

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

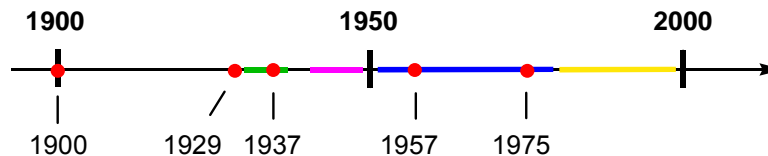
Books:

- 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

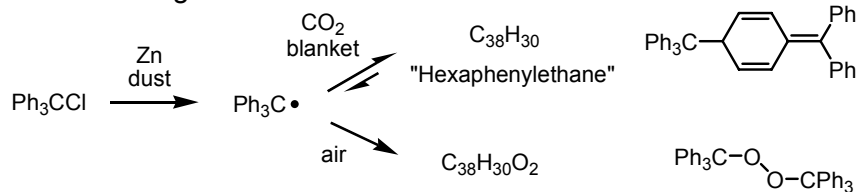
- *Synthesis* **1988**, 6, 417 and *Synthesis* **1988**, 7, 489;
- *ChemRev* **1991**, 91, 1237;

Brief History of Radical Chemistry



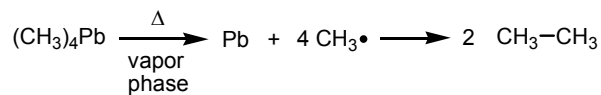
1 – Brief History of Radical Chemistry

• 1900 Gomberg



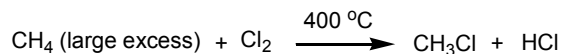
JACS **1900**, 22, 757; *TetLett* **1968**, 249; *Tet* **1974**, 30, 2009

• 1929 Paneth

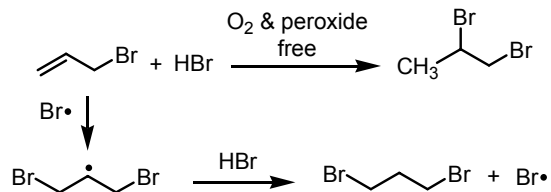


BerDtschChemGes **1929**, 62, 1335

• 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

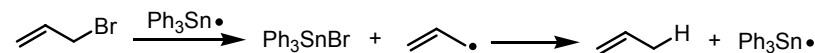
Advances in radical polymerization.

• 1950-1980

Advances in EPR and radical kinetics.

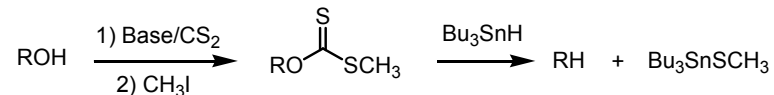
AccChemRes **1980**, 13, 317

• 1957 van de Kerk



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

• 1975 Barton & McCombie



JCS PT1 **1975**, 1, 1574

• 1980 – 1990s

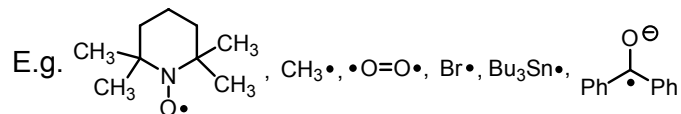
Applications to the synthesis of complex molecules.

Some Basic Concepts in Radical Chemistry

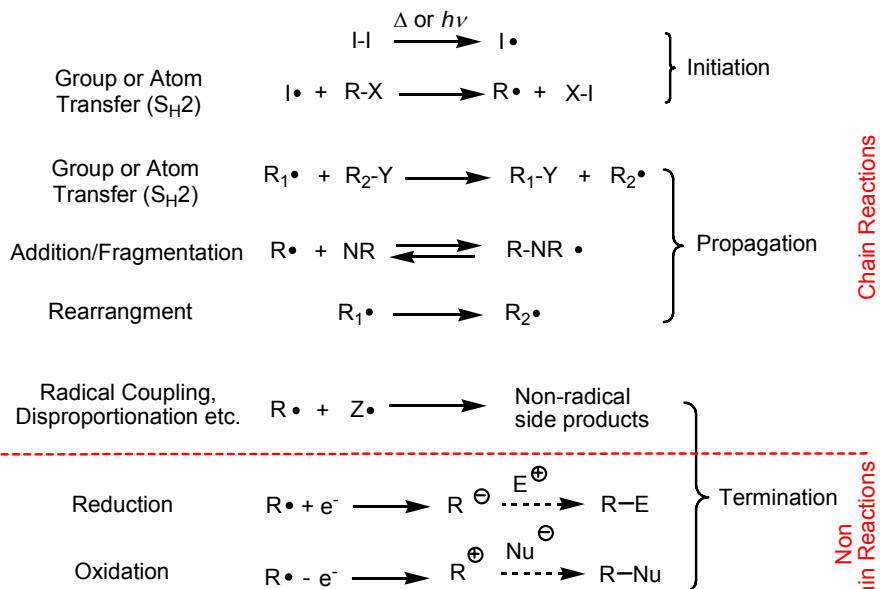
2 – Some Basic Concepts in Radical Chemistry

2.1 - Definition

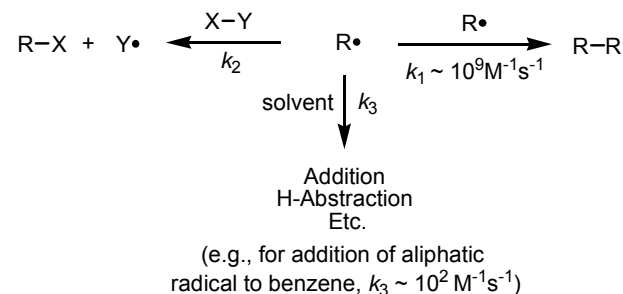
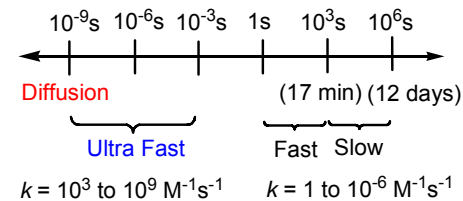
Radicals are species (atoms, molecules, ions) which contain an **unpaired electron**, $R\cdot$.



