Radicals and Radical Anions

INTRODUCTION

Radicals are species that contain one or more unpaired electrons. They are encountered in many reactions used in chemical industry (e.g., the production of polyethylene), in the processes responsible for the spoiling of foods (e.g., autoxidation by molecular oxygen), and in many biological systems (e.g., signaling by nitrogen oxide, NO). Radical anions, as their name implies, are radical species that have an unpaired electron and a negative charge.

In chemical structures, the unpaired electron of a radical is represented by a dot. Radical mechanisms are depicted in one of two ways. Most commonly, each individual step of the mechanism is written without the use of arrows to show electron movement. The resulting series of equations shows the order of events, and it is assumed that one-electron transfers are taking place throughout. A second method uses curved, half-headed arrows ($\rightarrow$) to show electron movement. The half-headed arrow is used to denote movement of a single

electron, whereas the normal arrowhead is used to denote movement of a pair of electrons.

Various studies indicate that although radicals tend to be pyramidal, the pyramids are shallow and the barriers to inversion are low. This means that the stereochemical results of radical reactions are very similar to those of carbocations, in other words, stereochemistry is usually lost at a reactive center.

Whereas most carbon free radicals are highly reactive species, there are notable exceptions.

FORMATION OF RADICALS

Many radicals are produced by homolytic cleavage of bonds. The energy for this kind of bond breaking comes from thermal or photochemical energy or from electron-transfer reactions effected by either inorganic compounds or electrochemistry. These kinds of processes initiate reactions that proceed by a radical mechanism. Compounds that readily produce radicals are called initiators or free radical initiators.

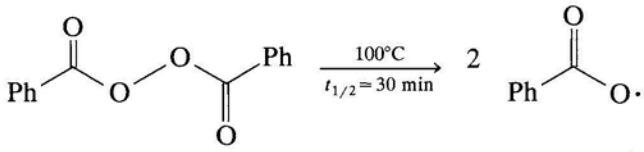
A. Homolytic Bond Cleavage

Radicals produced from chlorine and bromine can be generated photochemically and/or thermally. Because bromine atoms are less reactive than chlorine atoms, brominations are often done in the presence of both heat (Δ) and light ($h\nu$).

$$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$$

$$Br_2 \xrightarrow[\Delta]{h\nu} 2Br^{\bullet}$$

Many peroxides and azo compounds can be heated to generate radicals. Peroxides decompose readily because of the weak O—O bond, whereas azo compounds cleave readily because of the driving force provided by the formation of the stable nitrogen molecule. Common examples of these decompositions follow. (The $t_{1/2}$ is the time it takes one-half of the material to decompose.)



benzoyl peroxide

$$(CH_3)_3C{-}O{-}O{-}C(CH_3)_3 \xrightarrow[t_{1/2}=1\text{ h}]{150^\circ C} 2(CH_3)_3C{-}O\cdot$$

di-*t*-butyl peroxide

$$(CH_3)_2CN{=}NC(CH_3)_2 \xrightarrow[t_{1/2}=1\text{ h}]{85^\circ C} 2(CH_3)_2\dot{C}{-}CN + N_2$$

(CN groups on both carbons)

5-I

Example 5.1. ***Decomposition of AIBN [AIBN = azobisisobutyronitrile].***

Half-headed arrows show the movement of a single electron:

$$(CH_3)_2{-}C(C{\equiv}N:)\,{-}\,\ddot{N}{=}\ddot{N}\,{-}\,C(CH_3)_2(C{\equiv}N:) \xrightarrow{\Delta} 2(CH_3)_2{-}\dot{C}{-}C{\equiv}N: + :N{\equiv}N:$$

Why is the reaction shown in Example 5.1 a highly favorable process? **PROBLEM 5.1**

B. Hydrogen Abstraction from Organic Molecules

The carbon–hydrogen bond is relatively stable, so that direct formation of an organic radical by homolytic cleavage of a C—H bond is rarely observed. However, many radicals can remove hydrogen atoms from organic molecules to form carbon radicals. This process is known as hydrogen abstraction. For example,

$$F\cdot + CH_4 \longrightarrow HF + \cdot CH_3$$

Some radicals, like fluorine, are so reactive that they form radicals with almost any organic compound, whereas others are so stable that they can abstract hydrogen from very few organic compounds. An example of such a stable radical is **5-1**, formed from AIBN. When selectivity is desired in a radical initiator, a relatively stable radical like the one formed from AIBN is a good choice.

