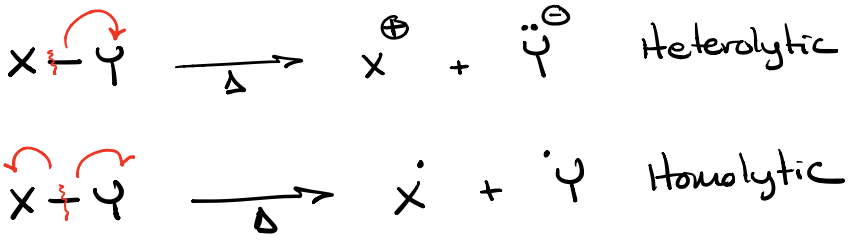
Free Radicals

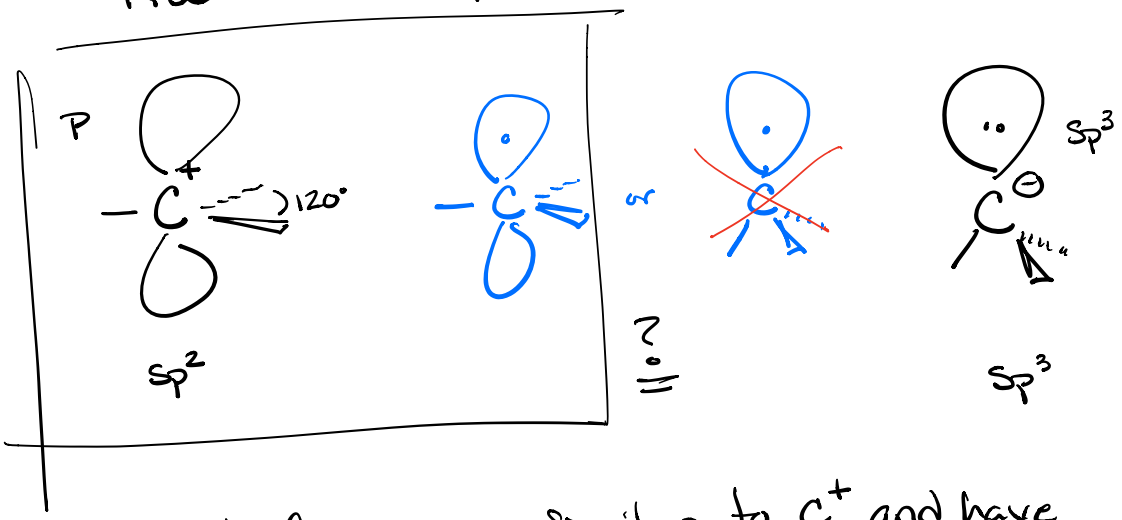


movement of $2e^-$

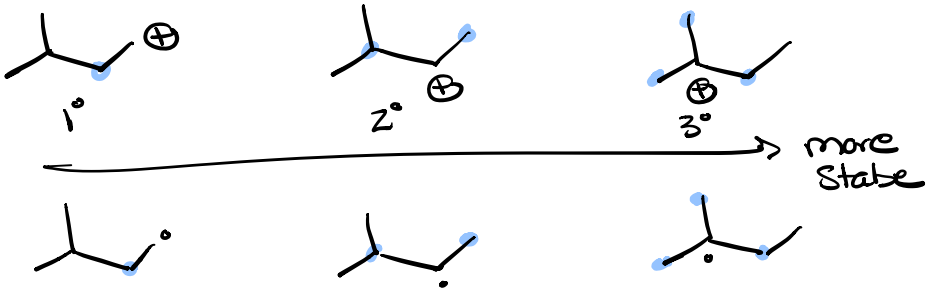
fish hook arrow movement of $1e^-$

Structure of Free Radical

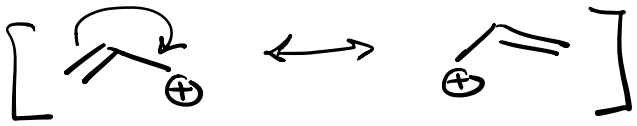
Free Radicals as sp^2



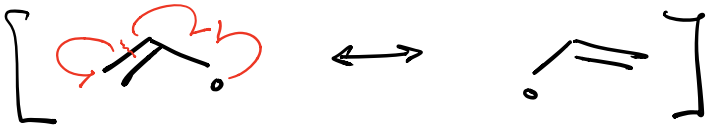
Free Radicals are very similar to C^+ and have all the same stability factors.