2.2 - Elementary Radical Reactions



2.3 - Timescales



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

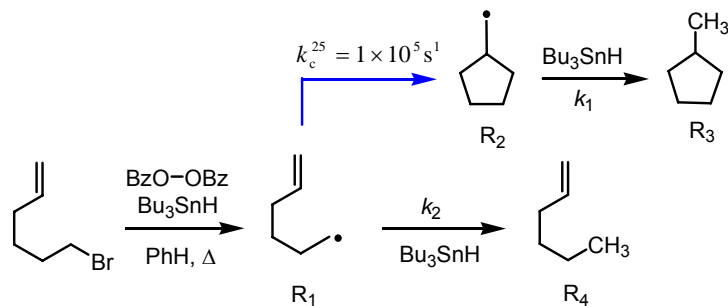
$$\frac{d}{dt}[R-X] = k_2[R\cdot][X-Y] \approx k_2 \times (10^{-8}) \times (1) \geq 10^{-7} Ms^{-1}$$

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

- ∴ 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



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

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

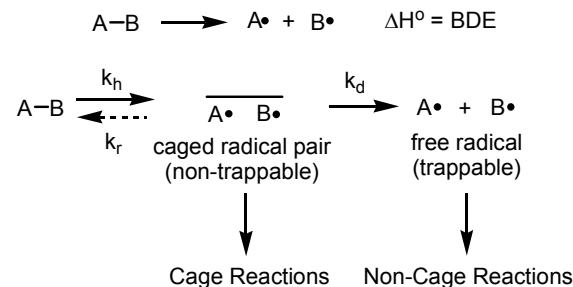
$$\frac{d[R_4]}{dt} = k_2 [R_1 \cdot][Bu_3SnH]$$

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

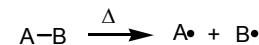
2.5 - Radical vs. Ionic Reactions

- 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 β -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

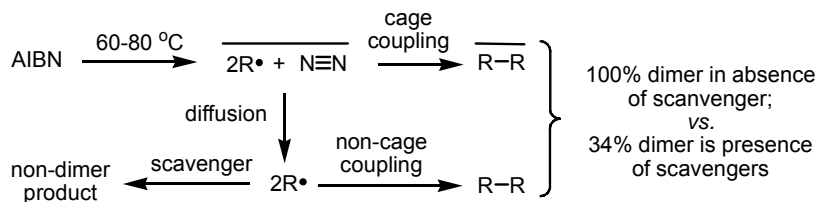


For $T_{\text{homolysis}} < 150^\circ\text{C} \Rightarrow BDE < 30\text{-}40 \text{ kcal mol}^{-1}$

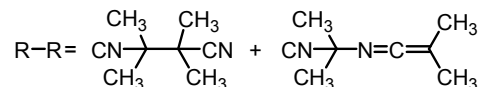
Radical Initiator	Radicals Produced	$t_{1/2}$ [at $T(^{\circ}\text{C})$]
Di- <i>t</i> -butyl peroxide 	$^t\text{BuO}\cdot, \text{CH}_3\cdot$	10h (126) 1h (150)
Dibenzoyl peroxide 	$\text{PhCO}_2\cdot, \text{Ph}\cdot$	7h (70) 0.5h (100)
Azobisisobutyronitrile (AIBN) 	$\text{CN}(\text{CH}_3)_2\text{C}\cdot$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



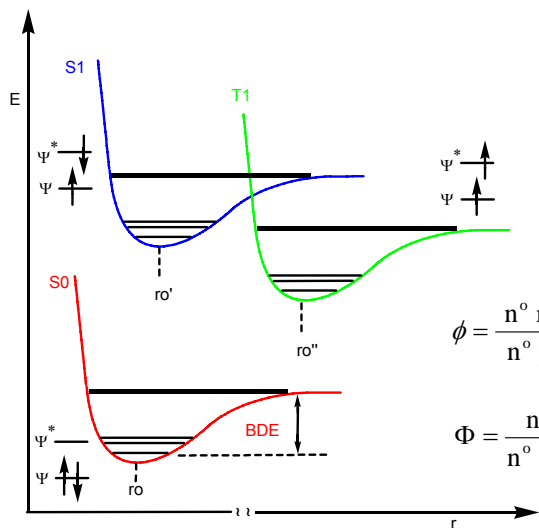
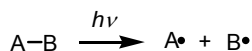
with $\text{R}\cdot = (\text{CH}_3)_2\dot{\text{C}}-\text{C}\equiv\text{N}$



JACS 1962, 84, 2596

3.3 – Photolysis

3.3.1 – Direct Photolysis



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

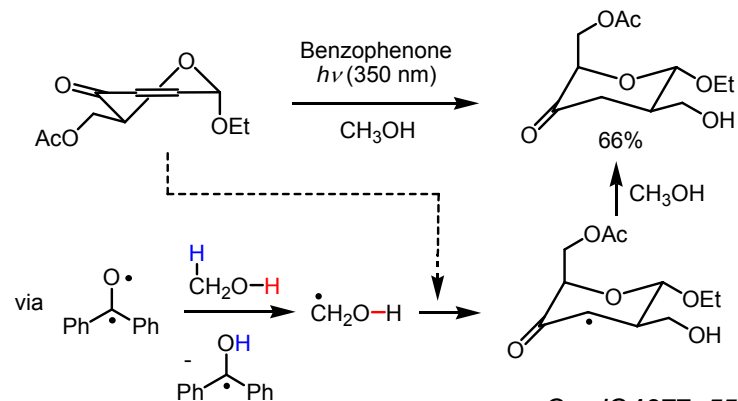
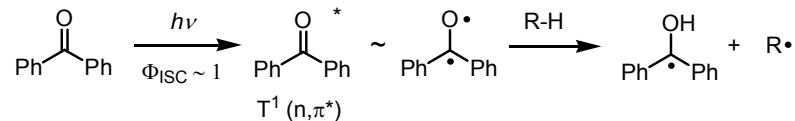
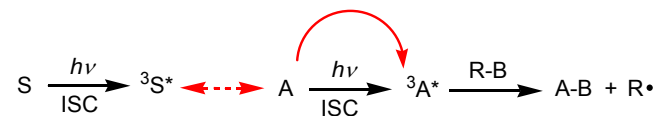
$$\phi = \frac{n^\circ \text{ reactant molecules consumed}}{n^\circ \text{ photon absorbed by reactant}} \leq 1$$

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

	λ (nm)	E (kcalmol ⁻¹)
Vis	780-380	37-75
UV	380-200	75-143

Compound Type	ΔH_{app} (kcalmol ⁻¹)
Cl-Cl	59
RO-OR	30 to 50
RN=NR	35 to 50
RO-NO	40
RO-Cl	48
R ₂ N-Cl	45
R ₃ Sn-SnR ₃	63

