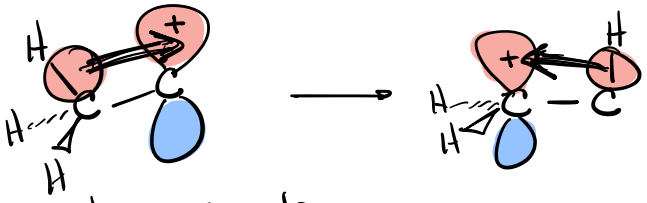
Allylic

Benzylic

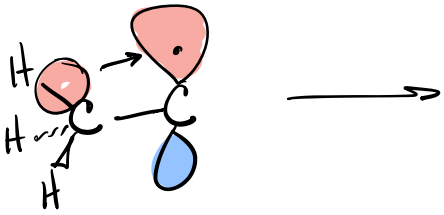
Common Patterns for Free Radical Rxns

→ No hydride or alkyl Shifts w/ Free Radicals

→ No rearrangements as we have w/ C+



Hyperconjugation

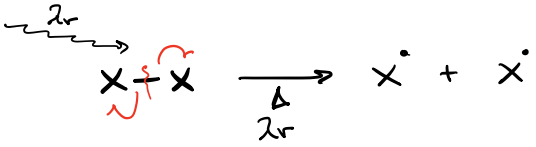


weak interaction

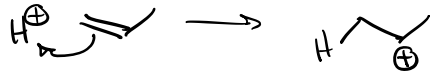
→ no shift observed

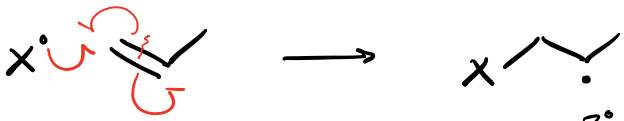
Free Radical not as e⁻ difficient as C+

① (Initiation) Homolytic Cleavage



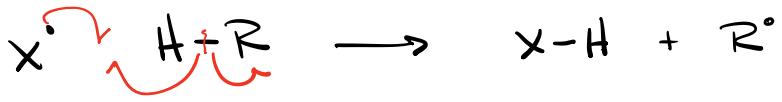
② Addition to π-bond



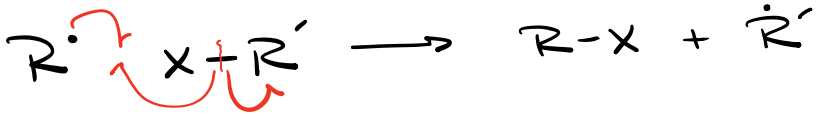


2° more Stable than 1°

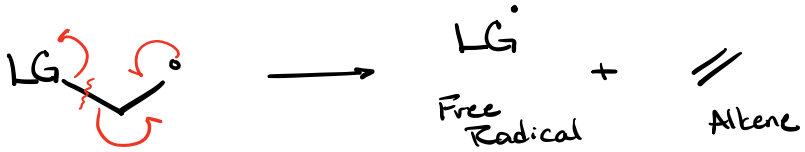
③ Hydrogen Abstraction (Radical as base)



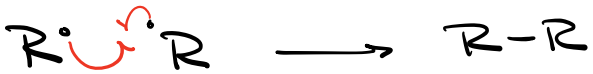
④ Halogen Abstraction



⑤ Elimination



⑥ Coupling (Termination)



