

## Outline

- Useful Literature;
- Brief History of Radical Chemistry;
- Some Basic Concepts in Radical Chemistry;
- Selected Methods for the Generation of Radicals;
- Structure of Some Carbon Centered Radicals;
- Radical Stability;
- Selected Examples of Chain Reactions Based on Stannanes;
- Organo-Silicon and Germanium Hydrides;
- The Persistent Radical Effect.

## Useful Literature

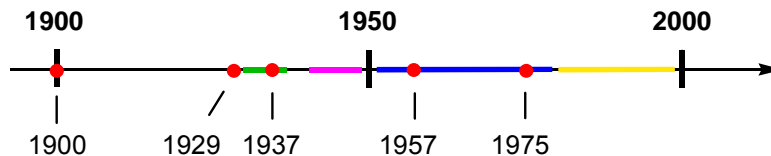
### Books:

- An Introduction to Free Radical Chemistry, Andrew Parson, 2000, Blackwell Science Ltd.; [a basic introduction](#);
- Radical Reactions in Organic Synthesis, Samir Zard, 2003, Oxford University Press; [highly recommended](#); [some schemes and examples in this seminar are taken from this reference](#);
- Radicals in Organic Synthesis Vols.1&2 , Ed. Philippe Renaud and Mukund Sibi, 2001, Wiley-VCH; [a very good, more comprehensive reference](#);
- Advanced Free Radical Reactions for Organic Synthesis, Hideo Togo, 2003, Elsevier; [contains experimental procedure](#);
- Free Radicals, Vols. 1 &2, Ed. Kochi, 1973, Wiley-Interscience;

### Key articles for the use of radicals in organic synthesis

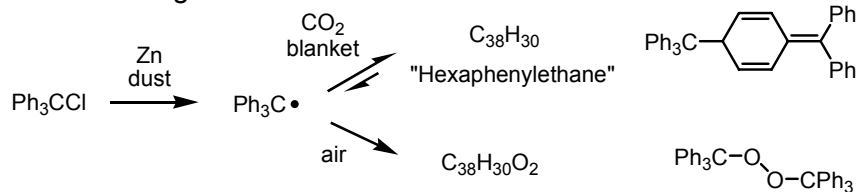
- *Synthesis* **1988**, 6, 417 and *Synthesis* **1988**, 7, 489;
- *ChemRev* **1991**, 91, 1237;

# Brief History of Radical Chemistry



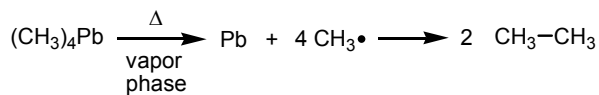
## 1 – Brief History of Radical Chemistry

### • 1900 Gomberg



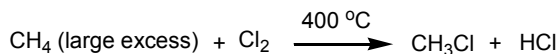
*JACS* **1900**, 22, 757; *TetLett* **1968**, 249; *Tet* **1974**, 30, 2009

### • 1929 Paneth

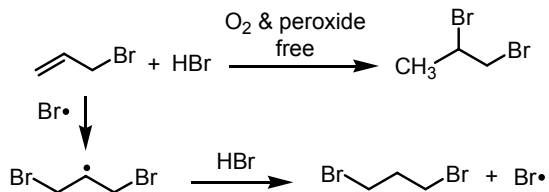


*BerDtschChemGes* **1929**, 62, 1335

### • Early 1930s



### • 1937 Kharasch



*JOC* **1937**, 2, 288; also in 1937 interpretation of vinyl polymerization in terms of a radical mechanism; see *JACS* **1937**, 59, 241.

### • 1940s

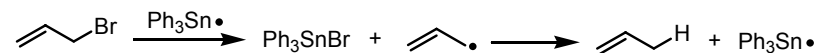
Advances in radical polymerization.

### • 1950-1980

Advances in EPR and radical kinetics.

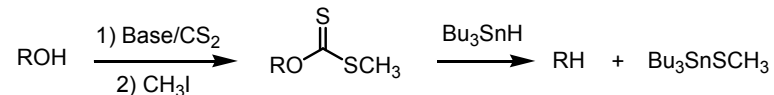
*AccChemRes* **1980**, 13, 317

### • 1957 van de Kerk



*JApplChem* **1957**, 7, 356; *AccChemRes* **1968**, 1, 299

### • 1975 Barton & McCombie



*JCS PT1* **1975**, 1, 1574

### • 1980 – 1990s

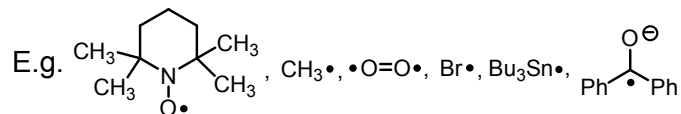
Applications to the synthesis of complex molecules.

# Some Basic Concepts in Radical Chemistry

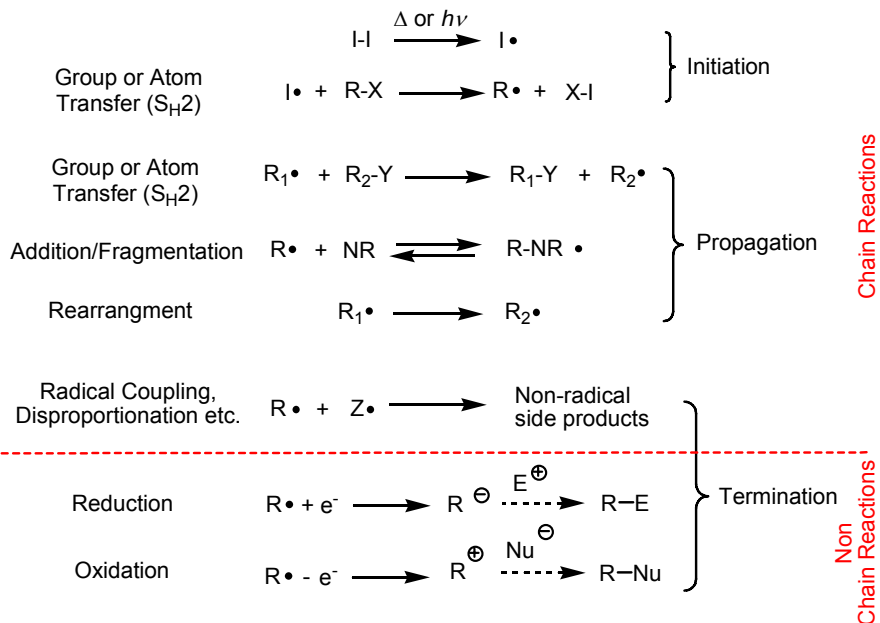
## 2 – Some Basic Concepts in Radical Chemistry

### 2.1 - Definition

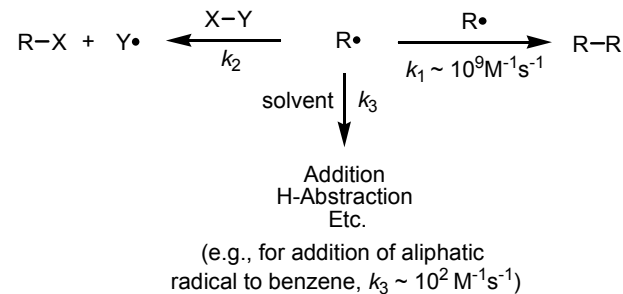
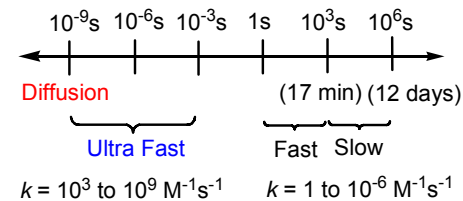
Radicals are species (atoms, molecules, ions) which contain an **unpaired electron**,  $R\cdot$ .