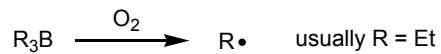
3.3.2 – Photolysis Mediated by a Sensitizer



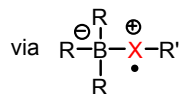
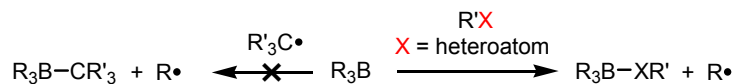
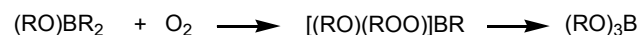
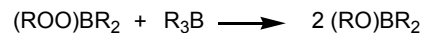
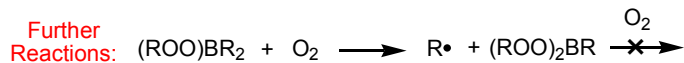
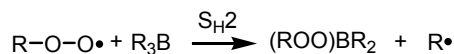
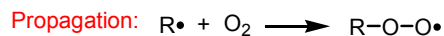
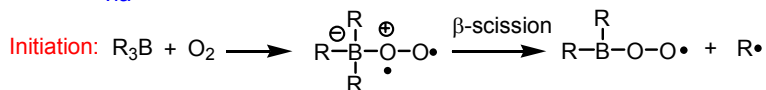
CanJC 1977, 55, 3978

Generation of Radicals/Structure of C-Centered Radicals

3.3 – Triethyl Borane: Generation of *Primary Radicals*

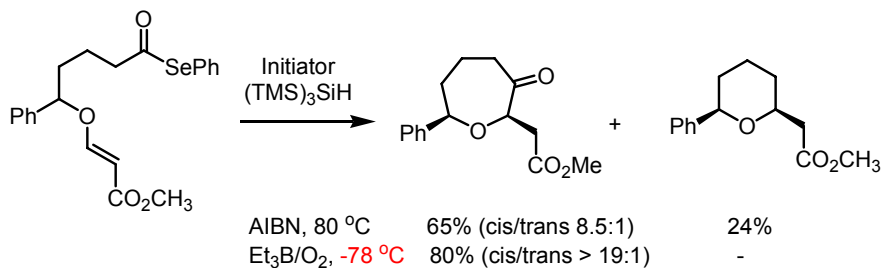


via



Lewis Acid-Base Complex
(X = O, S, NR⁺)

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



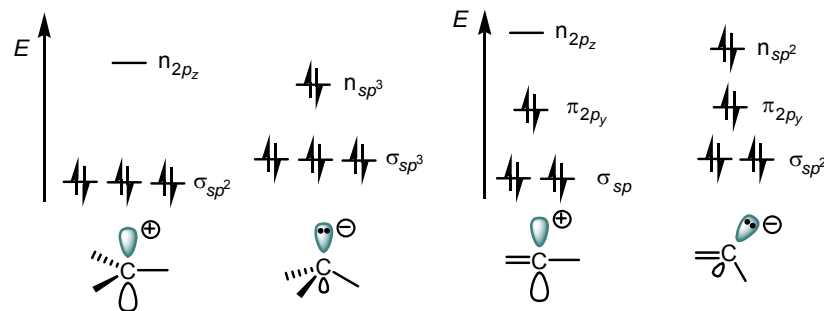
JOC **1996**, 61, 2252

4 – Structure of Some Carbon Centered Radicals

Determined by EPR, IR, theoretical calculations etc.

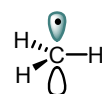
4.1 – Carbon-Centered Radicals

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



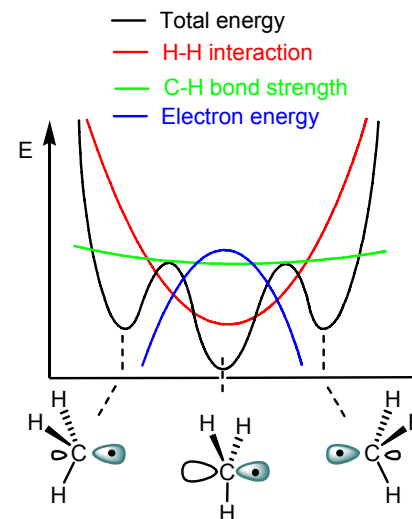
4.1.1 – Alkyl Radicals

4.1.1.1 – Methyl Radical



π -radical

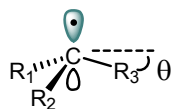
JChemPhys **1959**, 30, 15



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

σ -radical

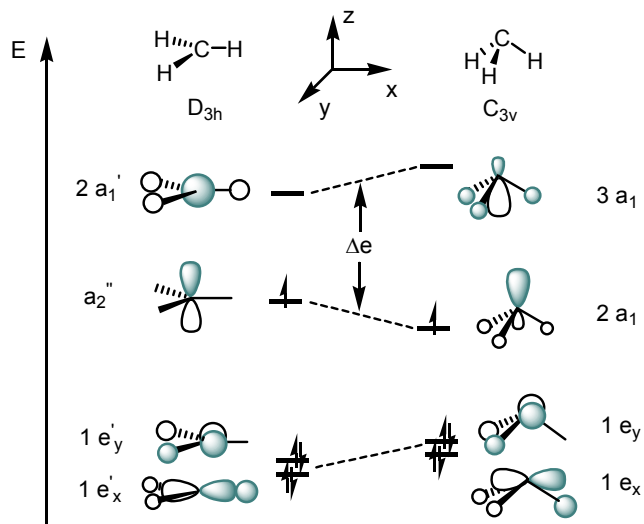
Pyramidalization of $\text{CH}_n\text{F}_{n-3}$ radicals according to EPR coupling constants (in G)

Radical	a^{F}	$a^{13\text{C}}$	θ ($^\circ$)
$\cdot\text{CH}_3$		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

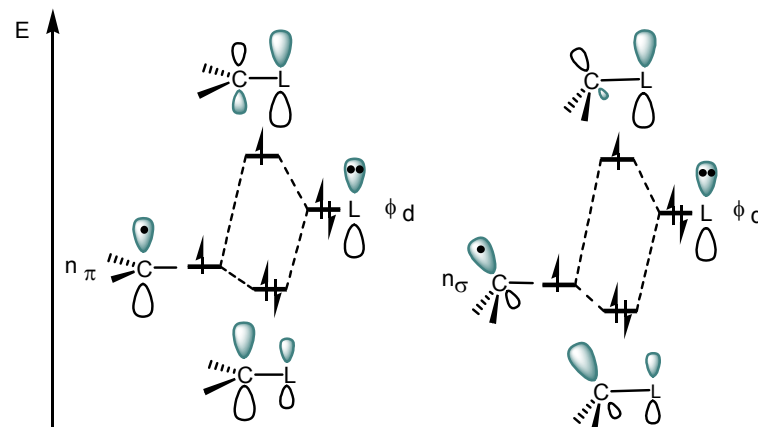
JChemPhys **1963**, 39, 2147; *JChemPhys* **1965**, 43, 2704

