

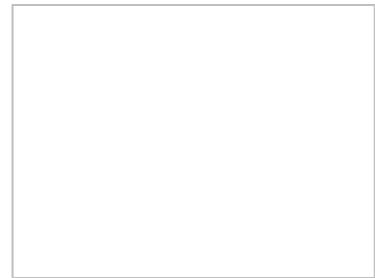


**Instituto de Química – USP**

**QFL 0450**

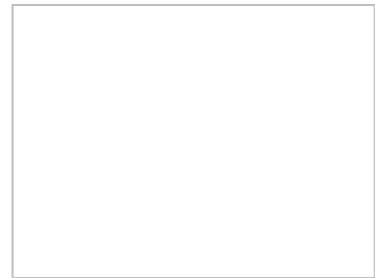
**Química Geral e Orgânica para Biomedicina**

**Reações Radicalares**





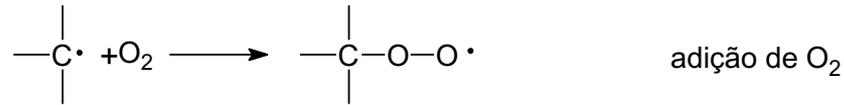
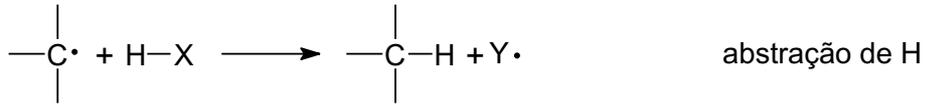
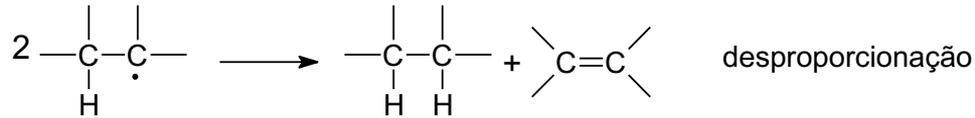
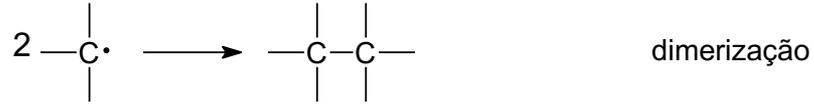
RL  $\Rightarrow$  elétrons não emparelhados  
(homólise)





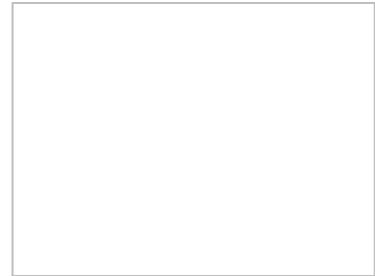
# Radicais Livres

$\tau$  reduzido devido a:



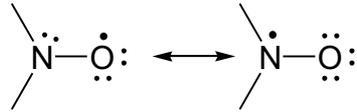
Entretanto:

- estáveis = resistem a reações bimoleculares
- inertes = não reativos até 300°C
- persistentes = reagem com oxigênio

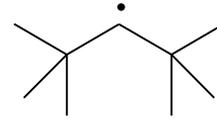




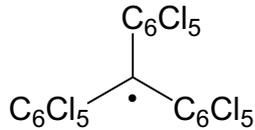
# Radicais Livres



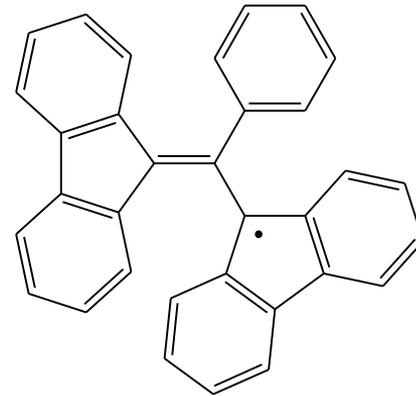
estáveis em diversas condições



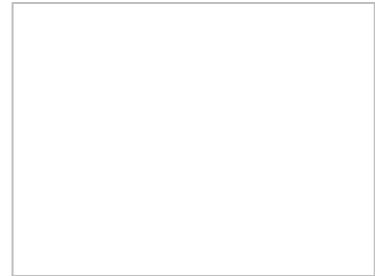
persistente



inerte



estável  
indefinidamente



## ressonância paramagnética eletrônica

*EPR - electron paramagnetic resonance*

*ESR - electron spin resonance*

R• tem momento magnético =  
paramagnético

logo, em um campo magnético  
terá duas orientações possíveis

$$h\nu = E = g\mu_B H$$

Presença de núcleos com  
momento magnético causa  
desdobramento no espectro de  
EPR