Rates of Hydrogen Abstraction and Relative Stability of Radicals

Because most radicals are electrophilic, the effects of structure on their rate of formation are very similar to those for the formation of carbocations. Thus, the rates of hydrogen abstraction are $1° < 2° < 3°$, corresponding to the order of stability of the resulting radicals: $1° < 2° < 3°$. Also, it is relatively easy to abstract a hydrogen from an allylic or benzylic position because the resulting radicals are stabilized by delocalization. In contrast, it is quite difficult to abstract vinyl and aromatic hydrogens because the electrophilicity of the resulting radicals is higher due to the higher *s* character of an sp^2-hybridized orbital relative to an sp^3-hybridized orbital. In these cases, the sp^2-hybridized orbital is perpendicular (orthogonal) to the π system; thus, the radical *cannot* be stabilized by resonance. Finally, it is difficult to abstract a hydrogen from the alcohol functional group. The resulting alkoxy radical is quite unstable due to the high electronegativity of oxygen.

The approximate relative stabilities of organic radicals are as follows:

$$\mathrm{Ph\cdot} < \mathrm{CH_2{=}CH\cdot} < \mathrm{RO\cdot} < \mathrm{RCH_2\cdot} < \mathrm{R_2CH\cdot} < \mathrm{R_3C\cdot} < \mathrm{PhCH_2\cdot} < \mathrm{RCH{-}CH_2\cdot}$$

C. Organic Radicals Derived from Functional Groups

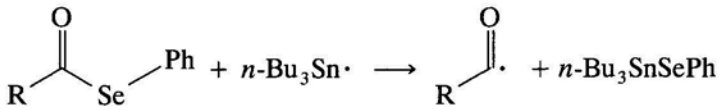
Reactive radicals are often produced by abstraction of a halogen atom from a substrate. A commonly used halogen-abstracting reagent is tri-*n*-butyltin radical, formed from tri-*n*-butyltin hydride using AIBN as an initiator. AIBN generates **5-1**, which abstracts a hydrogen atom from the tri-*n*-butyltin hydride, generating the tri-*n*-butyltin radical. This tin radical can abstract a halogen from a variety of substrates (e.g., alkyl, olefinic, or aryl chlorides, bromides, or iodides) to generate the corresponding radical and tri-*n*-butyltin halide.

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}{-}\mathrm{CN} + (n\text{-Bu})_3\mathrm{SnH} \longrightarrow (\mathrm{CH_3})_2\mathrm{CH}{-}\mathrm{CN} + (n\text{-Bu})_3\mathrm{Sn\cdot}$$

5-1

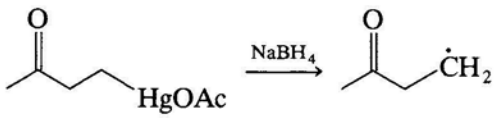
$$(n\text{-Bu})_3\mathrm{Sn\cdot} + \mathrm{RBr} \longrightarrow (n\text{-Bu})_3\mathrm{SnBr} + \mathrm{R\cdot}$$

Tri-*n*-butyltin radicals can also be used to generate radicals from selenium compounds. An example is the formation of acyl radicals from seleno esters.



Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1988**, *53*, 3377–3379.

Radicals can also be synthesized by the reduction of alkylmercury salts. For example, in the presence of sodium borohydride, compound **5-2** reacts to form the radical, **5-3**.



5-2 **5-3**

Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 931–934.

Despite their toxicity, alkylmercury salts have been used widely in research due to their versatility as synthetic intermediates.

3. RADICAL CHAIN PROCESSES

Most synthetically useful radical reactions occur as chain processes. A radical chain process is one in which many moles of product are formed for every mole of radicals produced. These chain processes include the following steps:

1. *Initiation.* One or more steps produce a radical from starting material.
2. *Propagation.* The radical enters a series of steps that results in the formation of product and a new radical that can start the series of propagation steps over again.
3. *Termination.* Removal of radicals from the propagation steps, thus ending a chain.