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

σ Component of Bonding



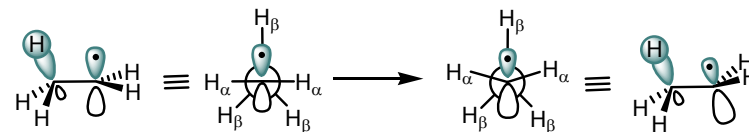
π Component of Bonding



$$\langle n_{\pi} | \phi_d \rangle > \langle n_{\sigma} | \phi_d \rangle$$

$$\Delta \varepsilon (n_{\pi} - \phi_d) < \Delta \varepsilon (n_{\sigma} - \phi_d)$$

4.1.1.3 – Ethyl Radical



σ -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 $\text{C}_{\beta}\text{-H}$.

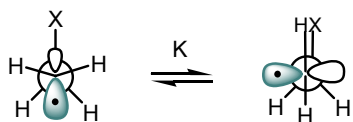
JACS **1981**, 103, 5046; *JCPhys* **1963**, 39, 2147

Structure of C-Centered Radicals/Radical Stability

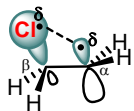
Replacement of a hydrogen by a σ -attractor/ π -donor group (e.g., Hal, OH, NH_2) or an alkyl group at the carbon radical center:

- 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 – β -Substituted Alkyl Radicals

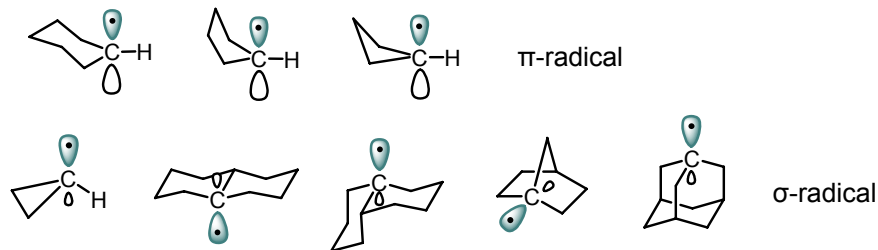


$K < 1$ for $X = \text{SiR}_3, \text{SnR}_3, \text{Cl}$
 $K \sim 1$ for $X = \text{F}, \text{NH}_2, \text{OH}$

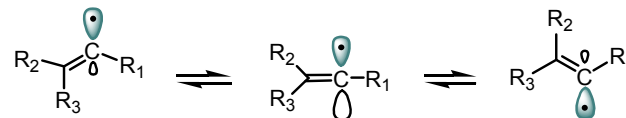


X	a_β (G)	
H	26.9	
F	23.4	
Me_3Si	17.7	
Me_3Sn	15.8	a_α (G)
Cl	10.2	21.8

4.1.1.5 – Cycloalkyl Radicals



4.1.1.6 – Vinyl Radicals

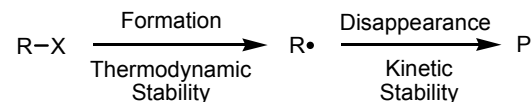


Either σ (more common) or π depending on the substituents.

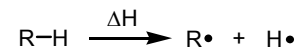
in *Free Radicals*, Kochi, 1973

Carbon-centered π radicals are flat and σ radicals usually invert very rapidly but stereoselective radical reactions are still possible!

5 – Radical Stability



5.1 – Thermodynamic Stability



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

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

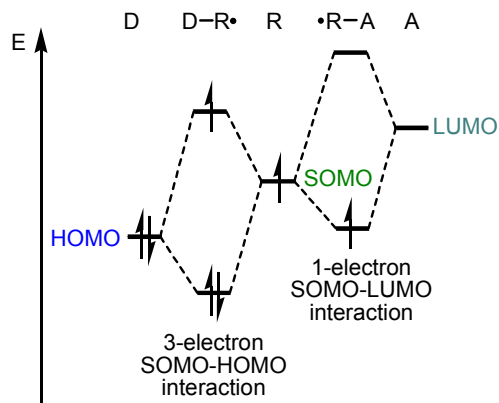
Radical Stability

Thermodynamic Radical Stability:

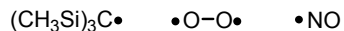
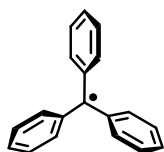
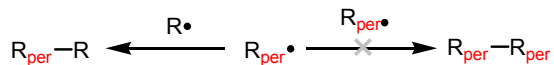
- 1) Hybridization: Alkyl > Alkenyl >> Alkynyl
- 2) Hyperconjugation: Tertiary > Secondary > Primary > Methyl
- 3) Resonance > Hyperconjugation; Amphiphilic character
- 4) Captodative