### 2.2 - Elementary Radical Reactions



### 2.3 - Timescales



$$\frac{d}{dt}[R-R] = k_1[R\cdot]^2 \approx 10^9 \times (10^{-8})^2 = 10^{-7} Ms^{-1}$$

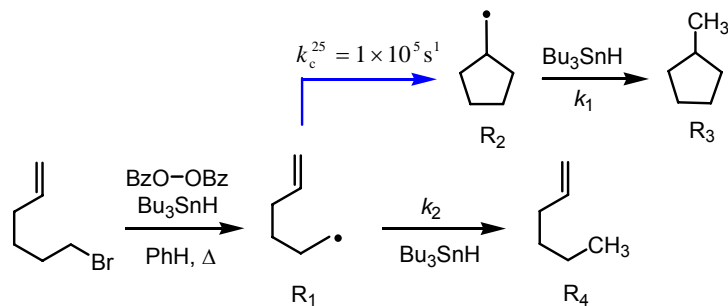
$$\frac{d}{dt}[R-X] = k_2[R\cdot][X-Y] \approx k_2 \times (10^{-8}) \times (1) \geq 10^{-7} Ms^{-1}$$

$$\Rightarrow k_{2, \text{minimum}} \geq 10 M^{-1}s^{-1} \text{ but in general, } k_2 \geq 10^2 M^{-1}s^{-1}$$

- ∴ 1)  $[R\cdot]$  should be as low as it is feasible
- 2)  $k_2$  should be as large as it is possible

# Basic Concepts / Generation of Radicals

## 2.4 - Radical Clocks and Probes



$$\frac{d[R_2]}{dt} = k_c [R_1 \cdot] - k_1 [R_2 \cdot][Bu_3SnH] = 0 \Leftrightarrow k_c [R_1 \cdot] = k_1 [R_2 \cdot][Bu_3SnH]$$

$$\frac{d[R_3]}{dt} = k_1 [R_2 \cdot][Bu_3SnH] = k_c [R_1 \cdot]$$

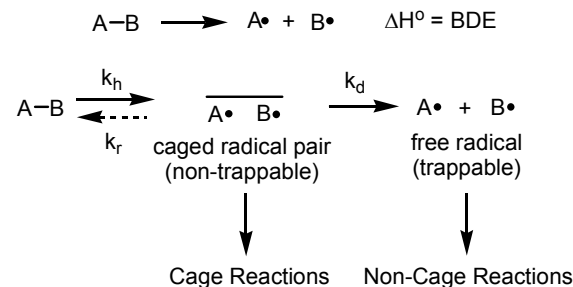
$$\frac{d[R_4]}{dt} = k_2 [R_1 \cdot][Bu_3SnH]$$

$$\frac{d[R_3]}{d[R_4]} = \frac{k_c [R_1 \cdot]}{k_2 [R_1 \cdot][Bu_3SnH]} \Rightarrow \frac{k_c}{k_2} = \frac{[R_3]}{[R_4]} [Bu_3SnH]$$

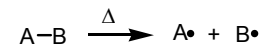
## 2.5 - Radical vs. Ionic Reactions

- Variations in radical reaction rates with the solvent are usually small;
- Radical reactions can often be run in essentially neutral media;
- Radical reactions are less sensitive to steric factors (no counterions and no solvating spheres; early TS)
- Radical intermediates are less prone to Wagner-Meerwein type rearrangements and  $\beta$ -elimination of (protected) OH and NH groups *but* H shifts are common;
- Radical reactions are usually compatible with O-H and N-H bonds;
- Stereochemical control in radical processes is usually more difficult.

## 3 – Selected Methods for the Generation of Radicals



### 3.1 – Thermolysis: Generation of *Primary* Radicals

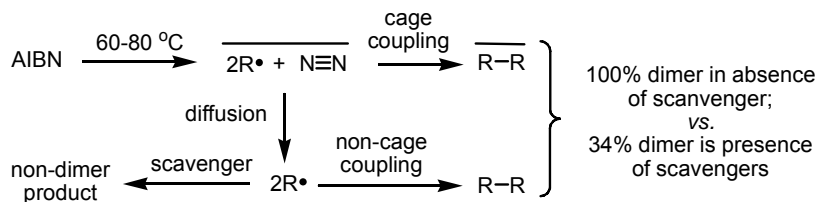


For  $T_{\text{homolysis}} < 150^\circ\text{C} \Rightarrow BDE < 30\text{-}40 \text{ kcal mol}^{-1}$

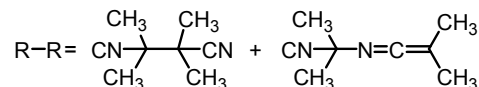
Radical Initiator	Radicals Produced	$t_{1/2}$ [at $T(^{\circ}\text{C})$ ]
Di- <i>t</i> -butyl peroxide 	$^t\text{BuO}\cdot, \text{CH}_3\cdot$	10h (126) 1h (150)
Dibenzoyl peroxide 	$\text{PhCO}_2\cdot, \text{Ph}\cdot$	7h (70) 0.5h (100)
Azobisisobutyronitrile (AIBN) 	$\text{CN}(\text{CH}_3)_2\text{C}\cdot$	5h(70) 2h (80)
Di- <i>t</i> -butyl peroxalate 	$^t\text{BuO}\cdot, \text{CH}_3\cdot$	12h (25)

For a graphical representation of  $t_{1/2}$  vs  $T(^{\circ}\text{C})$ , see *Tet* **1985**, 41, 3887

# Generation of Radicals



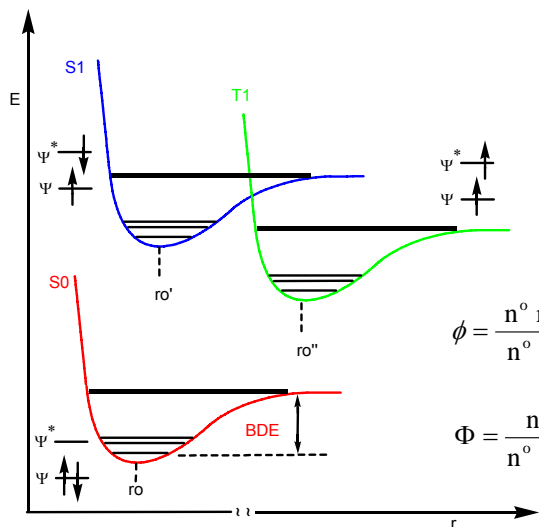
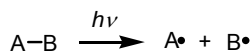
with  $\text{R}\cdot = (\text{CH}_3)_2\dot{\text{C}}-\text{C}\equiv\text{N}$



JACS 1962, 84, 2596

## 3.3 – Photolysis

### 3.3.1 – Direct Photolysis



$$E \text{ (kcalmol}^{-1}\text{)} = h \frac{c}{\lambda} = \frac{28600}{\lambda \text{ (nm)}}$$

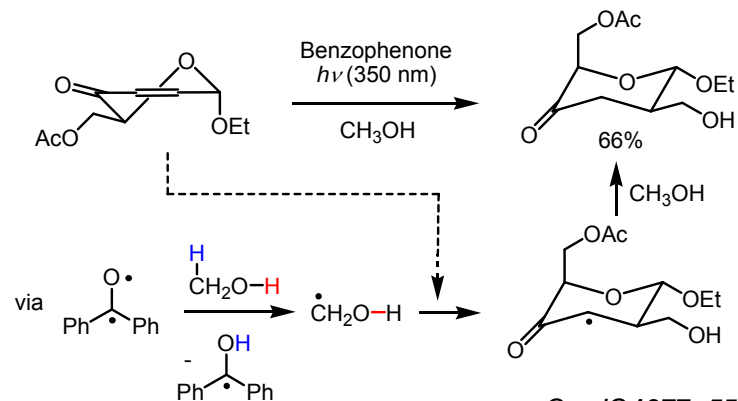
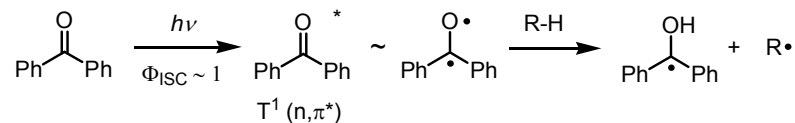
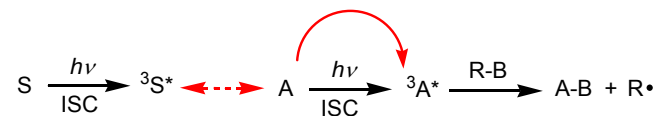
$$\phi = \frac{n^\circ \text{ reactant molecules consumed}}{n^\circ \text{ photon absorbed by reactant}} \leq 1$$

$$\Phi = \frac{n^\circ \text{ molecules of A produced}}{n^\circ \text{ photon absorbed by reactant}}$$