Initiation has been discussed in the previous section. In order for propagation to occur, many product molecules need to be formed from just one radical produced in the initiation step, and this occurs *only if the propagation steps are exothermic*. Termination steps include coupling, disproportionation, and abstraction. Abstraction by a chain-transfer agent removes a radical from a propagation step, and a new radical is generated in its place. If this newly generated radical is sufficiently stable, the chain transfer results in termination.

Hint 5.1

The propagation steps of a chain process must add up to the overall equation for the reaction. The overall equation will not contain any radicals. This means that the radical produced in the last propagation step must be the same as a reactant in the first propagation step.

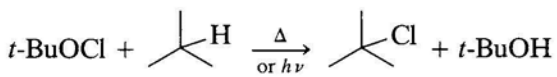
Hint 5.2 In radical reactions, the products are rarely generated by radical coupling.

Radical coupling reactions are those in which two radicals react to form a covalent bond. They are rarely a significant source of product, because both radicals are reactive intermediates and are present in extremely low concentrations. This means that the probability that they will react together is very small, and thus the rate of their reaction, which depends on their concentrations, is very low and other processes will compete effectively.

These various aspects of radical chain processes are illustrated in the following example.

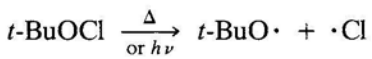
Example 5.2. ***Radical chain halogenation by t-butyl hypochlorite.***

The overall process is



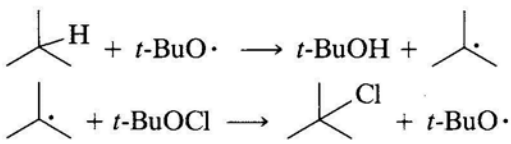
This can be broken down into initiation, propagation, and termination steps.

Initiation Step



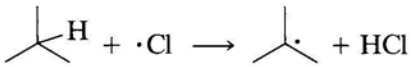
In continuing with the mechanism, consider *t*-BuO· to be the chain-carrying radical. This means that *t*-BuO· will be used up in the first propagation step but regenerated in the last propagation step. In this case, the last propagation step is the second step.

Propagation Steps



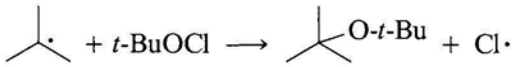
The radical formed in step 2 can start another reaction (step 1); that is why these processes are called chain processes. In this way, just one *t*-BuO· radical can initiate many sets of propagation steps. Addition of steps 1 and 2 gives the equation for the overall reaction; the radicals cancel when the addition is performed.

Is there another possible reaction pathway? Could the chlorine radical be the chain-carrying radical? If so, equation 3, an exothermic reaction, could represent one of the propagation steps.

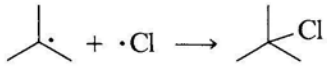
(3) 

Now a step must be found that forms the *t*-butyl chloride product *and* regenerates chlorine radical. This rules out equation 2 as a product-forming step because that reaction does not generate the same radical that is used in equation 3. Addition of equations 2 and 3 does not yield the overall reaction.

If we couple equation 3 with equation 4, we regenerate the chlorine radical but arrive at a different product for the reaction.

(4) 

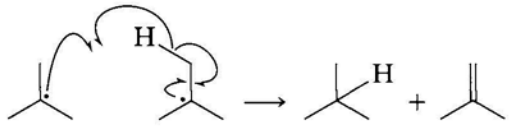
Another possible product-forming step would be reaction of the *t*-butyl radical with a chlorine atom. However, because this reaction removes radicals without forming new ones, it could not be one of the propagation steps of a chain process.