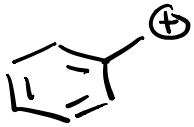
Resonance



Required a Single arrow

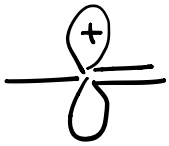


These require many more arrows 1 for each e⁻ moved



Benzylic Carbocation
Very Stable

Benzylic Radical

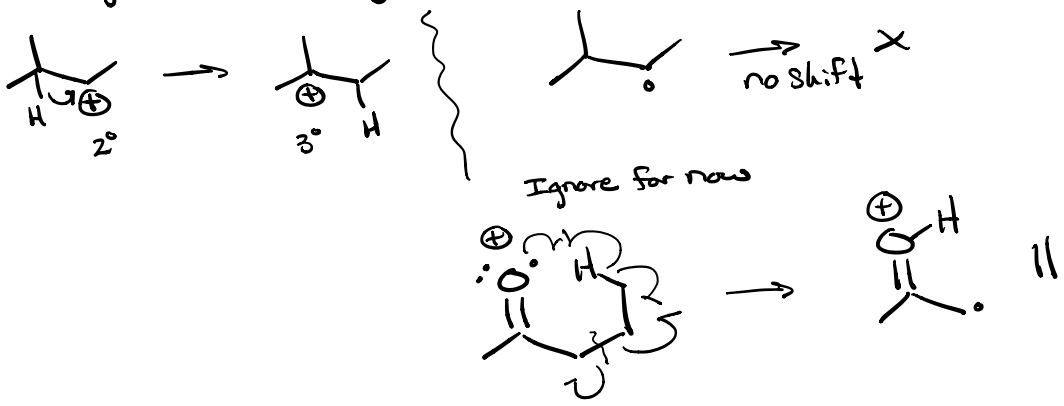


Sp Carbocation
no Resonance

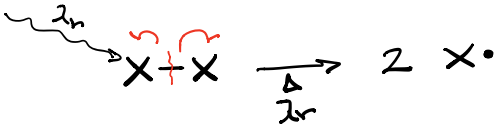
Sp free radical
no Resonance

Common Patterns or Steps in Radical Mechanisms

① No hydride or alkyl Shifts



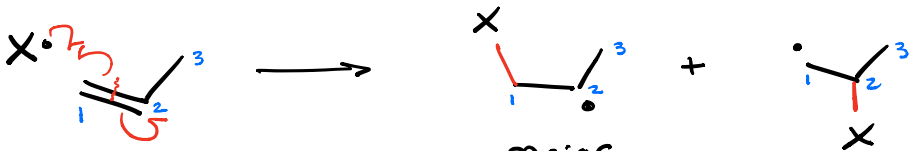
② Homolytic Cleavage (Initiation Step)



Δ Delta = heat

hν = light

③ Addition to π bonds

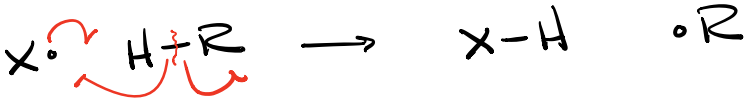


major

⇒ more stable

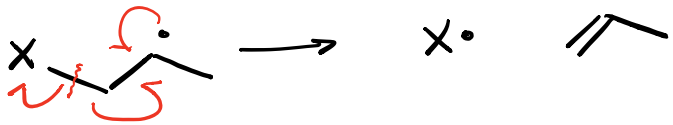
2° free radical

④ Hydrogen abstraction (Acid/Base)