	$\lambda$ (nm)	E (kcalmol <sup>-1</sup> )
Vis	780-380	37-75
UV	380-200	75-143

Compound Type	$\Delta H_{\text{app}}$ (kcalmol <sup>-1</sup> )
Cl-Cl	59
RO-OR	30 to 50
RN=NR	35 to 50
RO-NO	40
RO-Cl	48
R <sub>2</sub> N-Cl	45
R <sub>3</sub> Sn-SnR <sub>3</sub>	63

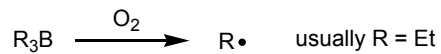
### 3.3.2 – Photolysis Mediated by a Sensitizer



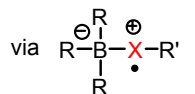
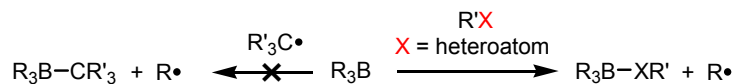
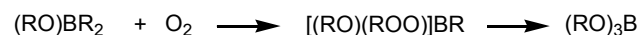
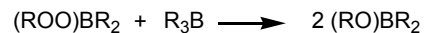
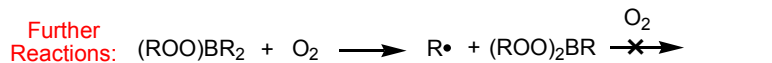
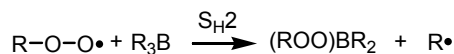
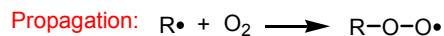
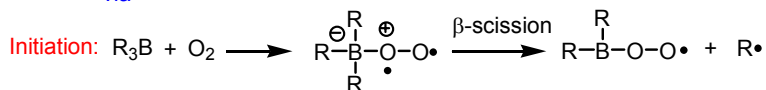
CanJC 1977, 55, 3978

# Generation of Radicals/Structure of C-Centered Radicals

## 3.3 – Triethyl Borane: Generation of *Primary Radicals*

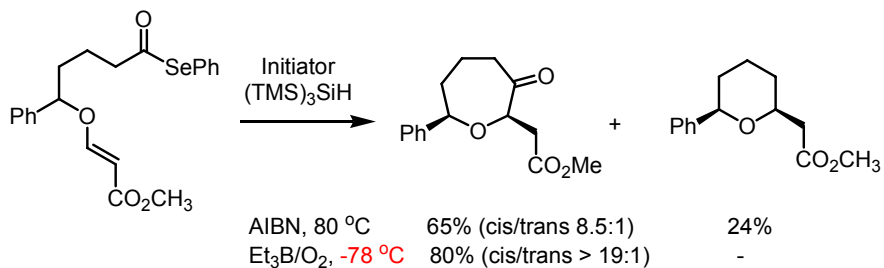


via



Lewis Acid-Base Complex  
(X = O, S, NR<sup>+</sup>)

*BullChemSocJpn* **1989**, 62, 143  
*ChemRev* **2001**, 101, 3415



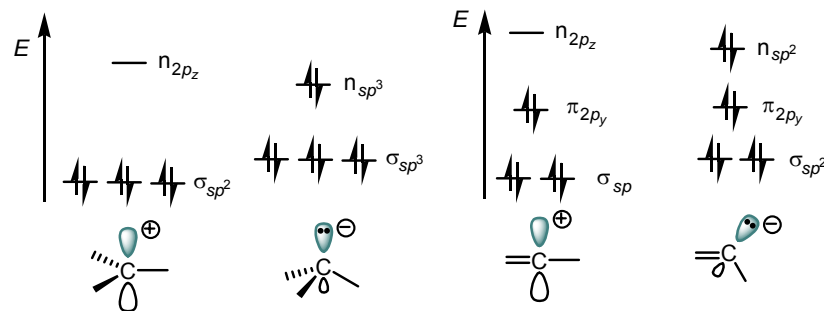
*JOC* **1996**, 61, 2252

## 4 – Structure of Some Carbon Centered Radicals

Determined by EPR, IR, theoretical calculations etc.

### 4.1 – Carbon-Centered Radicals

VSEPR for predicting preferred geometries of **closed shell** intermediates



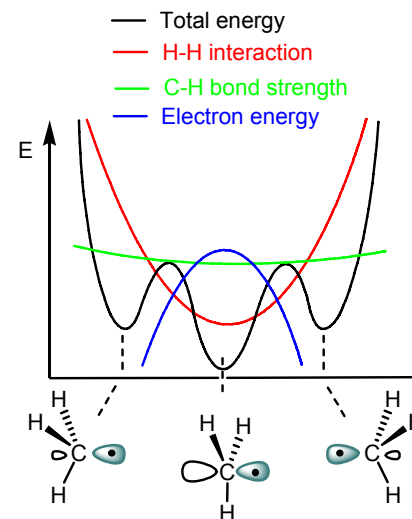
#### 4.1.1 – Alkyl Radicals

##### 4.1.1.1 – Methyl Radical



$\pi$ -radical

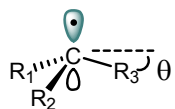
*JChemPhys* **1959**, 30, 15



From Organic Synthesis, Michael Smith, 2001, McGraw-Hill Science

# Structure of C-Centered Radicals

## 4.1.1.2 – Fluoromethyl Radicals



$R_1, R_2$  and  $R_3 = \text{H or F}$

$\sigma$ -radical

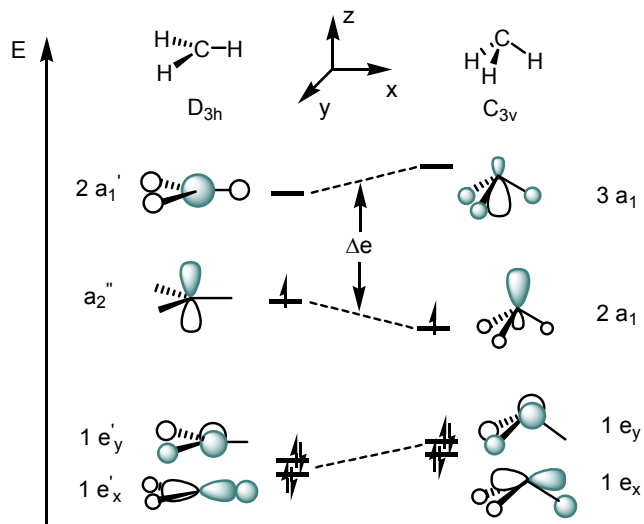
Pyramidalization of  $\text{CH}_n\text{F}_{n-3}$  radicals according to EPR coupling constants (in G)

Radical	$a^{\text{F}}$	$a^{13\text{C}}$	$\theta$ ( $^\circ$ )
$\cdot\text{CH}_3$		38.5	0
$\cdot\text{CH}_2\text{F}$	64.3	54.8	5
$\cdot\text{CHF}_2$	84.2	148.8	12.7
$\cdot\text{CF}_3$	142.4	271.6	17.8

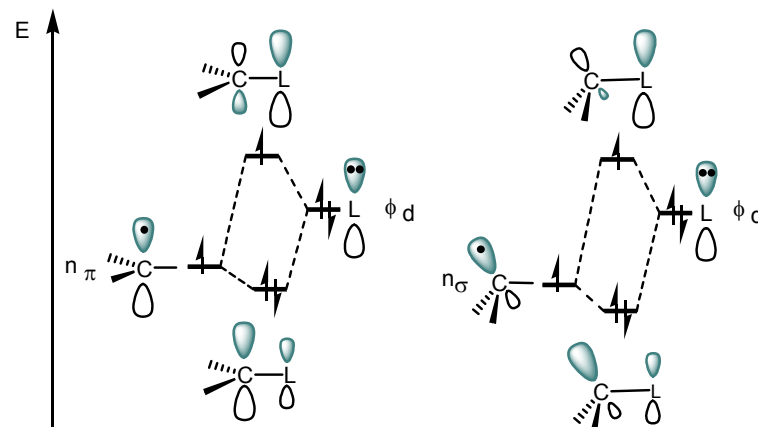
*JChemPhys* **1963**, 39, 2147; *JChemPhys* **1965**, 43, 2704

Walsh Diagram for Planar ( $D_{3h}$ ) to Pyramidal ( $C_{3v}$ ) Methyl

$\sigma$  Component of Bonding



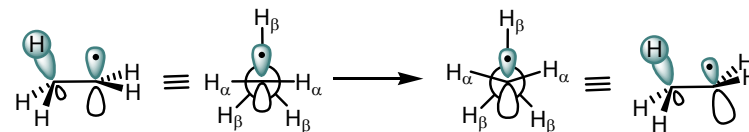
$\pi$  Component of Bonding



$$\langle n \pi | \phi d \rangle > \langle n \sigma | \phi d \rangle$$

$$\Delta \epsilon (n \pi - \phi d) < \Delta \epsilon (n \sigma - \phi d)$$

## 4.1.1.3 – Ethyl Radical



$\sigma$ -radical

Pyramidalization favoured by:

- low inversion barrier for C-centered radicals;
- Increased staggering between  $\text{C}_\alpha\text{-H}$  and  $\text{C}_\beta\text{-H}$ ;
- Increased hyperconjugation between SOMO and synperiplanar  $\text{C}_\beta\text{-H}$ .