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{14}\text{N}$ ,  $^{19}\text{F}$ ,  $^{31}\text{P}$   
( $^{12}\text{C}$  e  $^{16}\text{O}$  NÃO)

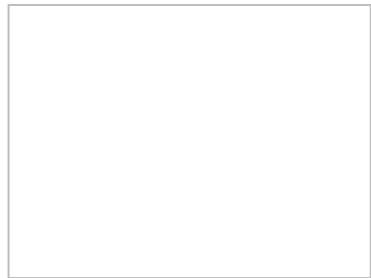
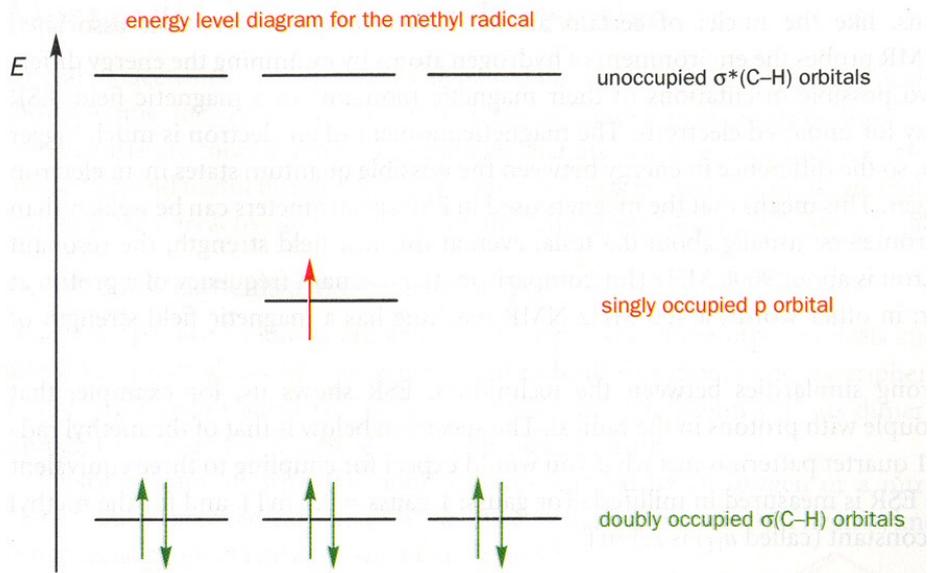
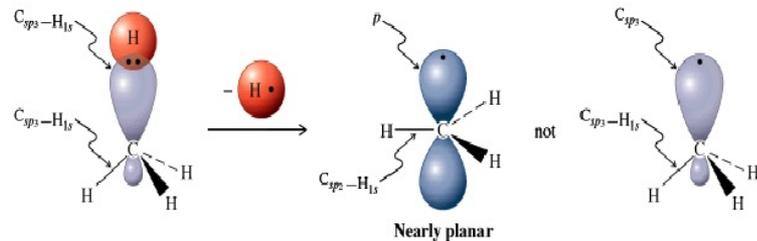
$$\text{N}^\circ \text{ de linhas} = 2 n I + 1$$

Escala de microondas !!