Chlorination

methyl CH_3 — methylene $-CH_2-$ — formyl $-\overset{|}{C}H$

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

CH_3Cl: methyl chloride

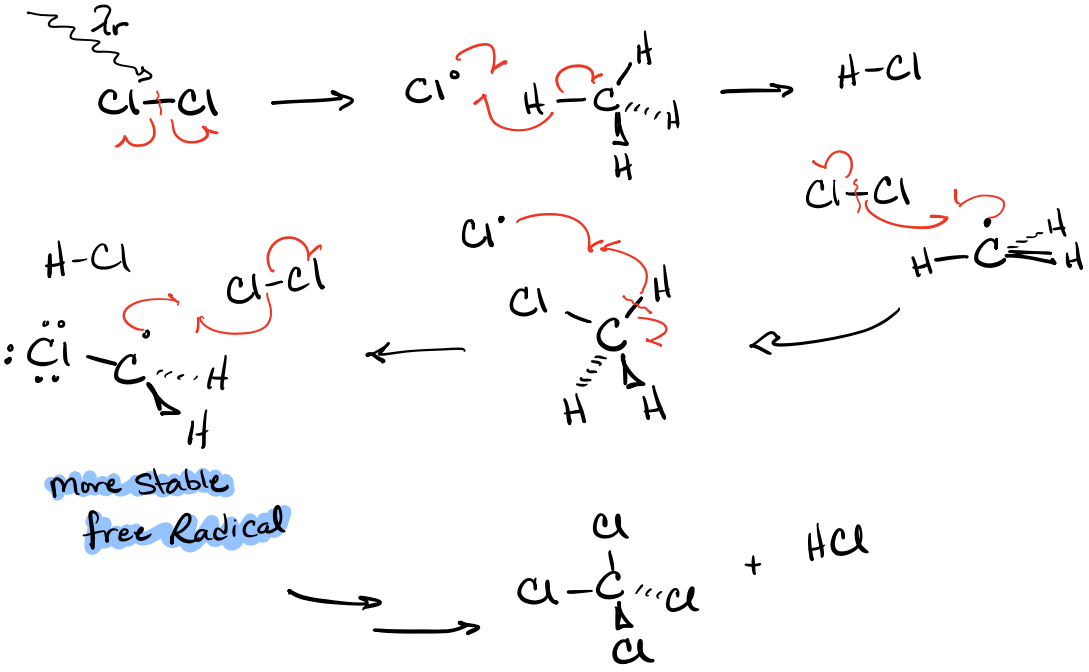
CH_2Cl_2: dichloro methane or methylene chloride

$CHCl_3$: trichloro methane or chloroform

CCl_4: Carbon tetrachloride

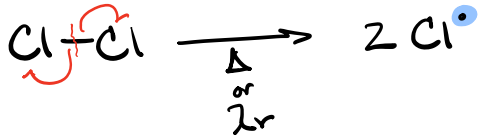
Difficult to Control

Mechanism

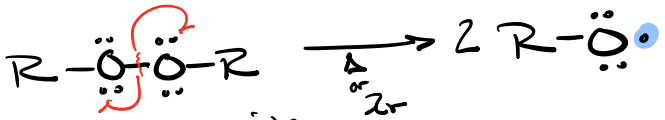


More Cl substituents act as free radical Stabilizer ⟹ lowers E_A for formation

Radical Initiators – molecules that easily form free radicals



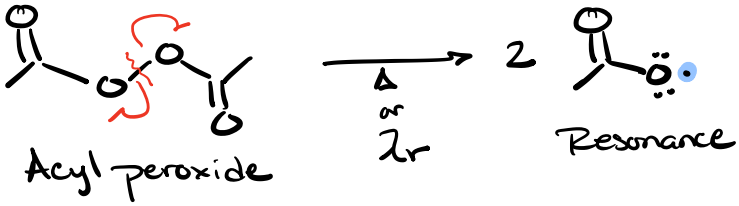
ΔH° = 243 kJ/mole



organic peroxides

ΔH° = 159 kJ/mole

$\xrightarrow[\text{peroxide}]{HBr}$

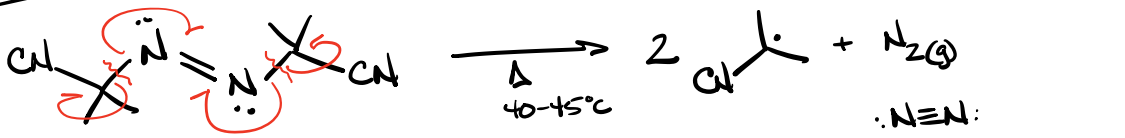


Acyl peroxide

Resonance

ΔH° = 121 kJ/mole

Very Common



Azo-bis-Isobutylnitrile

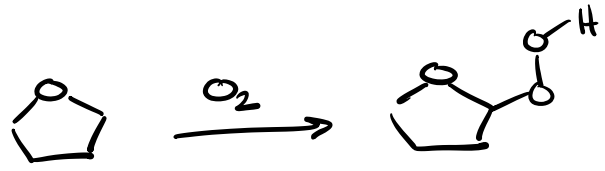
(AIBN)

:N≡N:

ΔH = < 121 kJ/mol

AIBN = Free Radical Rxn

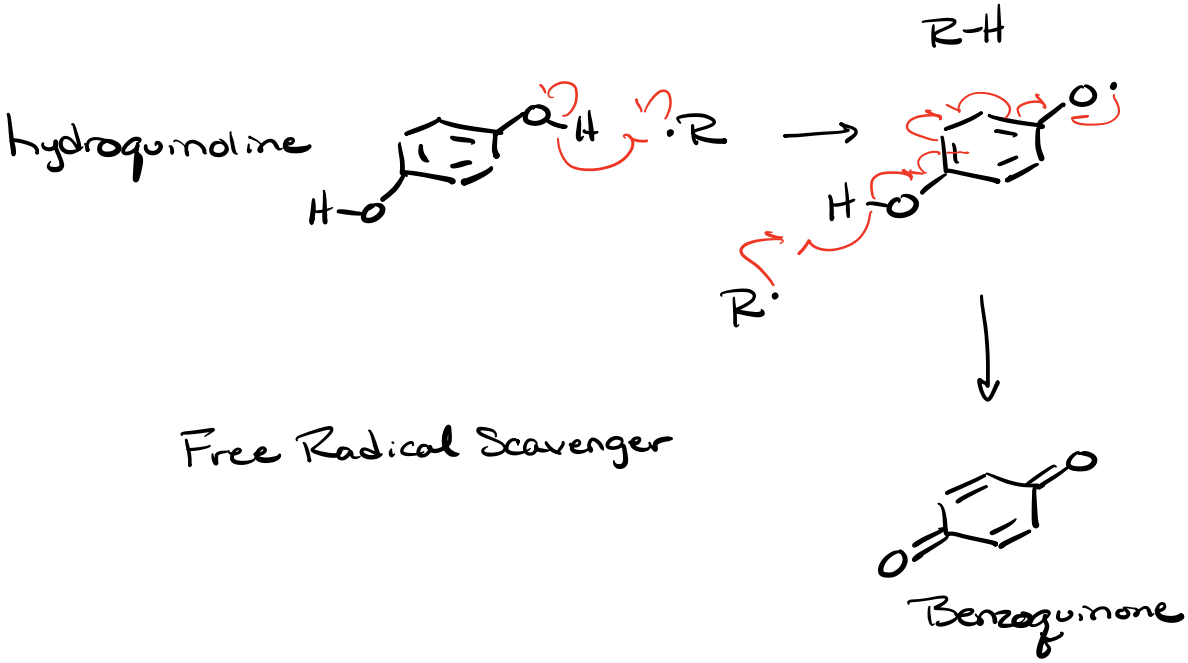
Free Radical Inhibitors



THF
Solvent

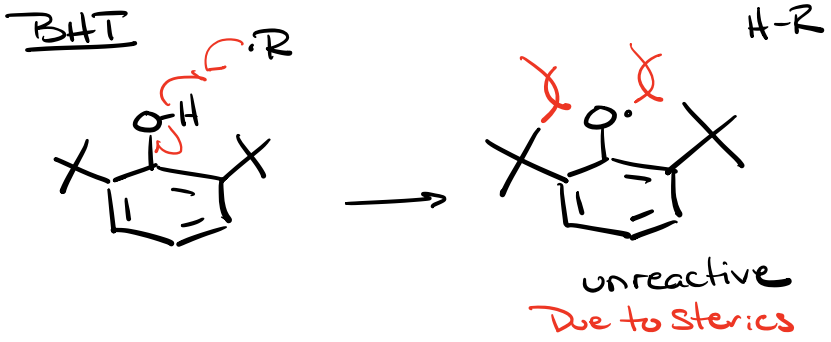
organic peroxide
Contact explosive

THF
w/ hydroquinoline as free radical inhibitor
"Stabilizer"