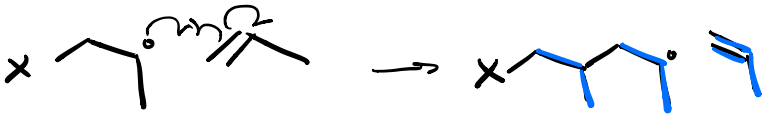


⑤ Halogen abstraction

⑥ Elimination



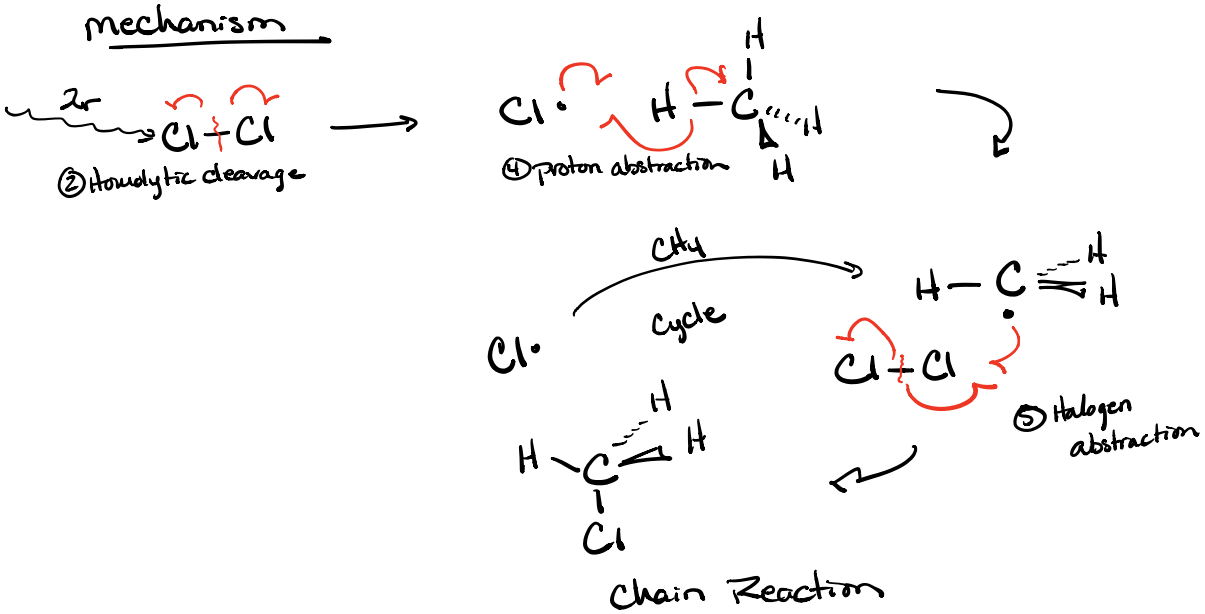
⑦ Coupling (Termination)



Chlorination

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl + HCl$$

mechanism

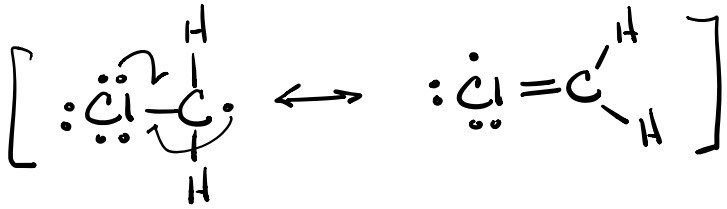


Doesn't Happen just once ...