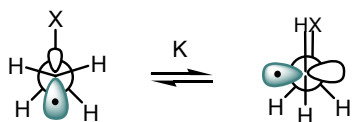
*JACS* **1981**, 103, 5046; *JCPhys* **1963**, 39, 2147

# Structure of C-Centered Radicals/Radical Stability

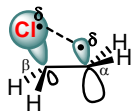
Replacement of a hydrogen by a  $\sigma$ -attractor/ $\pi$ -donor group (e.g., Hal, OH,  $\text{NH}_2$ ) or an alkyl group at the carbon radical center:

- promotes pyramidalization of the radical ( $\pi \rightarrow \sigma$ );
- raises its inversion barrier, although in most cases it remains sufficiently low ( $\sim 2 \text{ kcal mol}^{-1}$ ) for rapid inversion to take place.

## 4.1.1.4 – $\beta$ -Substituted Alkyl Radicals

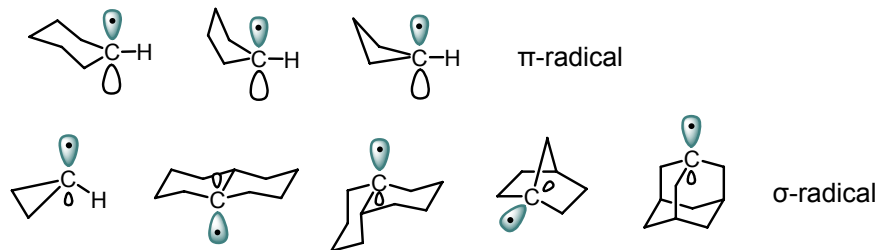


$K < 1$  for  $X = \text{SiR}_3, \text{SnR}_3, \text{Cl}$   
 $K \sim 1$  for  $X = \text{F}, \text{NH}_2, \text{OH}$

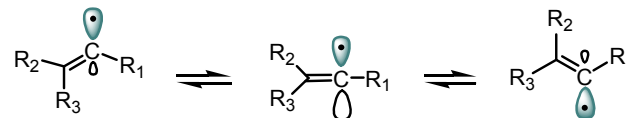


X	$a_\beta$ (G)	
H	26.9	
F	23.4	
$\text{Me}_3\text{Si}$	17.7	
$\text{Me}_3\text{Sn}$	15.8	$a_\alpha$ (G)
Cl	10.2	21.8

## 4.1.1.5 – Cycloalkyl Radicals



## 4.1.1.6 – Vinyl Radicals

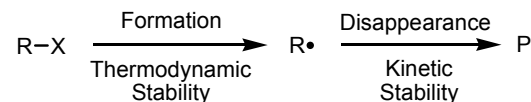


Either  $\sigma$  (more common) or  $\pi$  depending on the substituents.

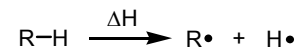
in *Free Radicals*, Kochi, 1973

Carbon-centered  $\pi$  radicals are flat and  $\sigma$  radicals usually invert very rapidly but stereoselective radical reactions are still possible!

## 5 – Radical Stability



### 5.1 – Thermodynamic Stability



$$\Delta H = \text{BDE}(\text{R-H}) = \Delta H_f^\circ(\text{H}\cdot) + \Delta H_f^\circ(\text{R}\cdot) - \Delta H_f^\circ(\text{R-H})$$

$$E_s(\text{R}\cdot) = \text{BDE}(\text{CH}_3\text{-H}) - \text{BDE}(\text{R-H})$$



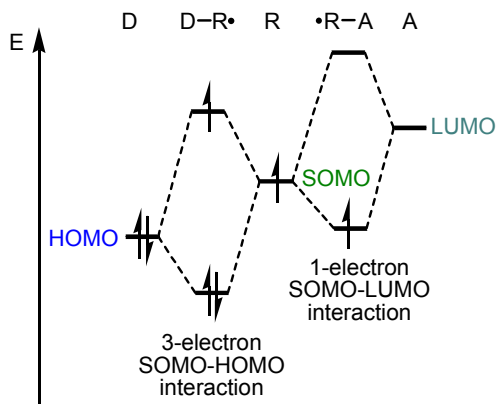
# Radical Stability

Thermodynamic Radical Stability:

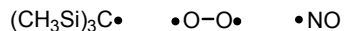
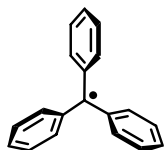
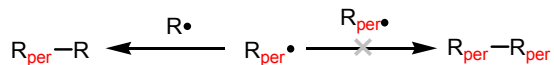
- 1) Hybridization: Alkyl > Alkenyl >> Alkynyl
- 2) Hyperconjugation: Tertiary > Secondary > Primary > Methyl
- 3) Resonance > Hyperconjugation; Amphiphilic character
- 4) Captodative

$$\Delta E_s = [E_s(\text{DHR}\cdot) + E_s(\text{WHR}\cdot)] - E_s(\text{DWR}\cdot)$$

$E_{s\text{add}}(\text{R}\cdot)$



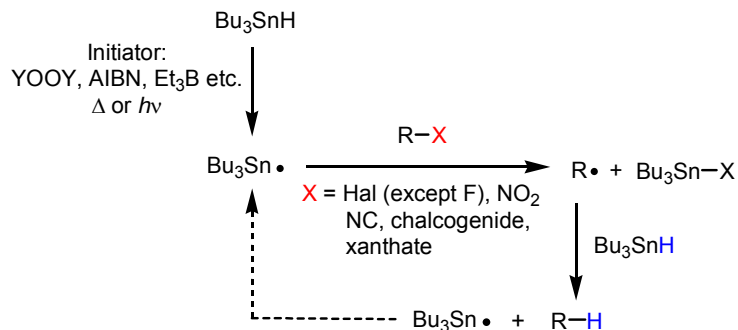
## 5.2 – Kinetic Stability



	R-H	BDE (R-H) kcal·mol <sup>-1</sup>	E <sub>s</sub> (R·) kcal·mol <sup>-1</sup>	
Hybridization	CH≡C-H	131	-26	
		111	-6	
	CH <sub>2</sub> =CH-H	110	-5	
		106	-1	
Hyperconjugation	CH <sub>3</sub> -H	105	0	
	CH <sub>3</sub> CH <sub>2</sub> -H	101	+4	
	(CH <sub>3</sub> ) <sub>2</sub> CH-H	99	+6	
	(CH <sub>3</sub> ) <sub>2</sub> C-H	95	+10	
	CH <sub>2</sub> =CHCH <sub>2</sub> -H	86	+19	
Resonance	PhCH <sub>2</sub> -H	85	+20	
	PhO-H	87	+18	
	NH <sub>2</sub> CH <sub>2</sub> -H	95	+10	
	CH <sub>3</sub> OCH <sub>2</sub> -H	93	+12	$E_{s\text{add}}(\text{R}\cdot)$ kcal·mol <sup>-1</sup>
	(CHO)CH <sub>2</sub> -H	92	+13	
Captodative Effect	(CH <sub>3</sub> O)(CH <sub>3</sub> )CH <sub>2</sub> -H	91	+14	12+4 = +16
	(CHO)(NH <sub>2</sub> )CH-H	73	+31	13+10 = +23
	Ph <sub>3</sub> C-H	77	+28	