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

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



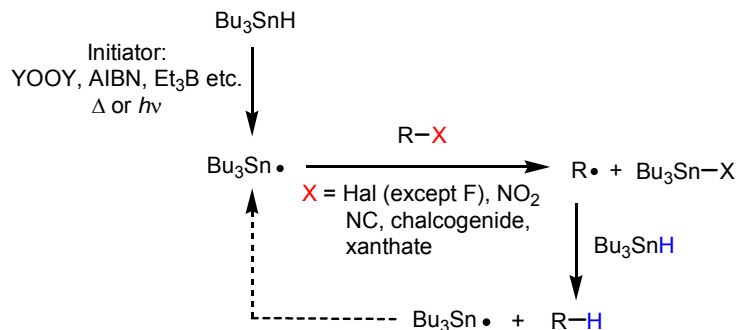
5.2 – Kinetic Stability



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

Selected Examples of Chain Reactions Based on Stannanes

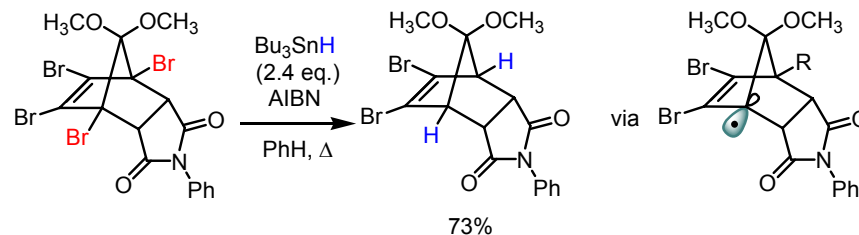
6.1 – Reduction



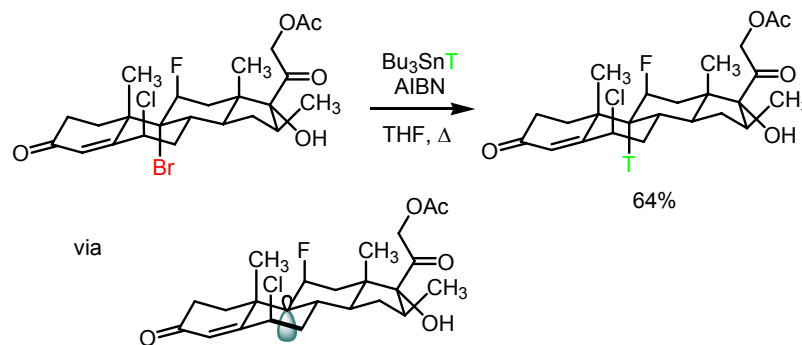
$\text{R-X} \xrightarrow{\text{Bu}_3\text{SnH}} \text{R-H}$	
R-X	$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\text{R}_{\text{alkyl}}\text{-I}$	$\geq 10^9$
$\text{R}_{\text{aryl/vinyl}}\text{-I}$	$10^7\text{-}10^8$
$\text{R}_{\text{alkyl}}\text{-Br}$	
$\text{R}_{\text{aryl/vinyl}}\text{-Br}$	
$\text{R}_{\alpha\text{-ester}}\text{-Cl}$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

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

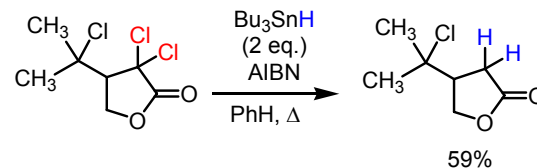
$\text{R}\cdot \xrightarrow{\text{Bu}_3\text{SnH}} \text{R-H}$	
$\text{R}_{\text{sp}2}\cdot$	$k_{30} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\text{C}_6\text{H}_5\cdot$	5.9×10^8
$(\text{CH}_3)_2\text{C=CH}\cdot$	3.5×10^8
$\text{R}_{\text{sp}3}\cdot$	$k_{30} \text{ (M}^{-1}\text{s}^{-1}\text{)}$
$\triangle\cdot$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



TL 1999, 40, 9289



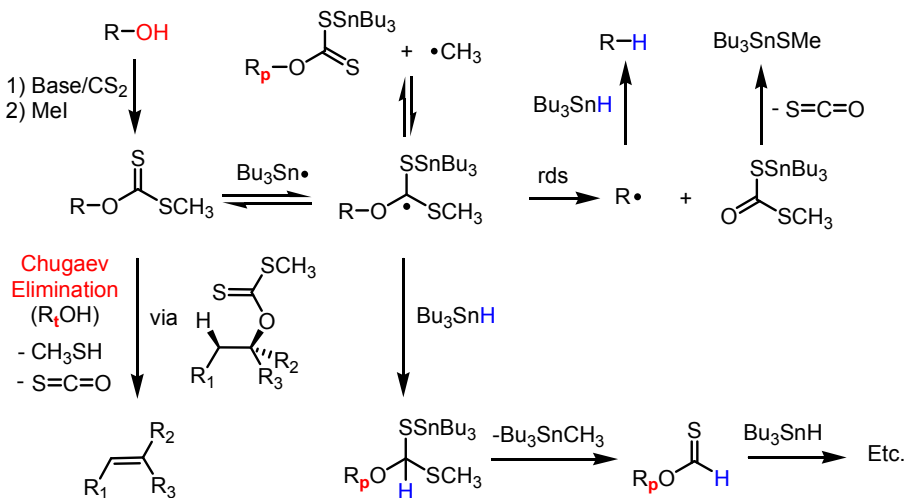
JOC 1979, 44, 151



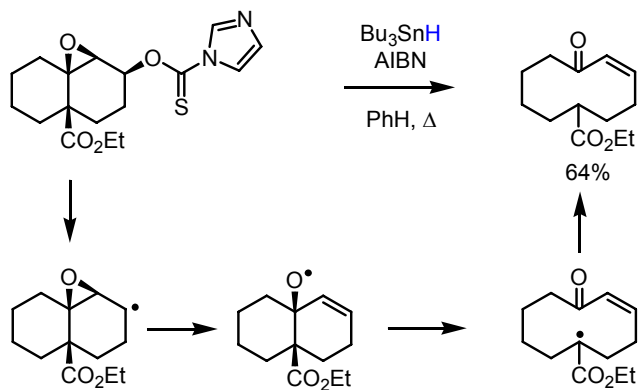
Synthesis 1984, 949

Selected Examples of Chain Reactions Based on Stannanes

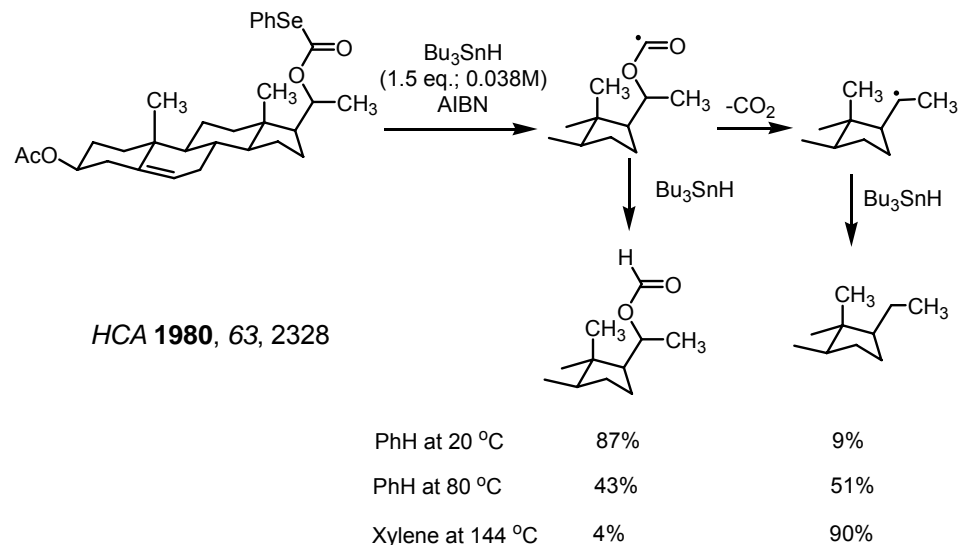
6.2 – The Barton-McCombie Deoxygenation Reaction