Termination Steps

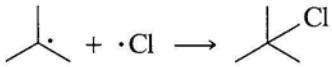
(1) Disproportionation

The disproportionation process involves the abstraction of hydrogen by one radical from another radical. Abstraction of a hydrogen atom from the carbon adjacent to the radical produces a double bond:

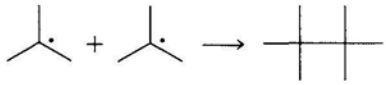


(2) Radical Coupling

Some possible coupling reactions follow:



t-BuO· + *t*-BuO· ⟶ *t*-BuOO-*t*-Bu



The following radical coupling does not affect the chain process because chlorine atoms are not involved in chain propagation.

$$\cdot Cl + \cdot Cl \longrightarrow Cl{-}Cl$$

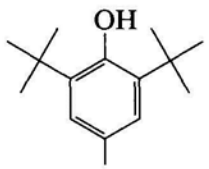
PROBLEM 5.2 **What other radical coupling reactions are possible for the reaction of *t*-butyl hypochlorite in Example 5.2?**

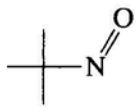
4. RADICAL INHIBITORS

Radical reactions can be slowed or stopped by the presence of substances called inhibitors.

Hint 5.3 A reaction that is slowed by the addition of a free radical inhibitor can be assumed to proceed by a radical mechanism.

Common radical inhibitors include 2,6-di-*t*-butyl-4-methylphenol (BHT), 2-nitroso-2-propane, and oxygen.

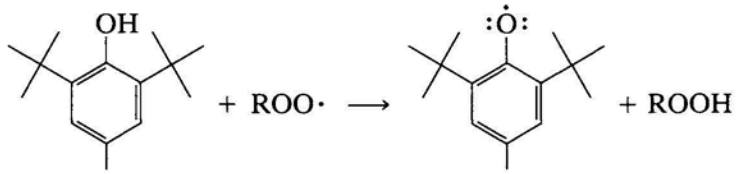




O_2

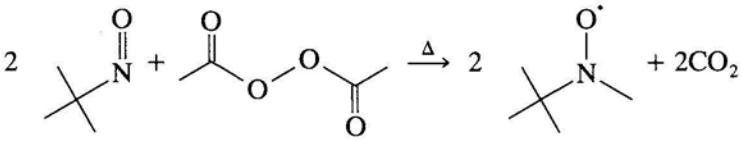
The acronym BHT stands for butylated hydroxytoluene, the common name for 2,6-di-*t*-butyl-4-methylphenol. It is used widely as an antioxidant in foodstuffs and food packaging. The reaction of oxygen with unsaturated fats gives, after several steps, alkylperoxy radicals (ROO·) that, upon further reaction, give smaller odiferous molecules that can ruin the palatability of foods. BHT acts as a scavenger for alkylperoxy radicals, ROO·, because hydrogen abstraction by ROO· gives the stable free radical, **5-4**. The hydroperoxide ROOH, which also is formed in the reaction, is much less reactive than ROO· and consequently causes much less oxidation. The new radical, **5-4**, which is formed from BHT, is relatively unreactive for two

reasons: (i) it is stabilized by resonance, and (ii) the groups attached to the ring sterically hinder further reaction.



5-4

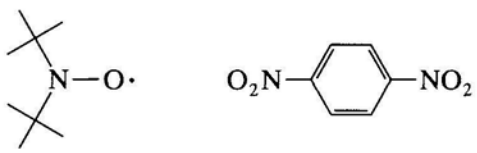
Radicals also can be trapped by addition to the nitroso group to form nitroxide radicals. In the following equation, diacetyl peroxide is a source of methyl radicals, which are trapped by the nitroso compound. (For further discussion of the fragmentation of radicals, see Section 7.)



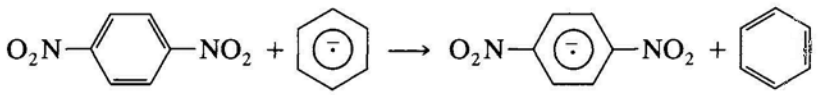
Oxygen can act as an inhibitor by reacting with radicals to produce less reactive hydroperoxyl radicals.

$$R\cdot + O_2 \longrightarrow ROO\cdot$$

Two compounds that effectively inhibit electron-transfer reactions are di-*t*-butyl nitroxide and 1,4-dinitrotoluene:



Transfer of an electron to 1,4-dinitrobenzene gives a radical anion so stable that it is unlikely to transfer an electron to anything else. The reaction of benzene radical anion with 1,4-dinitrobenzene proceeds to the right, because the radical anion of the 1,4-dinitrobenzene is much more stable than the radical anion of benzene itself.