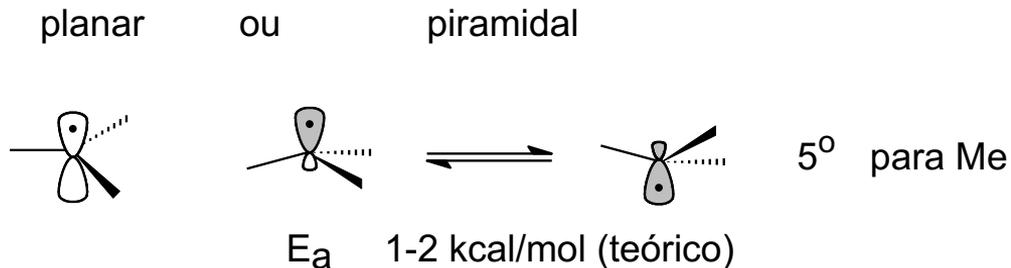
# Estrutura dos radicais

Radicais possuem uma estrutura trigonal planar ( $sp^2$ ):





# Estereoquímica de RL

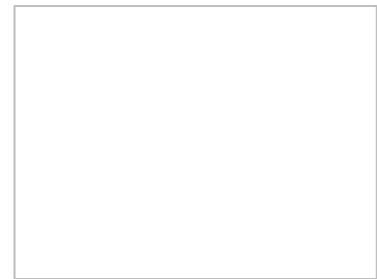


Estudos indicam que estrutura piramidal é preferida (caso t-butila)

Motivos:

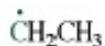
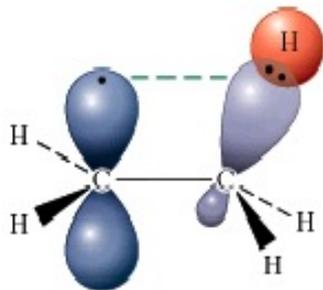
torsional (formas alternadas entre os substituintes)

hiperconjugação do orbital semipreenchido com hidrogênios substituintes



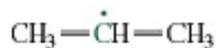
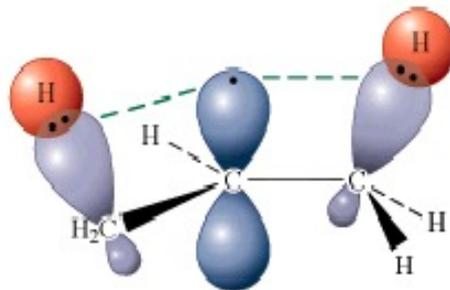
# Estabilidade Relativa dos Radicais

Um grupo alquila doa elétrons, estabilizando o radical. Assim, quanto mais grupos alquila estiverem ligados, mais estável será o radical. Doação de elétrons do grupo alquila para o radical ocorre por hiperconjugação. Hiperconjugação é a sobreposição com orbitais de ligações sigma.



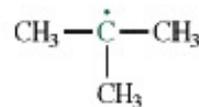
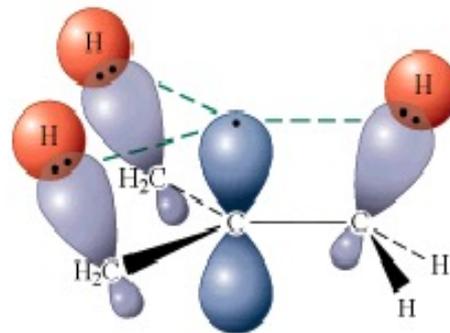
Ethyl radical

A

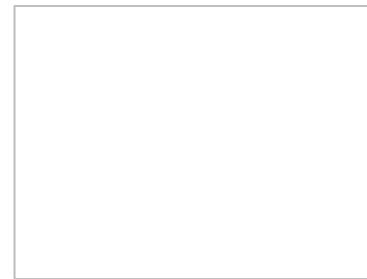


1-Methylethyl radical  
(Isopropyl)

