

ADVANCES IN  
FREE RADICAL CHEMISTRY

*Editor:* DENNIS D. TANNER

*Volume 1 • 1990*

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# ADVANCES IN FREE RADICAL CHEMISTRY

*A Research Annual*

*Editor:* DENNIS D. TANNER  
*Department of Chemistry*  
*Faculty of Science*  
*University of Alberta*

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VOLUME 1 • 1990



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ADVANCES IN  
FREE RADICAL CHEMISTRY

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# Introduction to the Series: An Editor's Foreword

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The field of organic chemistry has developed dramatically during the past forty years. Thus it appears to be an opportune time to publish a series of essays on various relevant themes in the 80s written by workers who are active in the discipline. This collection includes many of the important areas of current research interest. To cover such a broad area a very substantial effort is needed, as was the cooperation of a large number of colleagues and friends who have agreed to act as series editors. I have been gratified by the favorable response of research workers in the field to the invitation to contribute chapters in their own specialties. Each contributor has written a critical, lively and up-to-date description of his field of interest and competence, so that the chapters are not merely literature surveys. It is hoped that this new and continuing series will prove valuable to active researchers, and that many new ideas will be generated for future theoretical and experimental research. The wide coverage of material should be of interest to graduate students, postdoctoral fellows and those teaching specialized topics to graduate students.

Department of Chemistry  
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*Albert Padwa*  
*Consulting Editor*

# Preface

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Free radical chemistry has been an accepted area of research for almost 90 years. Initially, the subject was primarily the domain of physical chemists; however, from the mid-1930's organic, inorganic and bioorganic chemists have become active in the field. Treatises on radical reactions in the vapor phase [Rice and Rice, *The Aliphatic Free Radicals* [1935] and Steacie, *Atoms and Free Radicals* (1946)] and in solution [Walling, *Free Radicals in Solution* (1957)] were able to deal comprehensively with the existing literature. However, it soon became apparent that a systematic coverage of the field had become an almost impossible task for one author to attempt. Another approach was taken: to supply a collection of reviews of specific topics by experts in the field, and a number of excellent compendiums of this type have appeared in the last 25 years [*Methods in Free Radical Chemistry* (1969), ed. by Huyser; *Advances in Free-Radical Chemistry* (1965), ed. by Williams; *Free Radicals* (1973), ed. by Kochi]. In the last 10 or 15 years this branch of chemistry has expanded to such an extent that it is apparent that an even more limited approach has become desirable, and this series has been undertaken in the hope that it will fulfill this need.

The purpose of this series is to provide a vehicle in which investigators who have demonstrated a high degree of competence in some aspect of free radical chemistry can present a particular area of their interest. The topics covered will not be presented as a comprehensive review, but will be an attempt by the author to place his own work in perspective to that of other workers in the field.



The series will encompass a wide variety of topics which are of current interest, including reports of mechanistic studies using physical chemical methods, synthetic applications of radical reactions, and investigations of homolytic biochemical processes.

DENNIS D. TANNER  
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# Contents



<b>Contributors</b>	<b>ix</b>
<b>Introduction to the Series: An Editor's Foreword</b> <i>Albert Padwa</i>	<b>xi</b>
<b>Preface</b>	<b>xiii</b>
 <b>CHAPTER 1</b>	
<b>Free Radical Chain Reactions Involving Saturated and Unsaturated Alkylmercurials</b> <i>Glen A. Russell</i>	<b>1</b>
1. Introduction	1
2. Reactions Involving Hg(I) Intermediates	2
3. Self-Initiation of Free Radical Chain Processes with Hg(II) Substrates	10
4. Radical Attack at Mercury(II)	11
5. Formation of Donor and Acceptor Radicals by Addition of Alkyl Radicals to Polar Alkenes	14
5.1. Donor Species	14
5.2. Acceptor Species	17
6. Formation of Donor and Acceptor Radicals by $S_H2$ Reactions of Alkyl Radicals	22
6.1. Donor Radicals	22
6.2. Acceptor Radicals	24
7. Generation of Donor or Acceptor Radicals by an Addition-Elimination Process	28