# Selected Examples of Chain Reactions Based on Stannanes

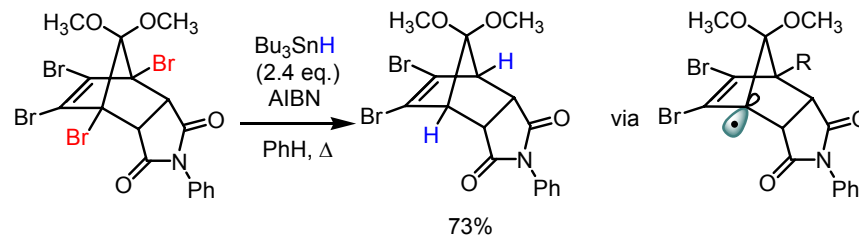
## 6.1 – Reduction



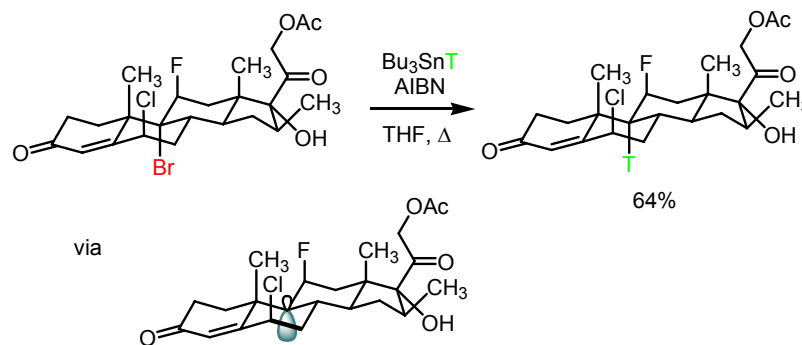
$\text{R-X} \xrightarrow{\text{Bu}_3\text{SnH}} \text{R-H}$	
R-X	$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\text{R}_{\text{alkyl}}\text{-I}$	$\geq 10^9$
$\text{R}_{\text{aryl/vinyl}}\text{-I}$	$10^7\text{-}10^8$
$\text{R}_{\text{alkyl}}\text{-Br}$	
$\text{R}_{\text{aryl/vinyl}}\text{-Br}$	
$\text{R}_{\alpha\text{-ester}}\text{-Cl}$	$10^5\text{-}10^6$
$\text{R}_{\text{alkyl}}\text{-SePh}$	
$\text{R}_{\text{alkyl}}\text{-Cl}$	$10^2\text{-}10^4$
$\text{R}_{\text{alkyl}}\text{-SPh}$	

(BDE:  $\text{R-I} < \text{R-Br} \ll \text{R-Cl}$ )

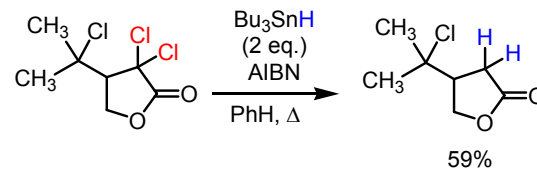
$\text{R}\cdot \xrightarrow{\text{Bu}_3\text{SnH}} \text{R-H}$	
$\text{R}_{\text{sp}2}\cdot$	$k_{30} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\text{C}_6\text{H}_5\cdot$	$5.9 \times 10^8$
$(\text{CH}_3)_2\text{C=CH}\cdot$	$3.5 \times 10^8$
$\text{R}_{\text{sp}3}\cdot$	$k_{30} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\triangle\cdot$	$8.5 \times 10^7$
$\text{CH}_3\cdot$	$1.2 \times 10^7$
$\text{R}_{\text{alkyl}}\text{CH}_2\cdot$	$2.7 \times 10^6$
$(\text{CH}_3)_2\text{CH}\cdot$	$1.5 \times 10^6$
$(\text{CH}_3)_3\text{C}\cdot$	$1.7 \times 10^6$
$\text{PhCH}_2\cdot$	$k_{25} = 3.6 \times 10^4$



TL 1999, 40, 9289



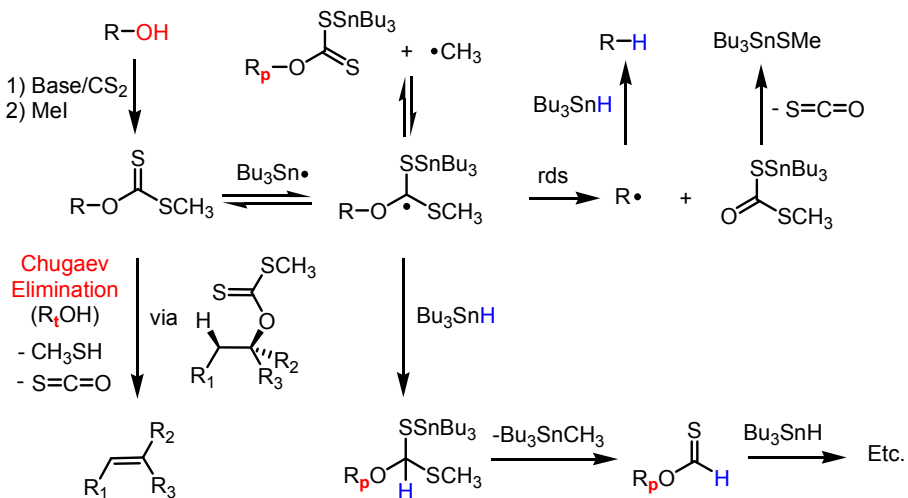
JOC 1979, 44, 151



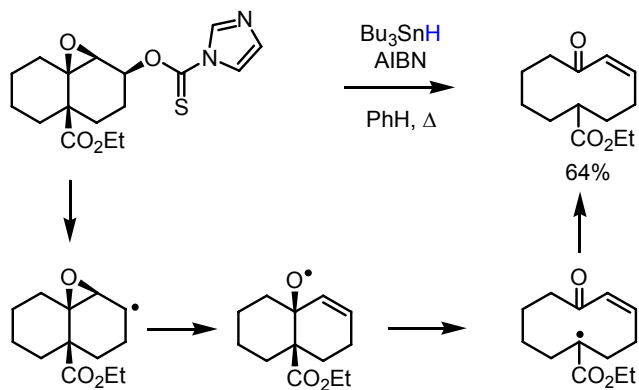
Synthesis 1984, 949

# Selected Examples of Chain Reactions Based on Stannanes

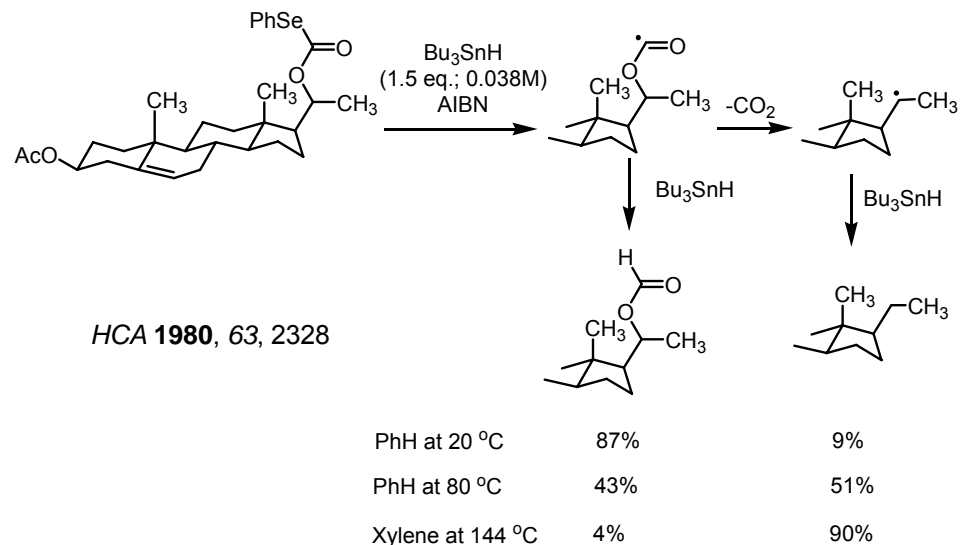
## 6.2 – The Barton-McCombie Deoxygenation Reaction