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

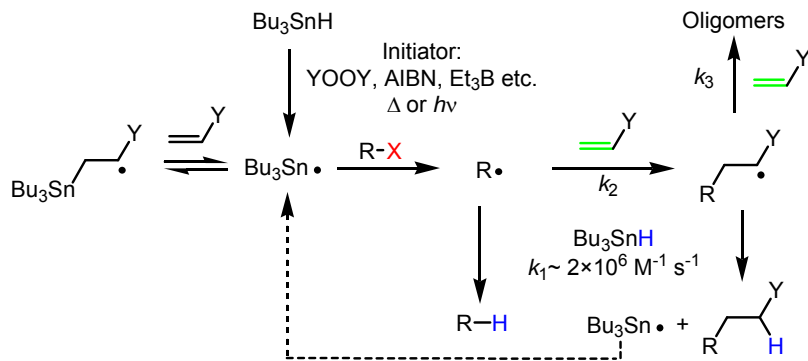


Synlett 1992, 987



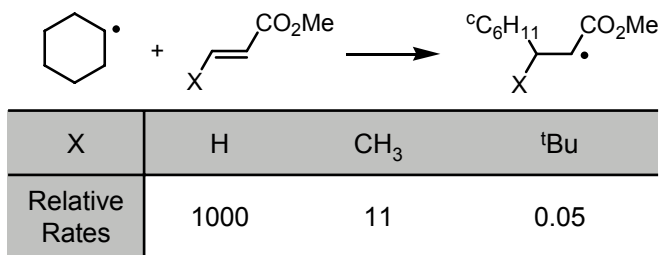
Selected Examples of Chain Reactions Based on Stannanes

6.3 – Addition to Olefins

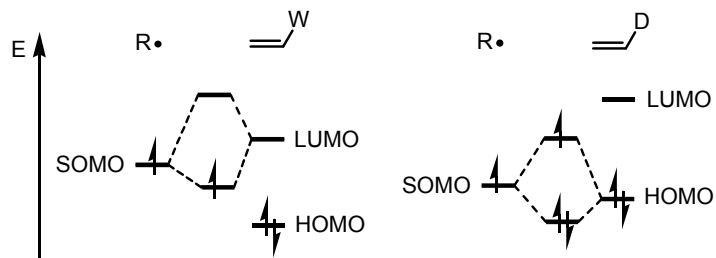


6.3.1 – Intermolecular Additions: Steric and Polar Effects

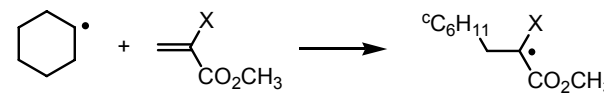
Intermolecular Additions to Olefins: **Steric Effects**



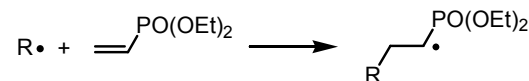
ACIEE 1983, 22, 753



Radical Additions to **Electron Poor** Olefins

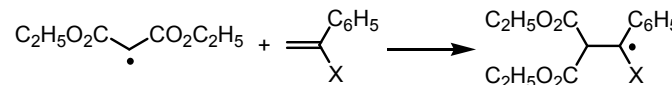


X	H	CH ₃	Cl	CO ₂ CH ₃	CN
Relative Rates	1	0.011	10	150	350

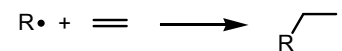


R•	Et	iPr	^t Bu
$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$	2.6×10^3	1.2×10^4	5.9×10^4

Radical Additions to **Electron Rich** Olefins



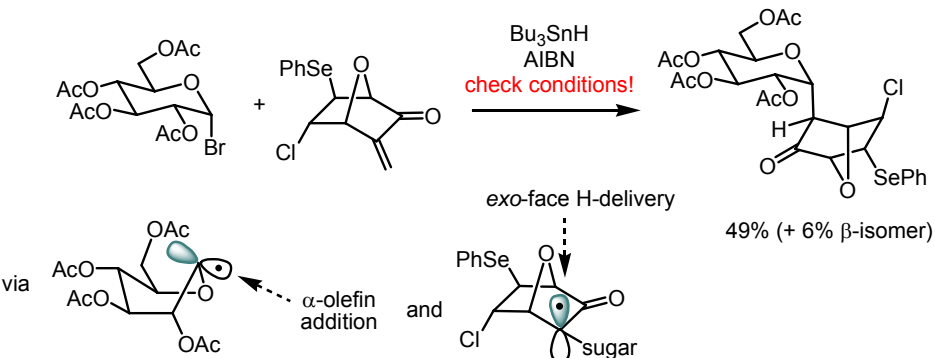
X		CH ₃	CO ₂ C ₂ H ₅
Relative Rates	23.0	3.5	1.0



R•	CH ₃	CH ₂ F	CF ₃
$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$	4.6×10^4	2.8×10^5	3.5×10^6

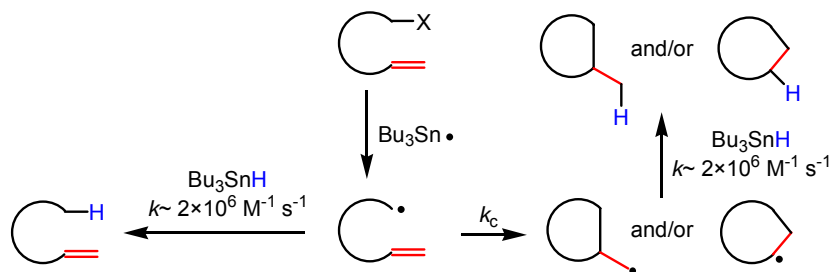
ACIEE 1983, 22, 753; AccChemRes 1976, 9, 183

Selected Examples of Chain Reactions Based on Stannanes



JOC 1992, 57, 2076

6.3.2 – Intramolecular Additions to Olefins: Regiochemistry and Rates



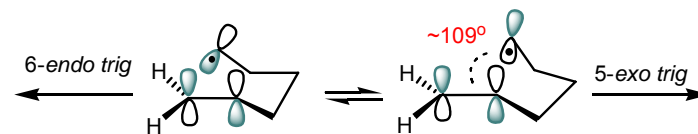
Baldwin Rules for Kinetically Controlled Ring Closures