7.1. Scope of the Reaction	28
7.2. Regiochemistry	36
7.3. Stereospecificity of Reactions of 1-Alkenyl Derivatives	38
7.4. Relative Reactivity of $\beta$ -Phenethenyl and $\beta$ -Phenethynyl Derivatives	40
7.5. Reactivities of Substrates Towards <i>tert</i> -Butyl Radicals	44
8. Free Radical Chain Reactions of Other Alkylmetal Reagents	44

## CHAPTER 2

### **Radical Cations as Reactive Intermediates in Aromatic Activation** **53** *J. K. Kochi*

1. Introduction	53
2. Electrophilic Aromatic Nitration	54
3. Aromatic Activation with Isoelectronic Mercury(II) and Thallium(III) Electrophiles	66
4. Oxidation of Arenes to Their Cation-Radicals	78
5. Oxidative Substitution of Methylarenes by Electron Transfer with Iron (III) Oxidants	82
6. Application of Marcus Theory to Electron Transfer Rates from Methylarenes	86
7. Reactivity of Aromatic Cation-Radicals. Nuclear vs Sidechain Substitution	93
8. Ambivalence of Aromatic Cation-Radicals. Ion-Pair vs Radical Pair Annihilation	101

## CHAPTER 3

### **Tandem Radical Cyclizations: A General Strategy for the Synthesis of Triquinane Sesquiterpenes** **121** *Dennis P. Curran*

1. Introduction	121
1.1. Triquinane Natural Products	122
1.2. Tin Hydride-Mediated Radical Cyclizations	123
1.3. The Tandem Radical Cyclization Strategy	125
2. Linear Triquinanes	127
2.1. Strategy	127
2.2. Model Studies	128
2.3. Linear Triquinane Hydrocarbons	131

3. Angular Triquinanes	146
3.1. Strategies and Model Reactions	146
3.2. Synthesis of Silphiperfolene	148
4. Propellane Triquinanes	151
4.1. Synthetic Strategies	151
4.2. Approaches to Modhephene	152
5. Conclusions	154

## CHAPTER 4

**Free Radical Thermochemistry** **159***Daniel D. M. Wayner and David Griller*

1. Introduction	159
2. Radical Buffers and Heats of Formation of Alkyl Radicals	161
3. The Appearance Energy Method	167
4. Photoacoustic Calorimetry	174
5. Electrochemistry of Free Radicals	182
6. Thermochemical Parameters for Ions and Radical Ions	185
7. Summary	189

## CHAPTER 5

**Nucleophilic Substitution by the  $S_{RN}1$  Mechanism on Alkyl Halides** **193***Roberto A. Rossi, Adriana B. Pierini, and  
Sara M. Palacios*

1. Introduction	193
2. Polar and SET Mechanisms as a Function of the Nucleophile-Substrate Pair	195
2.1. Theoretical Considerations	197
3. Perfluoroalkyl Iodides and Related Compounds	202
3.1. Reactions of $R_fI$ with Carbanions	202
3.2. Reactions of $R_fI$ with Thiols	208
3.3. Reaction of $R_fI$ with Other Nucleophiles	211
4. Bridgehead Halides	212
4.1. 1-Haladamantanes	213
4.2. 9-Bromo and 9,10-Dibromo Triptycenes	220
4.3. 1-Halo and 1,4-Dihalo Bicyclo[2.2.2]octanes	221
4.4. 4-Halotricyclanes	229
4.5. Concluding Remarks	230
5. Halocyclopropanes	231
5.1. 7-Bromonorcarane (7-Bromobicyclo[4.1.0]heptane)	232
5.2. Gem-Dihalocyclopropanes	233
6. Neopentyl Halides	237
7. Reactions of Organotin Alkali Metals with Alkyl Halides	244

## CHAPTER 6

**Two Decades of Spin Trapping****253***Edward G. Janzen and D. Larry Haire*

1. Introduction and Definitions	253
2. History and Development	254
3. ESR Spectroscopy and the Hyperfine Splitting Constants of Spin Adducts	255
4. Stability of Spin Traps and Spin Adducts	263
4.1. Dimerization	266
4.2. Disproportionation	267
4.3. Dissociative $\alpha$ -Cleavage	268
4.4. One Electron Redox Reactions	269
5. Rate Constants of Spin Trapping and Spin Adduct Decay	270
6. Factors Influencing Conformations and Hyperfine Splitting Constants of Spin Adducts	275
7. Solvent and Other Polar Effects	281
8. Spin Adduct Assignments—Chromatography and Mass Spectrometry	284
9. Artifacts in Spin Trapping	286
10. Summary and Future Directions	288