*JCS PT1* **1975**, 1, 1574; *ChemRev* **1989**, 89, 1413

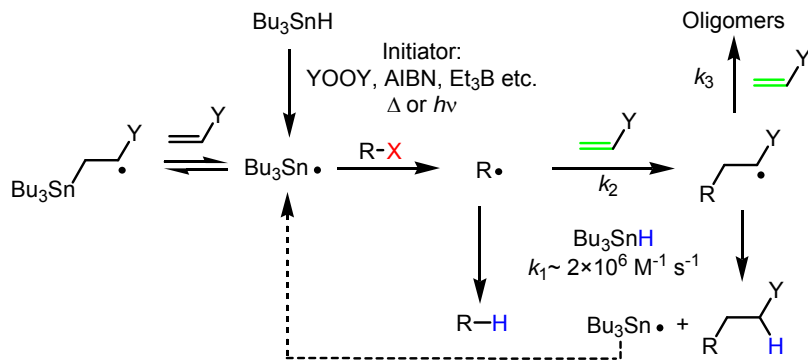


*Synlett* **1992**, 987



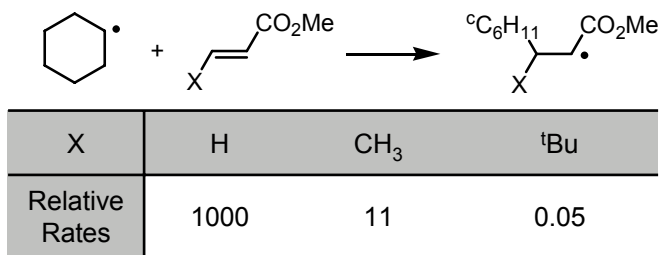
# Selected Examples of Chain Reactions Based on Stannanes

## 6.3 – Addition to Olefins

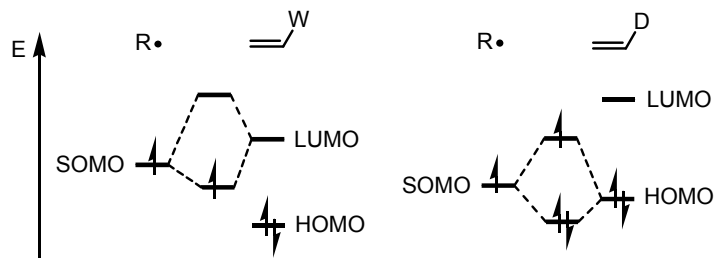


### 6.3.1 – Intermolecular Additions: Steric and Polar Effects

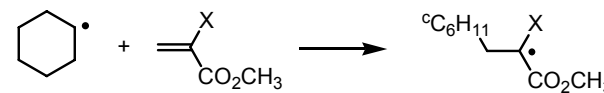
Intermolecular Additions to Olefins: **Steric** Effects



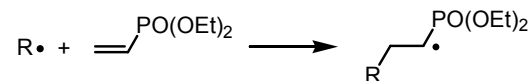
ACIEE 1983, 22, 753



Radical Additions to **Electron Poor** Olefins

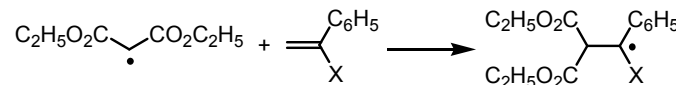


X	H	CH <sub>3</sub>	Cl	CO <sub>2</sub> CH <sub>3</sub>	CN
Relative Rates	1	0.011	10	150	350

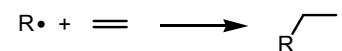


R <sup>•</sup>	Et	iPr	<sup>t</sup> Bu
k (M <sup>-1</sup> s <sup>-1</sup> )	2.6 × 10 <sup>3</sup>	1.2 × 10 <sup>4</sup>	5.9 × 10 <sup>4</sup>

Radical Additions to **Electron Rich** Olefins



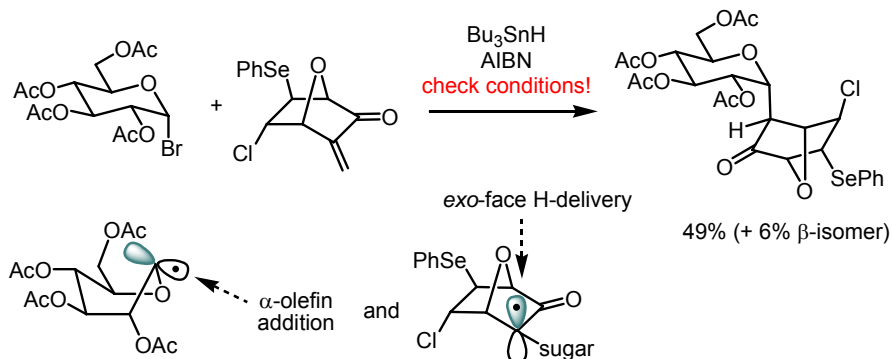
X		CH <sub>3</sub>	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>
Relative Rates	23.0	3.5	1.0



R <sup>•</sup>	CH <sub>3</sub>	CH <sub>2</sub> F	CF <sub>3</sub>
k (M <sup>-1</sup> s <sup>-1</sup> )	4.6 × 10 <sup>4</sup>	2.8 × 10 <sup>5</sup>	3.5 × 10 <sup>6</sup>

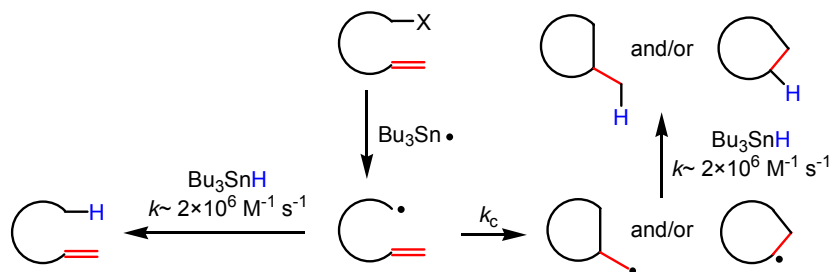
ACIEE 1983, 22, 753; AccChemRes 1976, 9, 183

# Selected Examples of Chain Reactions Based on Stannanes



JOC 1992, 57, 2076

## 6.3.2 – Intramolecular Additions to Olefins: Regiochemistry and Rates



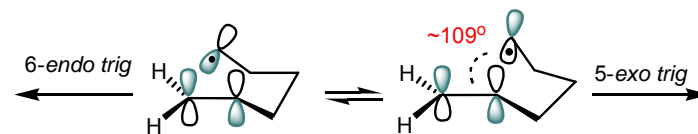
### Baldwin Rules for Kinetically Controlled Ring Closures

Favoured	Disfavoured
3-7 <i>exo-tet</i>	
3-7 <i>exo-trig</i>	5-6 <i>endo-tet</i>
3-7 <i>endo-dig</i>	3-5 <i>endo-trig</i>
6-7 <i>endo-trig</i>	3-4 <i>exo-dig</i>
5-7 <i>exo-dig</i>	

Ring Size	Exo:Endo Ratio	
	Calc.	Found
5:6	10:1	50:1
6:7	>100:1	10:1
7:8	1:5.8	<1:100

JOC 1987, 52, 959

JCS CC 1976, 734

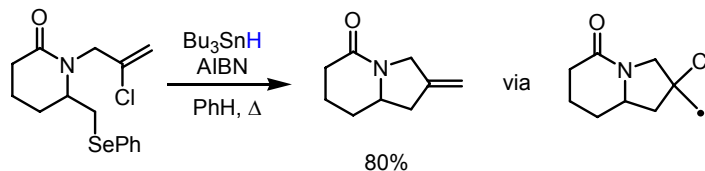
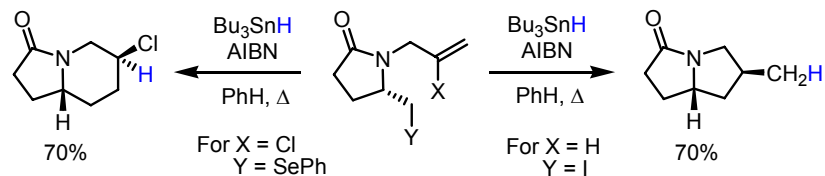