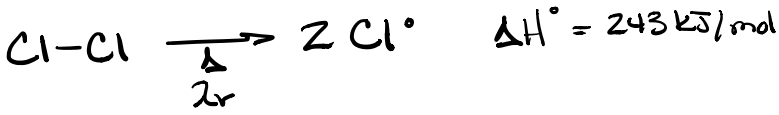
$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2 \xrightarrow[h\nu]{Cl_2} CHCl_3 \xrightarrow[h\nu]{Cl_2} CCl_4$$

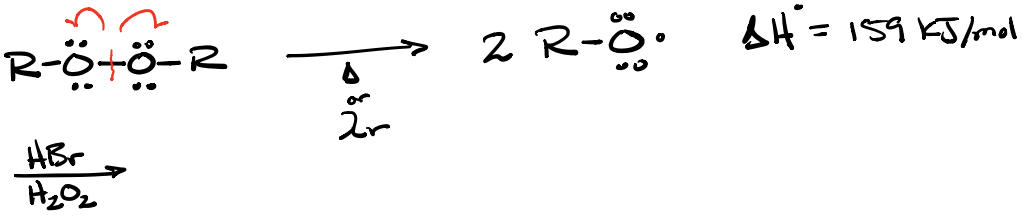
Chloro methane — Dichloro methane — Chloroform — Carbon tetrachloride