Although 1,3-dinitrobenzene sometimes is used for the inhibition of electron-transfer reactions, it is not as effective as the 1,4-isomer, because its radical anion is not as stable (see Problem 1.5).

Nitroxides are also used to remove radical anions from a reaction sequence. For example, di-*t*-butyl nitroxide has often been used to inhibit the $S_{RN}1$ reaction (see Section 10). Apparently, nitroxides remove radicals via coupling reactions (Hoffmann, A. K.; Feldman, A. M.; Gelblum, E.; Hodgson, W. G. *J. Am. Chem. Soc.* **1964**, *86*, 639–646).

Hint 5.4 A radical reaction that is initiated only by light can be prevented by omitting light. In this case, any reaction that takes place in the dark must proceed by a nonradical pathway.

5. DETERMINING THE THERMODYNAMIC FEASIBILITY OF RADICAL REACTIONS

The bond dissociation energies in Table 5.1 can be used to determine the feasibility of radical reactions. In general, a radical process will give reasonable synthetic yields only if all propagation steps are exothermic, so that many propagation steps can occur before termination. The number of propagation steps per initiation step is the *chain length* of the reaction. Highly exothermic propagation steps involve highly reactive radicals, like alkyl radicals, and have a long chain length. More stable radicals, like aryl radicals, may fail to react until they encounter another radical. In this case, there is no chain reaction.

In Example 5.3, calculations show that the radical chlorination of 2-methylpropane by *t*-butyl hypochlorite is an energetically feasible process for the synthesis of *t*-butyl chloride.

Example 5.3. ***Determination of the enthalpy change in chlorination by t-butyl hypochlorite.***

Consider the reactions shown in Example 5.2. If both propagation steps are exothermic, the chain length will be long enough that the thermochemistry of the initiation step(s) is unimportant relative to that of the propagation steps.

We will calculate the enthalpy change for the reactions in the propagation steps. In equation 1, the C—H bond broken has a bond dissociation energy (BDE) of 91.0 kcal/mol, and the O—H bond formed has a BDE of 103 kcal/mol. Therefore, this first reaction is exothermic by 91 − 103 or −12 kcal/mol.

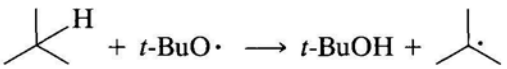
(1)  $\Delta H = -12$ kcal/mol

TABLE 5.1 Bond Dissociation Energies (BDEs, kcal/mol) at 298 K[a]

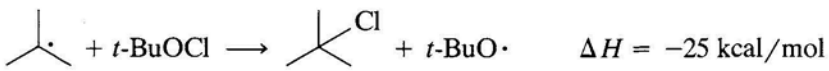
		Cl—Cl[b]	58	Br—Br[b]	46	I—I[b]	36	F—F[b]	37
		H—Cl[b]	103	H—Br[b]	87	H—I[b]	36	H—F[b]	135
CH_3—H	104	CH_3—Cl	73	CH_3—Br	70				
C_2H_5—H	98	C_2H_5—Cl	81	C_2H_5—Br	69	C_2H_5—I	53	C_2H_5—F	106
$CH_3CH_2CH_2$—H	98	*n*-C_3H_7—Cl	82	*n*-C_3H_7—Br	69				
$(CH_3)_2CH$—H	94.5	$(CH_3)_2CH$—Cl	81	$(CH_3)_2CH$—Br	68				
$(CH_3)_3C$—H	91.0	$(CH_3)_3C$—Cl	79	$(CH_3)_3C$—Br	63				
$PhCH_2$—H	85	$PhCH_2$—Cl	68	$PhCH_2$—Br	51				
CH_2=$CHCH_2$—H	85								
CCl_3—H	95.7	CCl_3—Cl	73	CCl_3—Br	54				
Ph—H	104			Ph—Br	71				
CH_2=CH—H	104								
$HOCH_2$—H	92								
CH_3O—H	102								
C_2H_5O—H	102								
i-C_3H_7O—H	103								
t-C_4H_9O—H	103	*t*-C_4H_9O—Cl	44[c]						
CH_3COO—H	112								
CH_3S—H	88								
PhS—H	75								
CH_3—CH_3	88								
PhCO—H	74	PhCO—Cl	74						
HCO—H	88								
CH_3CO—H	88								
CH_3COCH_2—H	92								

[a]All values from Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465–500, unless otherwise noted.