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

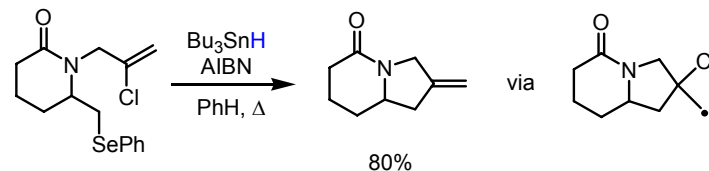
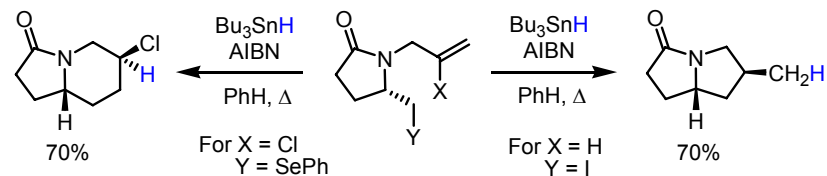


C-centered sp ³ Radicals	k_{25}^{exo} (s ⁻¹)	k_{25}^{endo} (s ⁻¹)	
	 2.3 × 10 ⁵	 4.1 × 10 ³	$E_a^{5exo} = 6.2 \text{ kcalmol}^{-1}$ $\Delta E_a = 1.7 \text{ kcalmol}^{-1}$
	 <0.7	 1.2 × 10 ²	 via 1,5-H shift
	 5.3 × 10 ³	 9.0 × 10 ³	
	 3.2 × 10 ⁶	 1 × 10 ⁵	
	 8.5 × 10 ⁶	 1 × 10 ⁵	
	 8.7 × 10 ²	 1.8 ×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

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

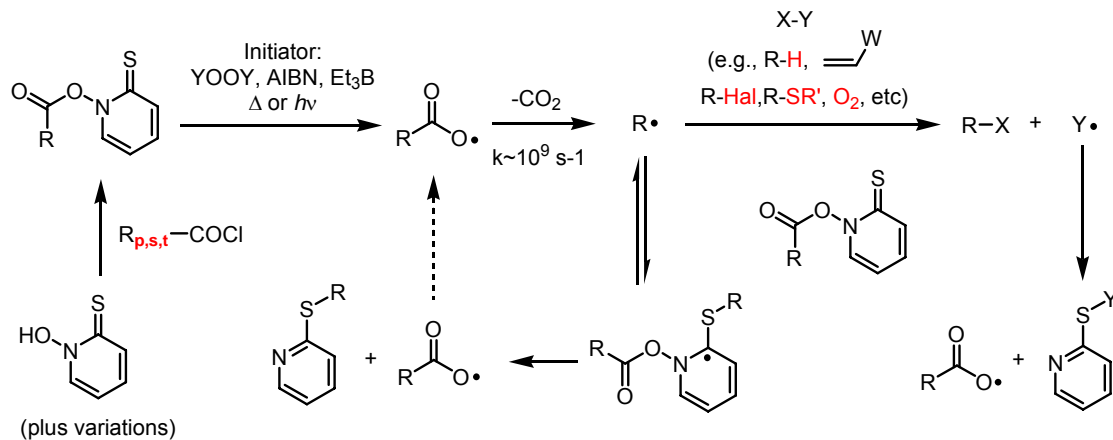


T 1992, 48, 2977
TL 1990, 31, 5397

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

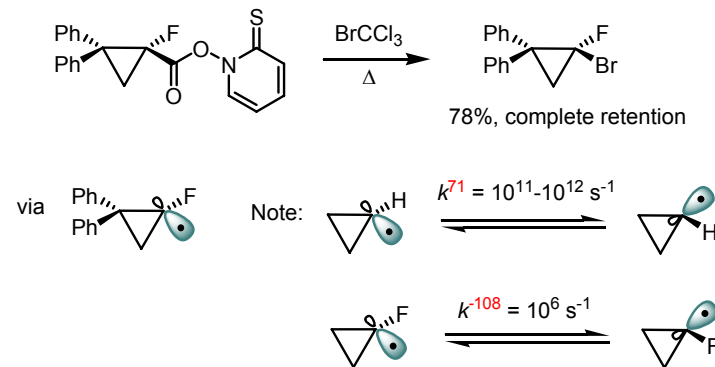
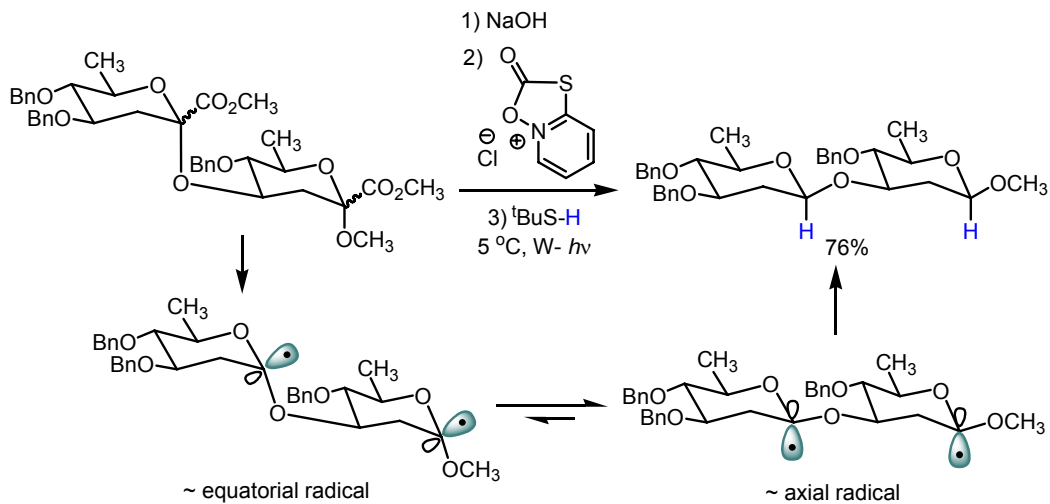
Selected Examples of Chain Reactions Based on Stannanes