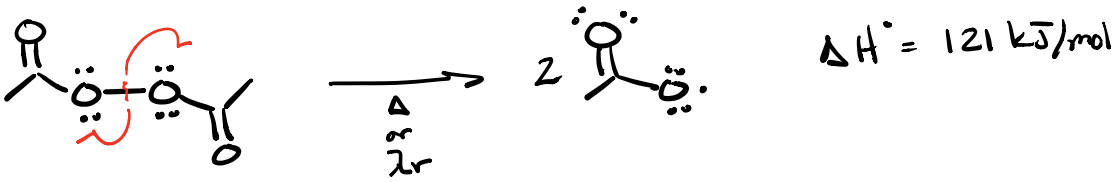
Higher Substitution = more reactive



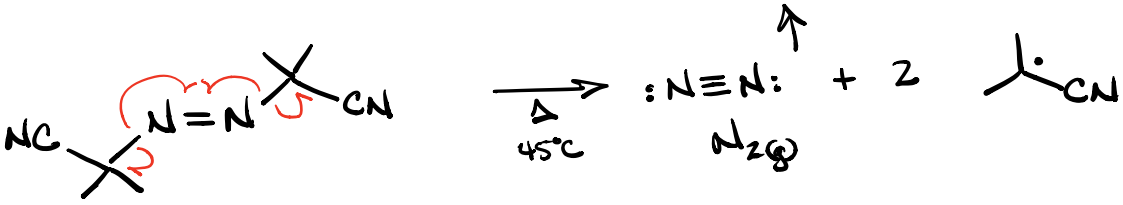
Radical Initiators







Acyl peroxide

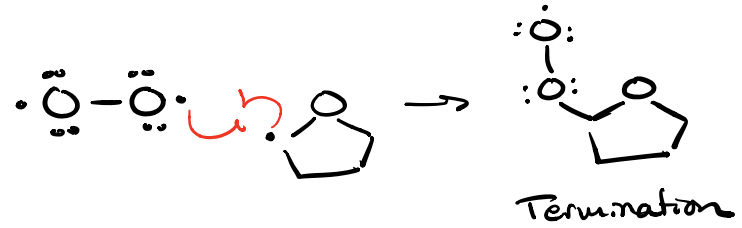


azo-bis-isobutylnitrile

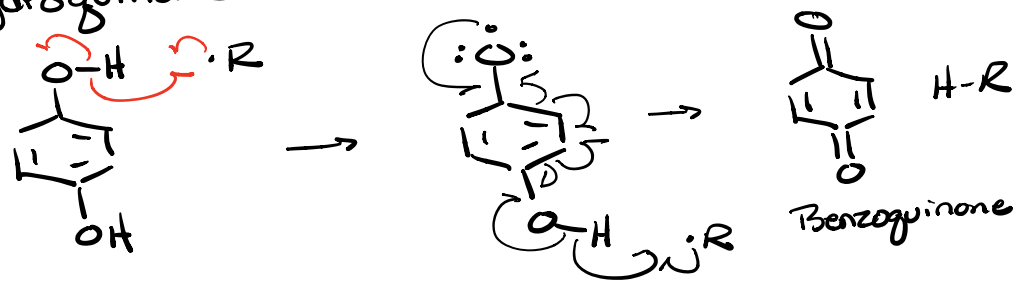
AIBN

Radical Inhibitors

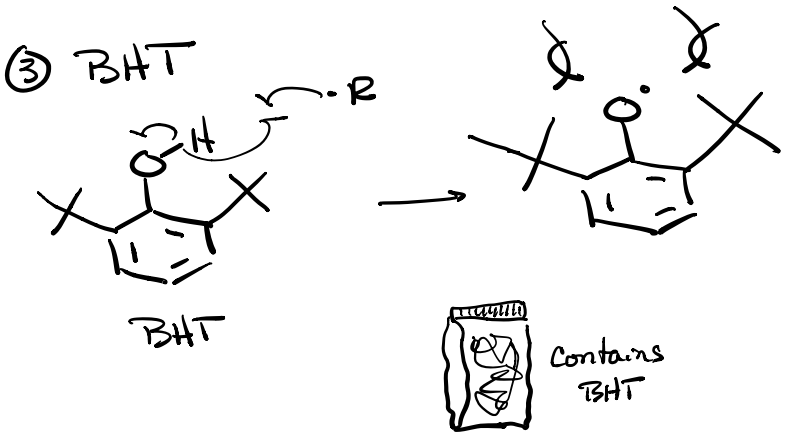
① Oxygen



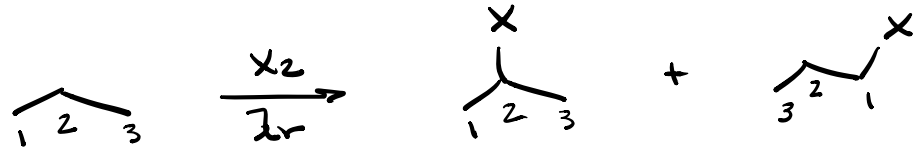
② Hydroquinone

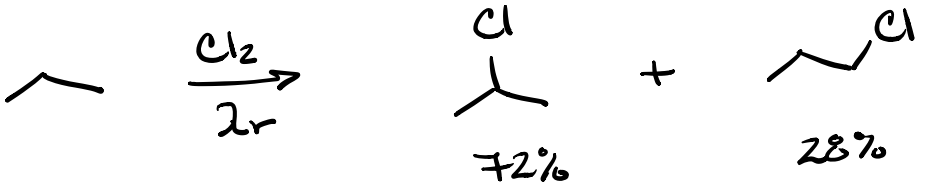


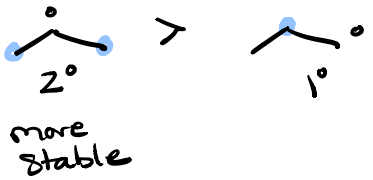
③ BHT



Regioselectivity







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

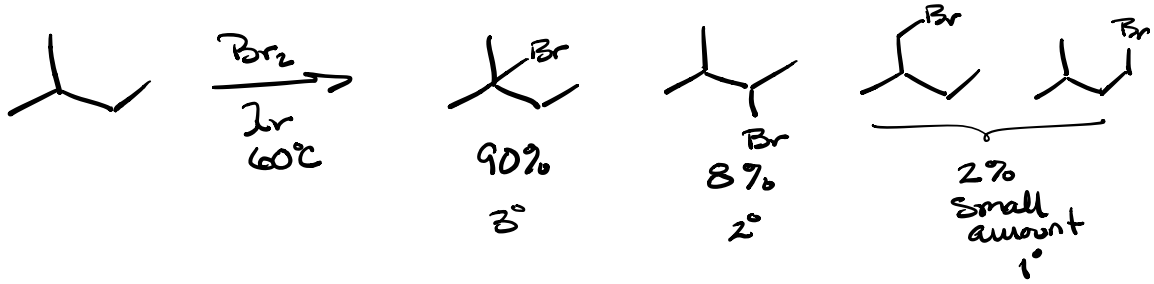
$$\frac{6 \times 72\%}{2 \times 28\%} = \frac{\text{Rate}_{2^\circ}}{\text{Rate}_{1^\circ}} = \frac{3.9}{1}$$