[b]*Handbook of Chemistry and Physics*, 63rd ed.; Weast, R. C.; Astle, M. J., Eds.; CRC Press: Boca Raton, FL, 1982–1983; F186ff.

[c]Walling, C.; Jacknow, B. B. *J. Am. Chem. Soc.* **1960**, *82*, 6108–6112.

For equation 2, the O—Cl bond broken has a BDE of 44 kcal/mol and the C—Cl bond formed has a BDE of 79 kcal/mol. Thus, the second reaction is exothermic by 44 − 79 kcal/mol or −35 kcal/mol. Because both reactions are substantially exothermic.

(2)  $\Delta H = -25$ kcal/mol

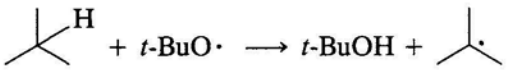
this should be a highly favorable process with a long chain length. The enthalpy change for the overall reaction is [(−12) + (−35)] or −47 kcal/mol.

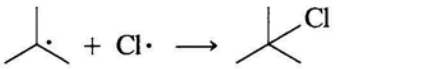
What are the defects in the following mechanism for the chlorination of 2-methylpropane by t-butyl hypochlorite? You will need to consider the **PROBLEM 5.3**

PROBLEM 5.3 *continued*

thermochemistry of the processes, as well as the fact that a chain process is not involved.

$$t\text{-BuOCl} \xrightarrow{\Delta} t\text{-BuO}\cdot + \cdot\text{Cl}$$





6. ADDITION OF RADICALS

Radical addition reactions are commonly used in organic synthesis. These additions range from the simple addition of halocarbons to π bonds to cyclization reactions with demanding stereoelectronic requirements.

A. Intermolecular Radical Addition

Hint 5.5

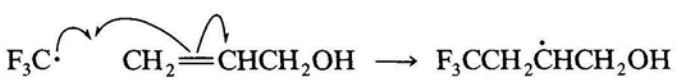
Common types of radicals that add to π bonds are those that can be generated from alkyl halides, mercaptans, thiophenols, thioacids, aldehydes, and ketones. Like the corresponding electrophilic additions to double bonds, many radical additions are either regiospecific or highly regioselective.

Example 5.4. ***Photochemical addition of trifluoroiodomethane to allyl alcohol.***

In the initation step of this reaction, light induces homolytic cleavage of the weak C—I bond.

$$CF_3I \xrightarrow{h\nu} \cdot CF_3 + \cdot I$$

The trifluoromethyl radical adds to the double bond, giving the most stable intermediate radical:



This radical then abstracts an iodide atom from trifluoroiodomethane to generate product and the chain-propagating radical, the trifluoromethyl radical.

$$F_3CCH_2\dot{C}HCH_2OH + ICF_3 \longrightarrow F_3CCH_2CHICH_2OH + \cdot CF_3$$

The product shown is the major regioisomer produced. For further details on this reaction, see Park, J. D.; Rogers, F. E.; Lacher, J. R. *J. Org. Chem.* **1961**, *26*, 2089–2095.

Examine the mechanistic steps for the reaction shown. **PROBLEM 5.4**

a. For each step, use half-headed arrows to show the movement of electrons, and dots to indicate all the unpaired electrons.

$$CH_2{=}CHC_6H_{13} + CBr_4 \xrightarrow[\Delta]{(PhCO_2)_2} Br_3CCH_2CHBrC_6H_{13}$$