# Free Radical Chain Reactions Involving Saturated and Unsaturated Alkylmercurials

GLEN A. RUSSELL

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## 1. INTRODUCTION

Alkylmercurials ( $\text{RHgX}$ ,  $\text{R}_2\text{Hg}$ ) are readily available organometallic reagents possessing moderate reactivity in electrophilic substitution, and low reactivity in nucleophilic attack at carbon.<sup>1</sup> Pyrolysis of organomercurials has been utilized as a method to generate alkyl radicals useful in homolytic aromatic substitution processes,<sup>2</sup> and in defining a set of  $\sigma$ -constants for substituent stabilization of benzylic radicals.<sup>3</sup> One of the most widely studied chain reactions of an organomercurial has been the

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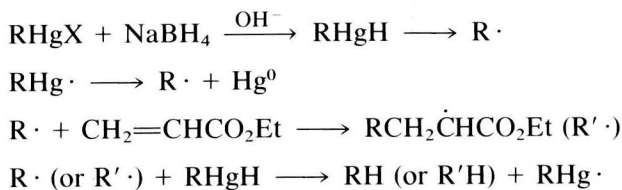
alkaline  $\text{NaBH}_4$  or  $\text{LiAlH}_4$  reduction of alkylmercury halides or carboxylates to yield the alkane,<sup>4-6</sup> or products derived from alkyl radical attack upon a suitable coreactant.<sup>7</sup> The reaction is widely applied for solvomer curation products.<sup>8-11</sup>

During the past several years, we have developed a series of free radical reactions in which  $\text{RHgX}$  or  $\text{R}_2\text{Hg}$  participate in the propagation step of a chain process which does not usually involve  $\text{RHg}\cdot$  as an intermediate, other than in the initiation step.<sup>12</sup> One group of these reactions involves the homolytic displacement of an alkyl radical from a mercury atom by an electron accepting carbon- or heteroatom-centered radical. This type of homolytic displacement is not unexpected since it has been recognized for some time in the cleavage of  $\text{R}_2\text{Hg}$  or  $\text{RHgX}$  by molecular halogens.<sup>13</sup> Competing electrophilic substitution by halogen can occur, but it has been possible to define conditions where either the free radical or ionic substitution will predominate.<sup>14</sup> Racemization of chiral alkyl groups in  $\text{R}_2\text{Hg}$  compounds is also recognized to occur by a radical chain mechanism in which the racemic  $\text{R}\cdot$  displaces a chiral group from  $\text{R}_2\text{Hg}$ .<sup>15</sup> Another group of reactions involves electron transfer to  $\text{RHgX}$  from an electron donating free radical or radical ion and leads directly to the alkyl radical, mercury metal and  $\text{X}^-$ .<sup>16</sup> This unusual reactivity of alkyl mercury(II) compounds towards both electron accepting and electron donating paramagnetic species is the focus of this chapter.

## 2. REACTIONS INVOLVING $\text{Hg(I)}$ INTERMEDIATES

Both the pyrolysis of  $\text{R}_2\text{Hg}$  and the alkaline  $\text{NaBH}_4$  reduction of  $\text{RHgCl}$  are reactions which involve unstable mercury(I) intermediates ( $\text{RHg}\cdot$ ) which readily dissociate into  $\text{R}\cdot$  and  $\text{Hg}\cdot$ .<sup>17</sup> In the borohydride reduction of  $\text{RHgX}$  ( $\text{X}$  = halide, carboxylate), attack of  $\text{R}\cdot$  upon  $\text{RHgH}$ ,<sup>18</sup> or of an adduct radical  $\text{RCH}_2\dot{\text{C}}\text{H}(\text{EWG})$  upon  $\text{RHgH}$ ,<sup>19,20</sup> occurs readily, Scheme 1.