2° position Replaced 3.9 x faster than 1°

Relative Rates for Chlorination

1 : 3.9 : 5.2

1° 2° 3° faster →

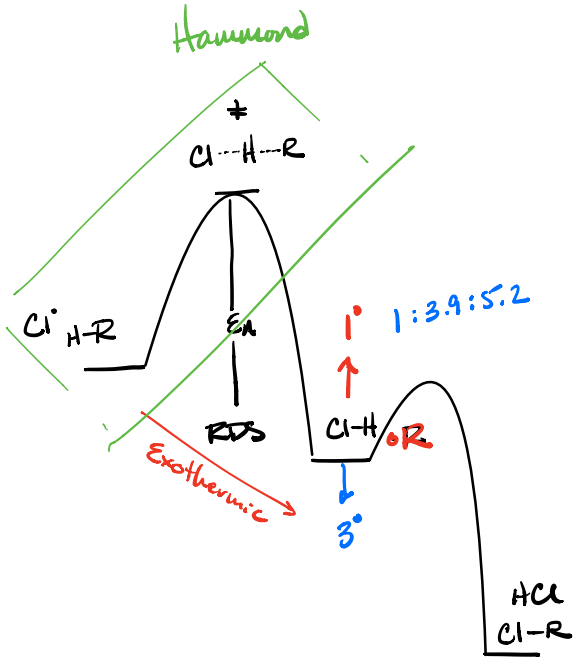


Relative Rates for Bromination

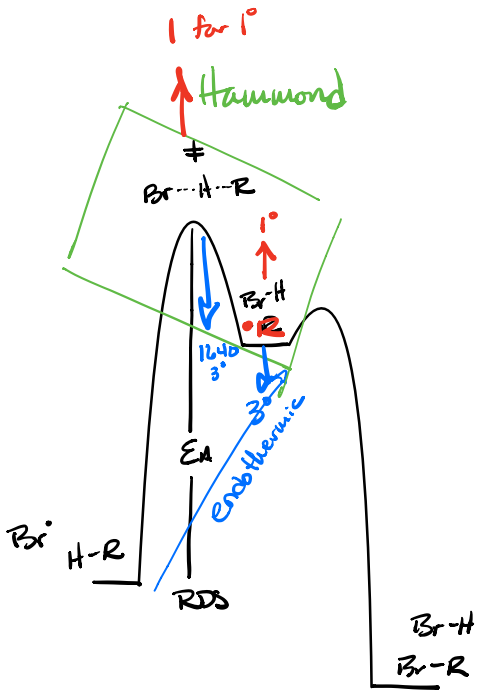
Br 1 : 82 : 1640

1° < 2° << 3° > ?

Cl 1 : 3.9 : 5.2



Stability of free Radical has little influence on ‡ & E_A

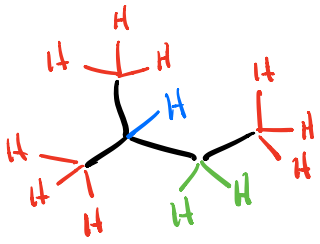


Stability of free Radical is directly linked to the stability of ‡ & E_A of Rxn

Bigger influence!

We will mostly focus on Brominations because of their Selectivity (Regioselectivity)

1° < 2° << 3°



9 1°
2 2°
1 3°

Quiz question