Step 1

$$PhC(=O)-O-O-C(=O)Ph \longrightarrow 2PhC(=O)-O$$

Step 2

$$PhC(=O)-O + Br-CBr_3 \longrightarrow PhC(=O)-O-Br + CBr_3$$

Step 3

$$CBr_3 + CH_2{=}CHC_6H_{13} \longrightarrow Br_3CCH_2\dot{C}HC_6H_{13}$$

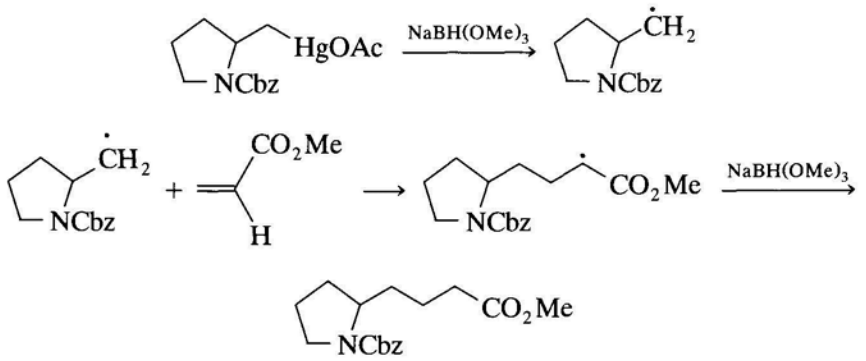
Step 4

$$Br_3CCH_2\dot{C}HC_6H_{13} + Br-CBr_3 \longrightarrow Br_3CCH_2CHBrC_6H_{13} + CBr_3$$

b. Identify the initation and propagation steps.
c. Why is the addition in step 3 regiospecific?

Example 5.5. ***Addition of a radical formed by reduction of a C—Hg bond.***

Addition of radicals formed from mercury compounds to alkenes often produce good-to-excellent yields. The following mechanism illustrates a reaction with a yield of 64%.



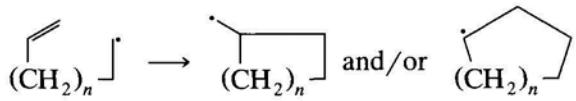
Note: Cbz = $-CO_2CH_2Ph$.

Danishefsky, S.; Taniyama, E.; Webb, R. R., II *Tetrahedron Lett.* **1983**, *24*, 11–14.

B. Intramolecular Radical Addition: Radical Cyclization Reactions

Generation of a radical in a molecule that contains a site of unsaturation presents an opportunity for cyclization. These types of radical cyclizations have been developed into very useful synthetic reactions. The synthetic utility of these cyclizations is enhanced by the ability to predict the regiochemistry of cyclization by applying the Baldwin rules. The Baldwin rules cover the formation of three- to seven-membered rings by various reactions and are based on consideration of both kinetic and thermodynamic factors. (See Beckwith, A. L. J.; Easton, D. J.; Serelis, A. K. *J. Chem. Soc., Chem. Commun.* **1980**, 482–483, and Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.)

The Baldwin rules distinguish two types of ring closure, *exo* and *endo*.



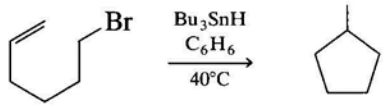
exo adduct *endo* adduct

With regard to radical cyclization, the most important guidelines are as follows:

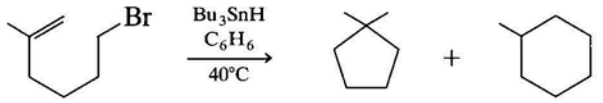
1. For unsubstituted ω-alkenyl radicals containing up to eight carbons, with the general structure previously shown, the preferred mode of cyclization is *exo*. (The symbol ω means that the alkene is at the terminus distant from the radical.) The reaction is controlled kinetically; the major product is the one that forms faster. The rates of formation of the two possible adducts are a result of the stereochemical requirements of their transition states. Often the *endo* product is more stable than the *exo* product. When this is the case, however, the more stable product is not the major product formed.

2. If the alkene is substituted at the nonterminal position, reaction to form the *exo* product is sterically hindered and the percentage of *endo* product increases. With substituted alkenes, the more stable product may predominate.