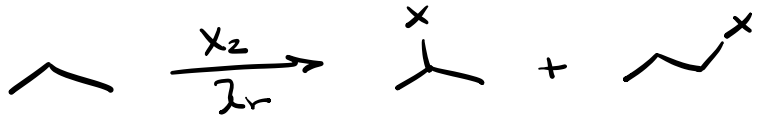


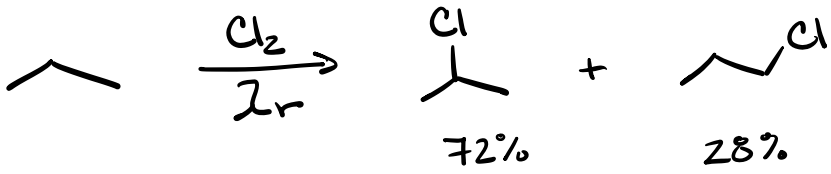
Free Radical Scavenger

Benzoquinone

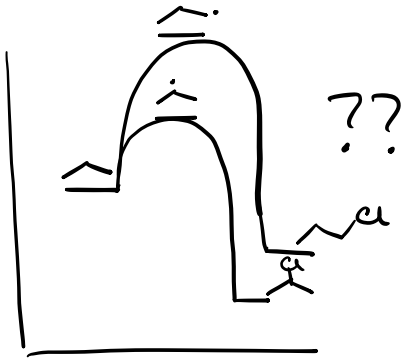


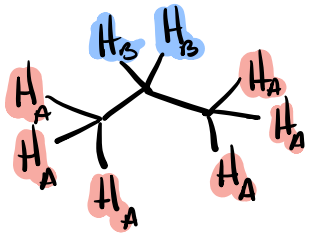
Regioselectivity





Might assume





Rate Calculation for 1° vs 2°

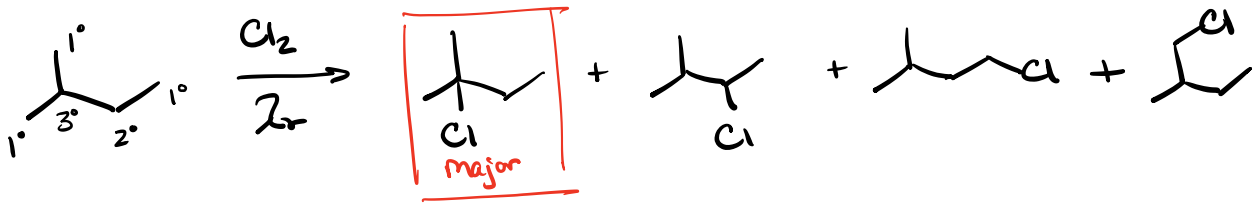
$$\frac{72\%}{28\%} = \frac{\text{Rate } 2^\circ \times 2H}{\text{Rate}_{1^\circ} \times 6H}$$

$$\frac{6 \times 72\%}{2 \times 28\%} = \frac{\text{Rate}_{2^\circ}}{\text{Rate}_{1^\circ}} = \frac{3.9}{1}$$

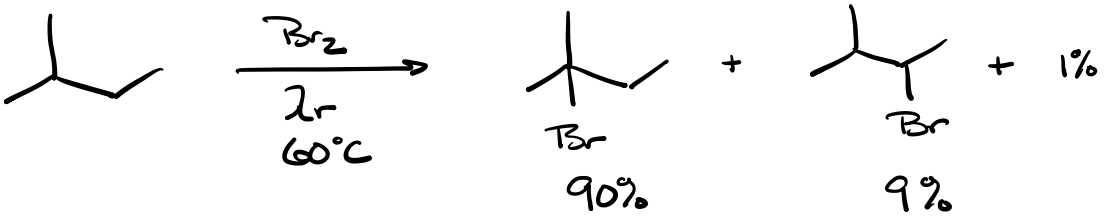
2° Proton 3.9× faster replaced than 1°

For Chlorination we find Relative Rates of

$$1 : 3.9 : 5.2$$
$$1^\circ < 2^\circ < 3^\circ$$



Bromination



Relative Rates of Bromination

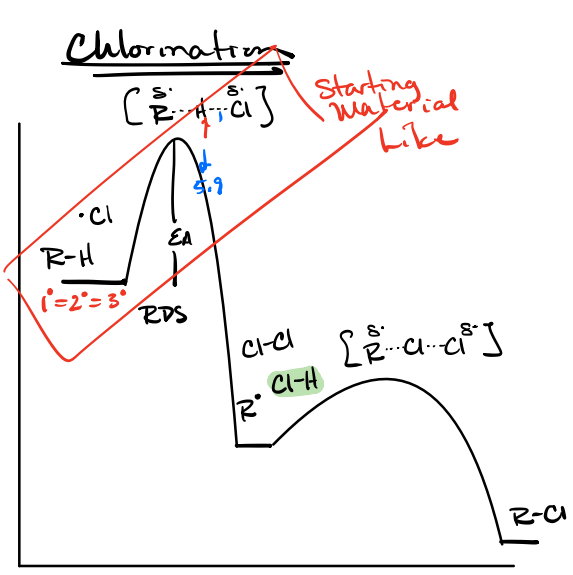
1 : 82 : 1640 ! Bromination

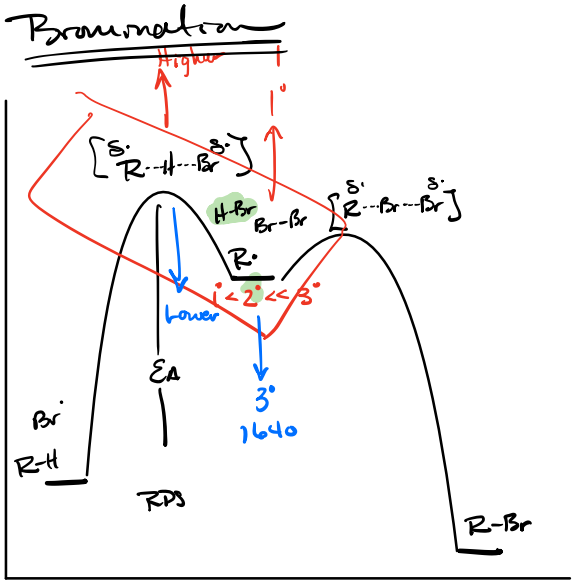
1° < 2° << 3°

1 : 3.9 : 5.2 Chlorination ???

way more selective

why?





Hammond !

HCl or HBr Stronger?