B

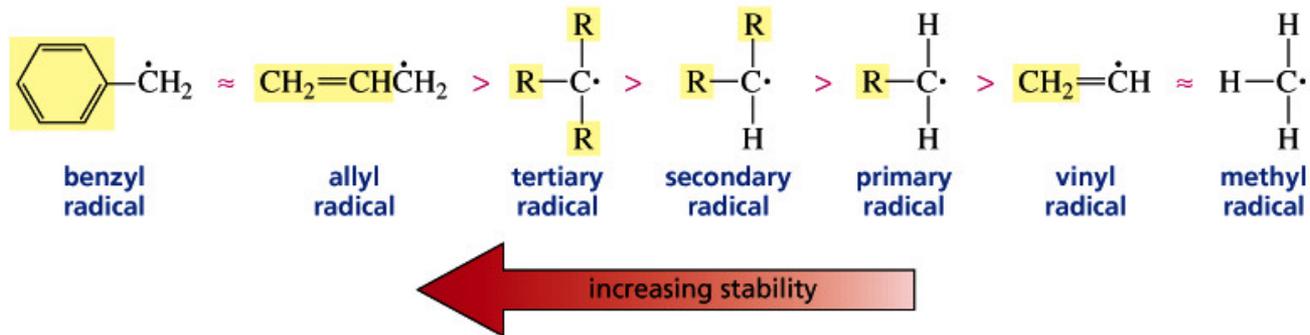


1,1-Dimethylethyl radical  
(*tert*-Butyl)

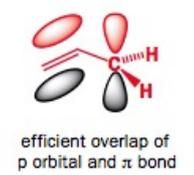
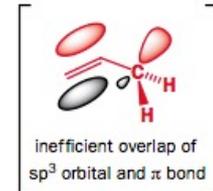
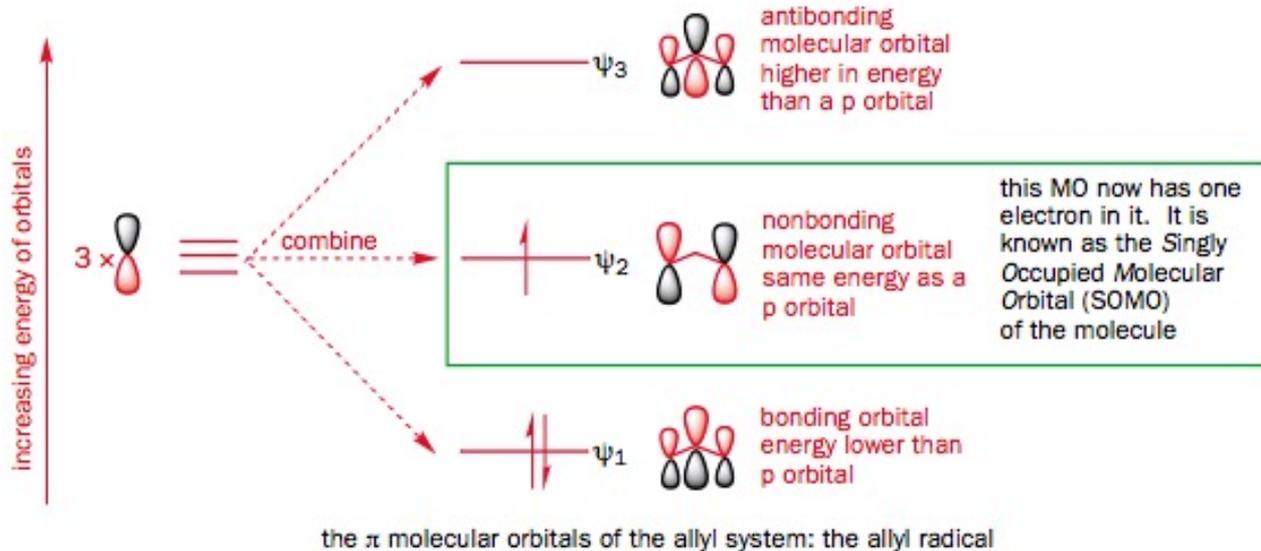
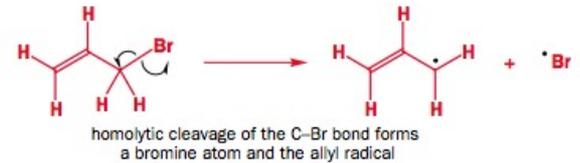