C-centered sp <sup>3</sup> Radicals	$k_{25}^{exo}$ (s <sup>-1</sup> )	$k_{25}^{endo}$ (s <sup>-1</sup> )	
	 2.3 × 10 <sup>5</sup>	 4.1 × 10 <sup>3</sup>	$E_a^{5exo} = 6.2 \text{ kcalmol}^{-1}$ $\Delta E_a = 1.7 \text{ kcalmol}^{-1}$
	 <0.7	 1.2 × 10 <sup>2</sup>	 via 1,5-H shift
	 5.3 × 10 <sup>3</sup>	 9.0 × 10 <sup>3</sup>	
	 3.2 × 10 <sup>6</sup>	 1 × 10 <sup>5</sup>	
	 8.5 × 10 <sup>6</sup>	 1 × 10 <sup>5</sup>	
	 8.7 × 10 <sup>2</sup>	 1.8 × 10 <sup>3</sup>	

in *Radical Reactions in Organic Synthesis*, Zard, 2003 and *Advanced Free Radical Reactions for Organic Synthesis*, Togo, 2003

## Selected Examples of Chain Reactions Based on Stannanes

C-centered $sp^3$ Radicals	$k^{25}_{exo}$ ( $s^{-1}$ )	$k^{25}_{endo}$ ( $s^{-1}$ )	
	$4.4 \times 10^7$	$5.2 \times 10^6$	
	$2.9 \times 10^5$	$2.2 \times 10^6$	
			$E_{a5exo} = 7.3$ $kcalmol^{-1}$
	$1.5 \times 10^5$	nd	
			$E_{a5exo} = 16.3$ $kcalmol^{-1}$
	$2 \times 10^{-1}$	-	
			$E_{a5exo} = 8.3$ $kcalmol^{-1}$
	$2.8 \times 10^4$	$6 \times 10^2$	
Other	$k^{25}_{exo}$ ( $s^{-1}$ )	$k^{25}_{endo}$ ( $s^{-1}$ )	
	$3.1 \times 10^8$	$6 \times 10^6$	
	$1.7 \times 10^9$	$3.6 \times 10^7$	
	$4 \times 10^8$ (30 °C)	$8 \times 10^6$ (30 °C)	

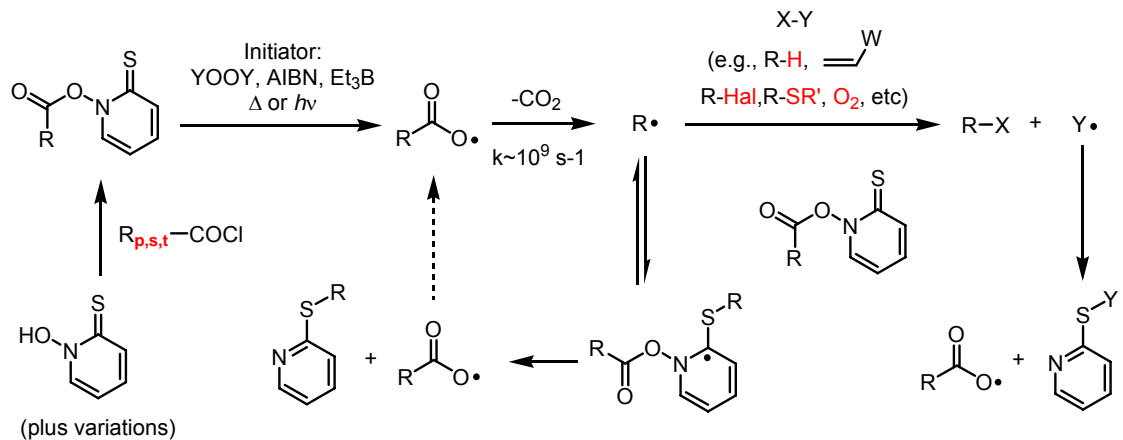


*T* 1992, 48, 2977  
*TL* 1990, 31, 5397

	$k^{80}$ ( $s^{-1}$ )
	$k_c = 8.7 \times 10^5$ $k_o = 4.7 \times 10^8$
	$k_c = 1.0 \times 10^6$ $k_o = 1.1 \times 10^7$
	$k_c = 6 \times 10^6$
	$k_c = 4.2 \times 10^7$

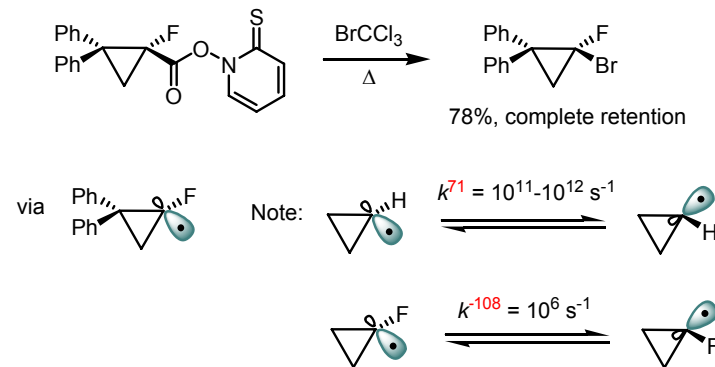
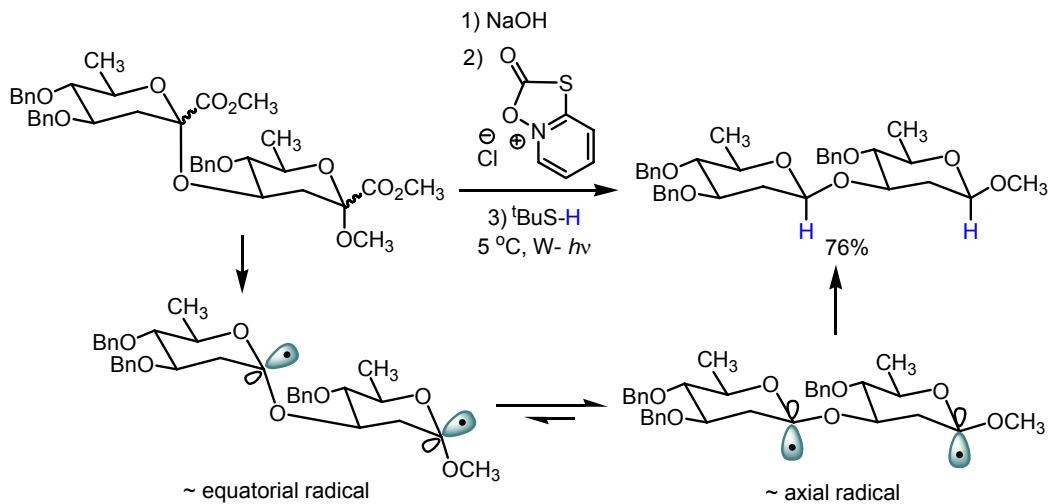
# Selected Examples of Chain Reactions Based on Stannanes

## 6.4 – The Barton-McCombie Decarboxylation



R = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub>	t <sub>1/2</sub> = 31 min
	k = 4.2 × 10 <sup>6</sup> M <sup>-1</sup> s <sup>-1</sup>
R = (CH <sub>3</sub> ) <sub>2</sub> CH, t <sub>1/2</sub> = 26 min	
R = (CH <sub>3</sub> ) <sub>3</sub> C, t <sub>1/2</sub> = 14 min	

JCS CC 1983, 939; Tet 1985, 41, 3901



JOC 1991, 56, 2193

TetLett 1991, 32, 2565

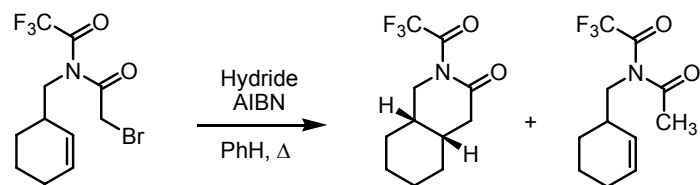
# Organo-Silicon and -Germanium Hydrides