6.4 – The Barton-McCombie Decarboxylation



R = CH ₃ (CH ₂) ₁₄	t _{1/2} = 31 min
	k = 4.2 × 10 ⁶ M ⁻¹ s ⁻¹
R = (CH ₃) ₂ CH, t _{1/2} = 26 min	
R = (CH ₃) ₃ C, t _{1/2} = 14 min	

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



JOC 1991, 56, 2193

TetLett 1991, 32, 2565

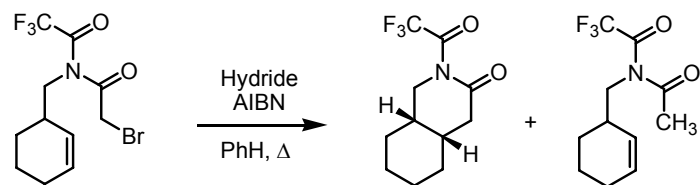
Organo-Silicon and -Germanium Hydrides

7 – Organo-Silicon and -Germanium Hydrides

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

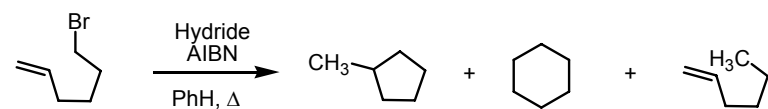
Reaction with Et ₃ Si·		Reaction with (Me ₃ Si) ₃ Si·	
R-X	k ²⁷ (M ⁻¹ s ⁻¹)	R-X·	k ²⁷ (M ⁻¹ s ⁻¹)
CH ₃ CH ₂ -I	4.3×10 ⁹	^c C ₆ H ₁₁ -OC(S)SCH ₃	1.1×10 ⁹
Ph-I	1.5×10 ⁹	(CH ₃) ₃ C-Br	1.2×10 ⁸
CH ₂ =CHCH ₂ Br	1.5×10 ⁹	ⁿ C ₁₀ H ₂₁ -SePh	9.6×10 ⁷
(CH ₃) ₃ C-Br	1.1×10 ⁹	^c C ₆ H ₁₁ -NC	4.7×10 ⁷
CH ₃ (CH ₂)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

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



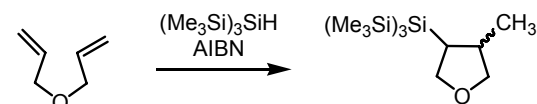
For Bu₃SnH 65% 24%
For Ph₃GeH 85% -

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



For Bu₃SnH 83% 1.2% 15%
For (Me₃Si)₃SiH 93% 2.0% 4.1%

AccChemRes **1992**, 25, 188



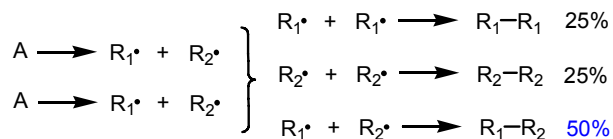
63% (cis:trans 3:1)

JOC **1992**, 57, 3994

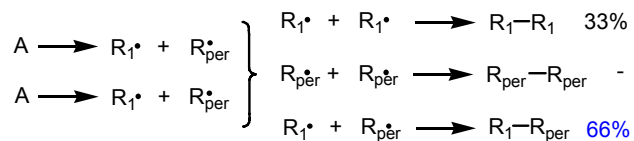
The Persistent Radical Effect

8 – The Persistent Radical Effect

Dimerization Reactions for Transient Radicals

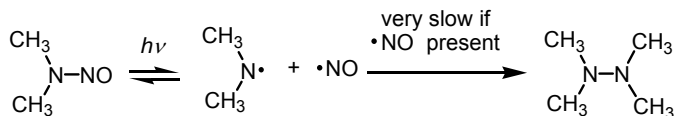


Dimerization Reactions Between a Transient and a Persistent Radical

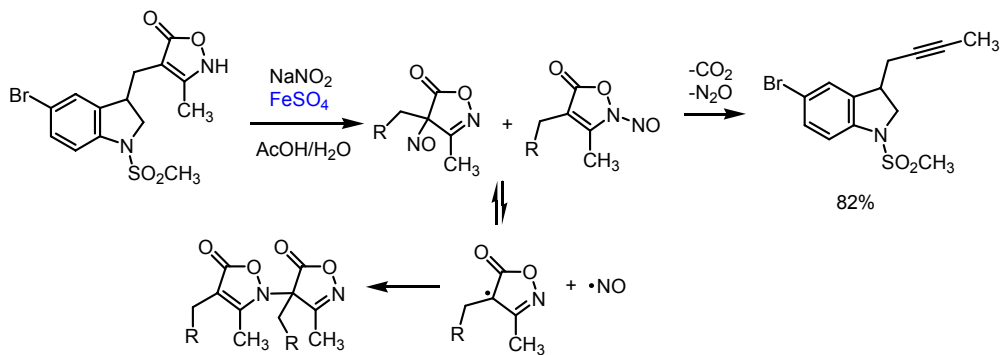


in practice almost total selectivity

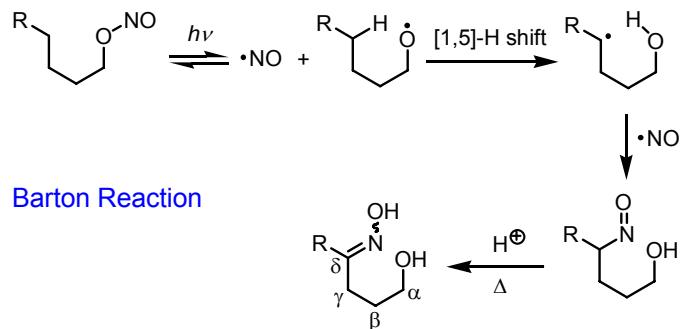
ChemRev **2001**, 101, 3581; *ChemEurJ* **2001**, 7, 1159



JACS **1986**, 108, 3925

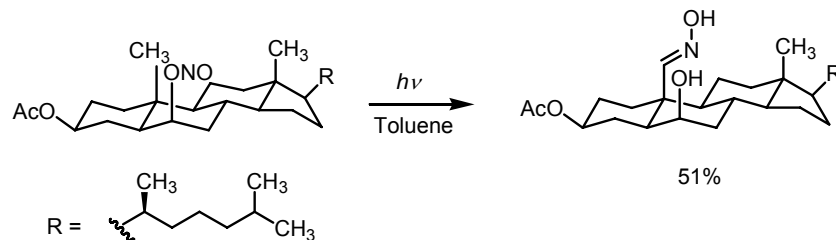


CC **2001**, 1304



Barton Reaction

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



Synthesis **1971**, 501