### Scheme 1

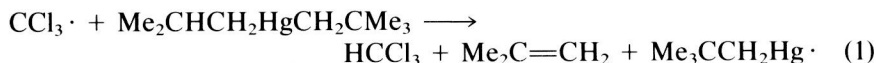


For such processes involving  $\text{RHg}\cdot$ , the structure of the alkyl group has little effect on the reactivity of its precursor; competitive reactions in-

volving *tert*-butyl and *n*-butylmercury chlorides with  $\text{NaBH}_4$  lead to approximately equal amounts of *tert*-butylation and *n*-butylation products, particularly when a reactive radicalphile (e.g.,  $\text{CH}_2=\text{C}(\text{Cl})\text{CN}$ ) is present to trap  $\text{R}\cdot$ .<sup>21,22</sup>

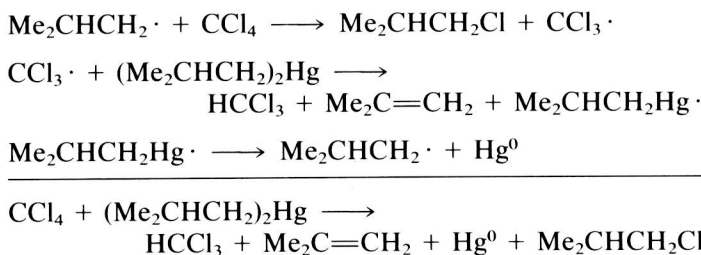
Further evidence for the formation of  $\text{R}\cdot$  in the  $\text{NaBH}_4$  reduction of  $\text{RHgCl}$  involves the cyclization of  $\text{R}\cdot = 5\text{-hexenyl}\cdot$  and the formation of alcohols in the presence of oxygen via the reaction  $\text{R}\cdot + \text{O}_2 \rightarrow \text{ROO}\cdot$ ;  $\text{ROO}\cdot + \text{RHgH} \rightarrow \text{RHg}\cdot + \text{ROOH}$ ;  $\text{ROOH} + \text{NaBH}_4 \rightarrow \text{ROH}$ .<sup>23,24</sup> A common intermediate ( $\text{R}\cdot$ ) is implicated by the similar distribution of products upon the reduction of *cis-exo*-2-acetoxynorbor-5-ene-3-mercuric bromide by  $\text{Bu}_3\text{SnH}$ ,  $\text{NaBH}_4$  or  $\text{HCuP}(\text{Bu})_3$ , and in the  $\text{Bu}_3\text{SnH}$  reduction of *endo*-2-chloro-*exo*-3-acetoxynorborn-5-ene.<sup>25</sup>

Another route to  $\text{RHg}\cdot$  intermediates involves a  $\beta$ -hydrogen abstraction from  $\text{R}_2\text{Hg}$ , Reaction 1.<sup>26</sup>



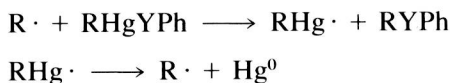
Reaction of dialkylmercurials with  $\text{CCl}_4$  with peroxide initiation is reported to involve Reaction 1 and the chain sequence of Scheme 2.

#### Scheme 2



Radicals do not usually attack halogen atoms in  $\text{RHgX}$  because of the strong mercury-halogen bond. However, photolysis of  $\text{RHgYPh}$  ( $\text{Y} = \text{S}, \text{Se}$ ) in benzene does yield  $\text{RYPh}$  and  $\text{Hg}^0$  by the steps of Scheme 3.<sup>27</sup>

#### Scheme 3 ( $\text{R} = \text{alkyl}$ )



Benzylmercurials  $(\text{PhCH}_2)_2\text{Hg}$ ,  $\text{PhCH}_2\text{HgYPh}$  (with  $\text{Y} = \text{S}, \text{Se}$ ), or  $\text{PhCH}_2\text{HgCl}$  also undergo a photostimulated free radical chain decom-

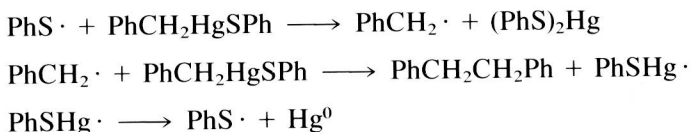


position whose rate is decreased by the presence of radical traps such as  $\text{Ph}_2\text{C}=\text{CH}_2$  or  $(t\text{-Bu})_2\text{NO}\cdot$ .<sup>28</sup> Attack of a benzyl radical in a  $\text{S}_{\text{H}}2$  fashion at the benzyl–mercury bond leads to bibenzyl and a  $\text{Hg}(\text{I})$  intermediate (Reaction 2).