# Estabilidade Relativa dos Radicais

relative stabilities of radicals

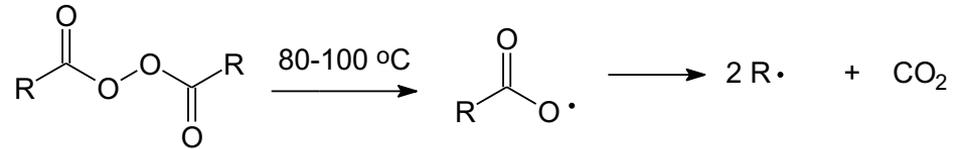


# Radical Alílico

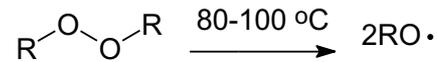


# Fontes de RL

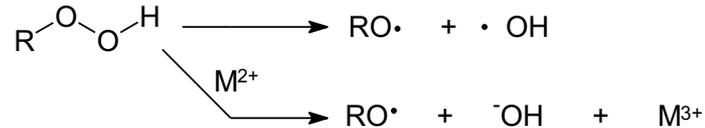
Peróxidos:



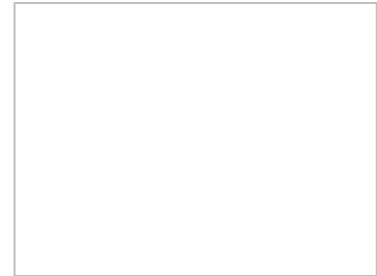
peranidrido



peróxido



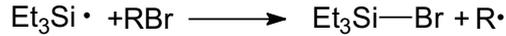
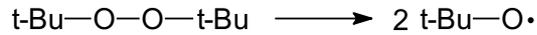
hidroperóxido





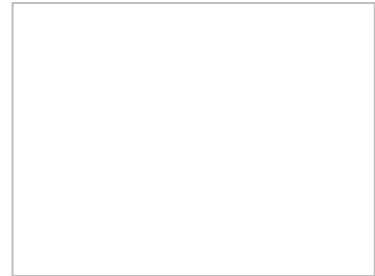
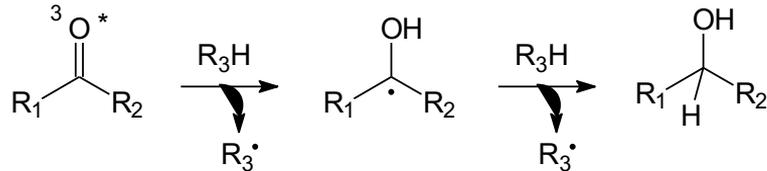
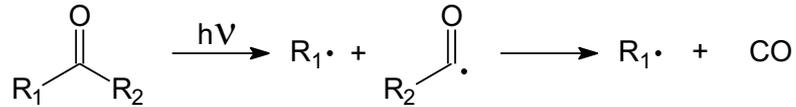
# Iniciadores radicalares

## Azo-compostos



## Brometos de alquila

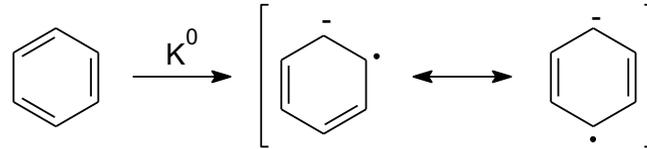
## Fotoquímica de cetonas



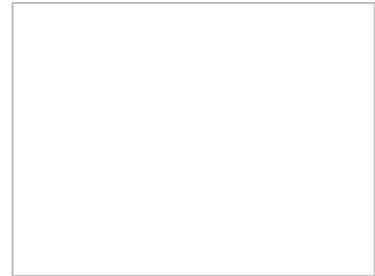
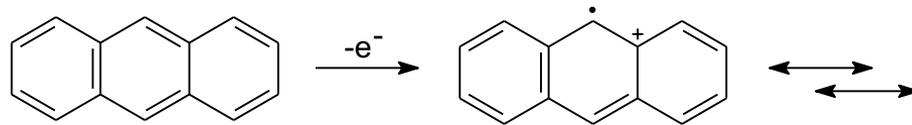


# Radicais carregados

- redução  $\Rightarrow$  ânion radical (correlacionam com o potencial de redução  $\rightarrow$  LUMO)