## 7 – Organo-Silicon and -Germanium Hydrides

BDE [(CH <sub>3</sub> ) <sub>3</sub> M-X] (kcalmol <sup>-1</sup> )						
X	H	CH <sub>3</sub>	Cl	Br	I	OEt
(CH <sub>3</sub> ) <sub>3</sub> C-X	95	86	84	70	54	82
(CH <sub>3</sub> ) <sub>3</sub> Si-X	90	90	112	96	77	111
(CH <sub>3</sub> ) <sub>3</sub> Ge-X	82	76	116	104	63	107
(CH <sub>3</sub> ) <sub>3</sub> Sn-X	74	65	94	83	69	84

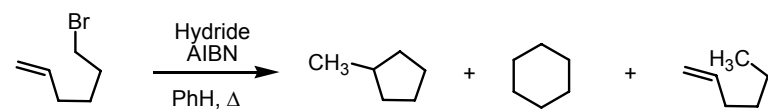
Reaction with Et <sub>3</sub> Si·		Reaction with (Me <sub>3</sub> Si) <sub>3</sub> Si·	
R-X	k <sup>27</sup> (M <sup>-1</sup> s <sup>-1</sup> )	R-X·	k <sup>27</sup> (M <sup>-1</sup> s <sup>-1</sup> )
CH <sub>3</sub> CH <sub>2</sub> -I	4.3×10 <sup>9</sup>	<sup>c</sup> C <sub>6</sub> H <sub>11</sub> -OC(S)SCH <sub>3</sub>	1.1×10 <sup>9</sup>
Ph-I	1.5×10 <sup>9</sup>	(CH <sub>3</sub> ) <sub>3</sub> C-Br	1.2×10 <sup>8</sup>
CH <sub>2</sub> =CHCH <sub>2</sub> Br	1.5×10 <sup>9</sup>	<sup>n</sup> C <sub>10</sub> H <sub>21</sub> -SePh	9.6×10 <sup>7</sup>
(CH <sub>3</sub> ) <sub>3</sub> C-Br	1.1×10 <sup>9</sup>	<sup>c</sup> C <sub>6</sub> H <sub>11</sub> -NC	4.7×10 <sup>7</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> -Br	5.4×10 <sup>8</sup>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> -Br	2.0×10 <sup>7</sup>
Ph-Br	1.1×10 <sup>8</sup>	(CH <sub>3</sub> ) <sub>3</sub> C-NO <sub>2</sub>	1.2×10 <sup>7</sup>
CH <sub>2</sub> =CHCH <sub>2</sub> -Cl	2.4×10 <sup>7</sup>	<sup>n</sup> C <sub>10</sub> H <sub>21</sub> -SPh	5×10 <sup>6</sup>
(CH <sub>3</sub> ) <sub>3</sub> C-Cl	2.5×10 <sup>6</sup>		
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> -Cl	3.1×10 <sup>5</sup>		
Ph-Cl	6.9×10 <sup>5</sup>		

	k <sup>30</sup> (M <sup>-1</sup> s <sup>-1</sup> )		
	Bu <sub>3</sub> SnH	(Me <sub>3</sub> Si) <sub>3</sub> SiH	Et <sub>3</sub> SiH
<sup>n</sup> C <sub>7</sub> H <sub>15</sub> ·	2.7×10 <sup>6</sup>	4.6×10 <sup>5</sup>	8.5×10 <sup>2</sup>
<sup>n</sup> C <sub>7</sub> F <sub>15</sub> ·	2×10 <sup>8</sup>	5.1×10 <sup>7</sup>	7.5×10 <sup>5</sup>



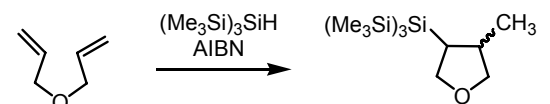
For Bu<sub>3</sub>SnH 65% 24%  
For Ph<sub>3</sub>GeH 85% -

*Heterocycles* **1989**, 28, 723  
*JOC* **1999**, 64, 1151



For Bu<sub>3</sub>SnH 83% 1.2% 15%  
For (Me<sub>3</sub>Si)<sub>3</sub>SiH 93% 2.0% 4.1%

*AccChemRes* **1992**, 25, 188



63% (cis:trans 3:1)

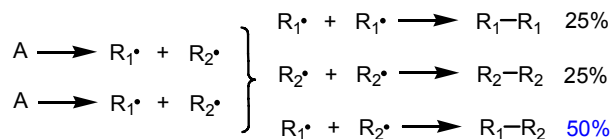
*JOC* **1992**, 57, 3994



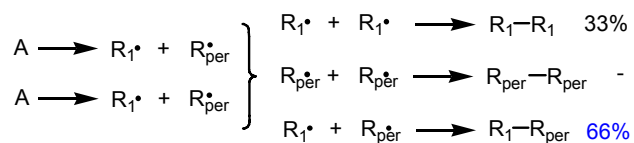
# The Persistent Radical Effect

## 8 – The Persistent Radical Effect

### Dimerization Reactions for Transient Radicals

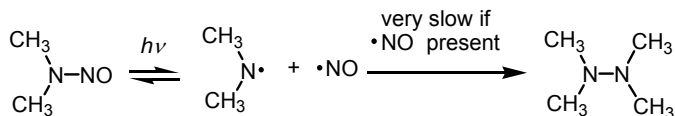


### Dimerization Reactions Between a Transient and a Persistent Radical

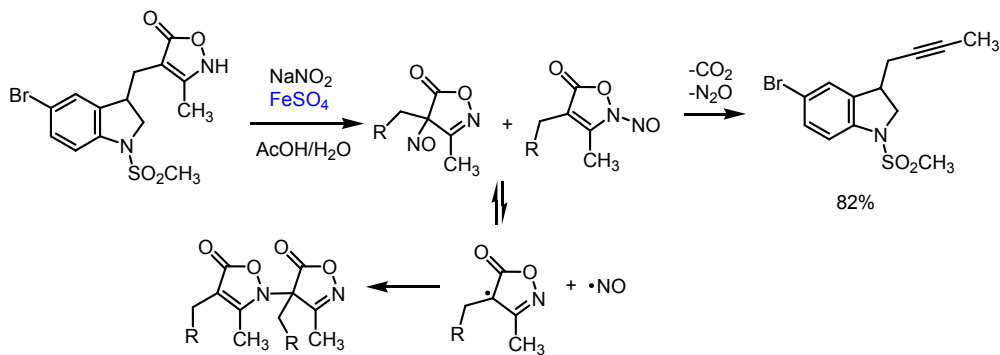


in practice almost total selectivity

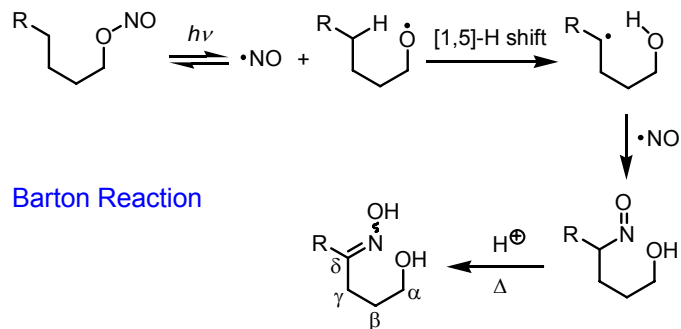
*ChemRev* **2001**, 101, 3581; *ChemEurJ* **2001**, 7, 1159



*JACS* **1986**, 108, 3925

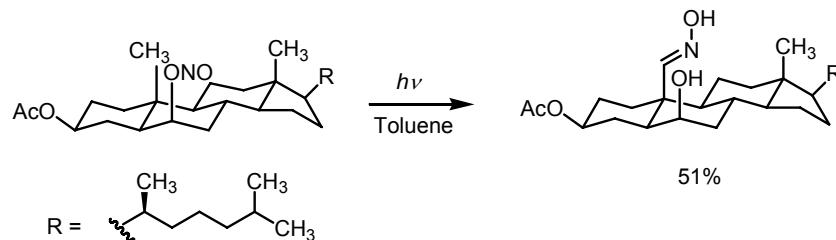


*CC* **2001**, 1304



Barton Reaction

*JACS* **1960**, 82, 2640; *JACS* **1961**, 83, 4076



*Synthesis* **1971**, 501