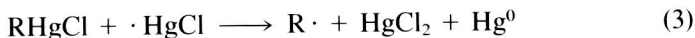
With  $\text{Z} = \text{PhCH}_2$  or  $\text{YPh}$  ( $\text{Y} = \text{S}, \text{Se}$ ) the  $\text{Hg}(\text{I})$  intermediate decomposes to  $\text{Hg}^0$  and  $\text{PhCH}_2\cdot$  or  $\text{PhY}\cdot$ . In the case of  $\text{Z} = \text{PhS}\cdot$ , the decomposition of  $\text{PhCH}_2\text{HgSPh}$  follows the steps of Scheme 4.

#### Scheme 4



In the presence of a very reactive  $\text{PhYYPh}$  ( $\text{Y} = \text{Se}$  or  $\text{Te}$ ), the benzyl radical can be trapped to yield  $\text{PhCH}_2\text{YPh}$  but  $\text{PhSSPh}$  is too unreactive to compete with  $\text{PhCH}_2\text{HgSPh}$  in Scheme 4.<sup>28</sup> In the presence of  $\text{BrCCl}_3$ ,  $(\text{PhCH}_2)_2\text{Hg}$  reacts by a chain mechanism to form  $\text{PhCH}_2\text{Br}$  and  $\text{PhCH}_2\text{CCl}_3$  in a nearly 1:1 ratio. Here,  $\text{CCl}_3\cdot$  takes the place of  $\text{PhCH}_2\cdot$  in Reaction 2 to yield  $\text{PhCH}_2\text{CCl}_3$  and  $\text{PhCH}_2\cdot$  which attacks  $\text{BrCCl}_3$  to give  $\text{PhCH}_2\text{Br}$  and  $\text{CCl}_3\cdot$ .

Mercury(I) halide intermediates will continue chain reactions by  $\text{S}_{\text{H}}2$  reaction with reagents such as  $\text{RY}-\text{YR}$  ( $\text{Y} = \text{S}, \text{Se}, \text{Te}$ ),  $\text{Cl}-\text{SO}_2\text{Ph}$ ,  $\text{PhSe}-\text{SO}_2\text{Ph}$ , or  $\text{Br}-\text{CCl}_3$ . The monomeric  $\cdot\text{HgCl}$  also reacts with  $\text{RHgCl}$  according to Reaction 3. Reaction 3 is a process where rate is controlled by the stability of the incipient alkyl radical.



Thus, in competitive experiments with mixtures of two alkyl mercury halides, the relative reactivities of  $\text{R} = t\text{-Bu}(1.0):c\text{-C}_6\text{H}_{11}(0.01):n\text{-Bu}(0.0001)$  are observed in  $\text{PhH}$  at  $40^\circ\text{C}$ .<sup>29</sup>

$\text{Hg}(\text{I})$  intermediates can also be formed by a free radical addition–elimination sequence from  $\text{R}'\text{CH}=\text{C}(\text{H})\text{HgZ}$  ( $\text{R}' = t\text{-Bu}, \text{Ph}, \text{Cl}$ ).<sup>30–33</sup> In the case where  $\text{Z} = \text{halogen}$ , the  $\text{XHg}\cdot$  intermediate will undergo electron transfer with anions such as  $\text{PhSO}_2^-$ ,  $(\text{EtO})_2\text{PO}^-$ , or  $\text{PhPO}(\text{Bu})\text{O}^-$  to yield  $\text{Hg}^0$ ,  $\text{X}^-$ , and the radical derived from the anion (Reaction 4).



Addition of  $\text{A}\cdot$  in a regioselective manner to the starting vinylmercury halide will regenerate  $\cdot\text{HgX}$  (Scheme 5).