- oxidação  $\Rightarrow$  cátion radical (correlacionam com o potencial de oxidação  $\rightarrow$  HOMO)





# Estrutura vs. Reatividade

- técnicas rápidas permitem obter velocidades absolutas
- velocidade abstração de hidrogênio é determinada pela força da ligação “H—substituente”

$\text{CH}_3\text{—H}$	104 kcal/mol	Energia
$\text{CH}_3\text{CH}_2\text{—H}$	98 kcal/mol	de
$(\text{CH}_3)_2\text{CH—H}$	94,5 kcal/mol	Dissociação
$(\text{CH}_3)_3\text{C—H}$	91 kcal/mol	





$k_{\text{abs}} \Rightarrow \text{terciário} > \text{secundário} > \text{primário}$

*reatividade do radical*

primário > secundário > terciário > benzil ~ alil

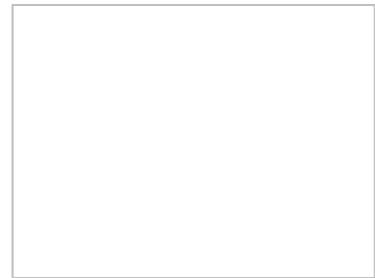
## Escala de estabilidade

(Leroy, Peters & Wilante, 1982)



### Energia termoquímica de estabilização

baseado no calor de formação pela incorporação de R·  
e balanço das energias de ligação



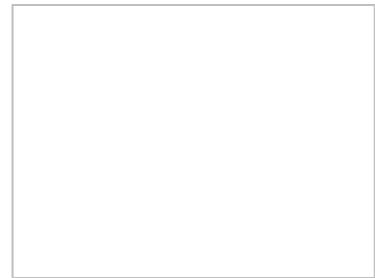


# Reações de Substituição

Halogenação: importante método de funcionalização

<u>Comparação da entalpia de reação</u>	F	Cl	Br	I
$X_2 \rightarrow X^\bullet$	+37	+58	+46	+36
$X^\bullet + CH_4 \rightarrow HX + CH_3^\bullet$	-30	+2	+18	+34
$CH_3^\bullet + X_2 \rightarrow XCH_3 + X^\bullet$	-73	-27	-25	-21
<b><math>CH_4 + X_2 \rightarrow XCH_3 + HX</math></b>	<b>-103</b>	<b>-25</b>	<b>-7</b>	<b>+13</b>

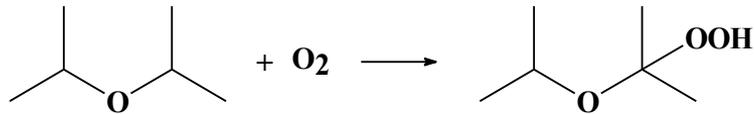
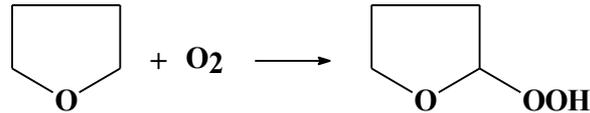
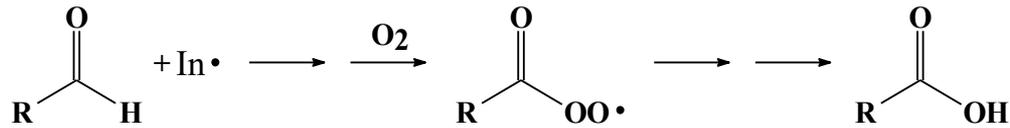
$F_2$  - quase explosivo,  $Cl_2$  - favorável  $\sim$   $Br_2$ ,  $I_2$  - desfavorável



# Autoxidação

-bastante seletiva (H “ativado”) - substratos do tipo benzílico alílico ou terciário.

- aldeídos e éteres são especialmente susceptíveis a autoxidação





## Adição de HX a olefinas

- adição de HBr: na presença de  $\text{In}\cdot$  ou luz produz bromoalcanos com orientação anti-Markovnikoff
- adição de HCl: polimerização inviabiliza utilização pois quebra de HCl no passo de propagação
- adição de HF e HI: não ocorre por motivos energéticos