Example 5.6. ***exo and endo ring closure in radical cyclization.***



exo adduct

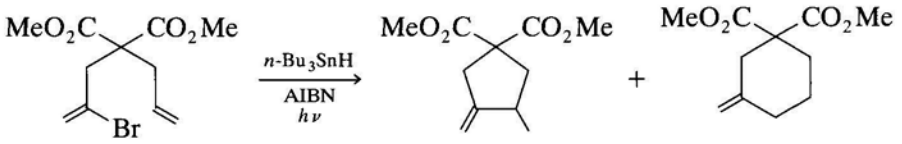


exo adduct *endo* adduct

Julia, M.; Descoins, C.; Baillarge, M.; Jacquet, B.; Uguen, D., Graeger, F. A. *Tetrahedron* **1975**, *31*, 1737–1745.

Example 5.7. ***Intramolecular cyclization of a vinyl radical.***

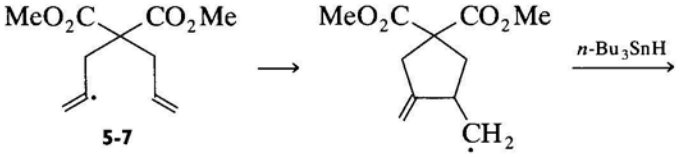
The overall reaction is as follows:



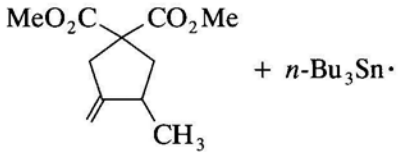
5-5 **5-6**

Stork, G.; Baine, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2321–2323.

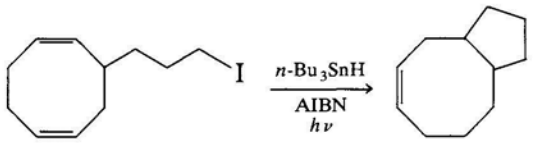
The vinyl radical, **5-7**, is formed by the process shown in Section 2. Cyclization of **5-7** can give an *exo* adduct or an *endo* adduct. The resulting radical abstracts hydrogen from n-Bu_3SnH to form products, **5-5** and **5-6**, as well as tri-*n*-butyltin radical, which continues the chain. As is predicted by the guidelines, the *exo* product (**5-5**) predominates, in this case by a factor of 2.



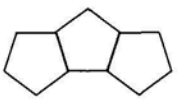
5-7



PROBLEM 5.5 **Consider the following reaction:**

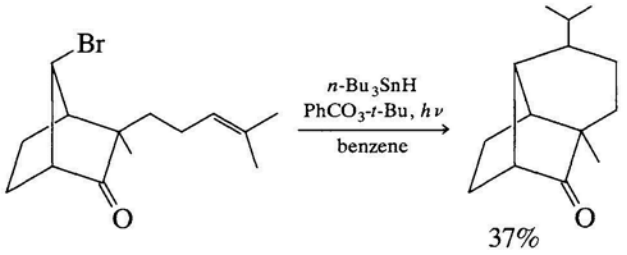


a. Write the initiation and propagation steps.
b. The following structure represents a minor product isolated from the reaction mixture. Show how it might have been formed.



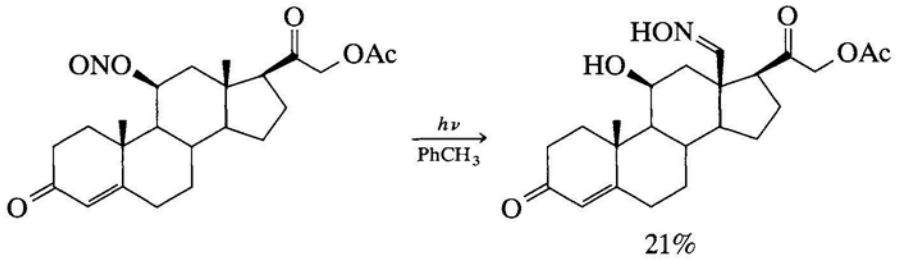
Winkler, J. D.; Sridar, V. *J. Am. Chem. Soc.* **1986**, *108*, 1708–1709.

PROBLEM 5.6 **Write the initiation and propagation steps for the following reaction:**



Hart, D. J. *Science* **1984**, *223*, 883–887.

PROBLEM 5.7 **Propose a mechanism for the following transformation.**



Barton, D. H. R.; Beaton, G. M.; Geller, L. E.; Bechet, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2640.