ADVANCES IN
FREE RADICAL CHEMISTRY

Editor: DENNIS D. TANNER

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Department of Chemistry
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LIST OF CONTRIBUTORS

Dennis P. Curran	Department of Chemistry University of Pittsburgh Pittsburgh, Pennsylvania
David Griller	Division of Chemistry National Research Council of Canada Ottawa, Ontario Canada
Larry Haire	Department of Chemistry and Biochemistry Guelph-Waterloo Centre for Graduate Work in Chemistry University of Guelph Guelph, Ontario Canada
Edward G. Janzen	Director Magnetic Resonance Imaging Facility University of Guelph Guelph, Ontario Canada
J. K. Kochi	Department of Chemistry University of Houston Houston, Texas
Sara M. Palacios	Departamento de Quimica Organica Facultad de Ciencias Quimicas Universidad Nacional de Cordoba Cordoba, Argentina

Adriana B. Pirini	Departamento de Quimica Organica Faculdad de Ciencias Quimicas Universidad Nacional de Cordoba Cordoba, Argentina
Roberto A. Rossi	Departamento de Quimica Organica Facultad de Ciencias Quimicas Universidad Nacional de Cordoba Cordoba, Argentina
Glen A. Russell	Department of Chemistry Iowa State University Ames, Iowa
Daniel D. M. Wayner	Division of Chemistry National Research Council of Canada Ottawa, Ontario Canada

Introduction to the Series: An Editor's Foreword

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
Emory University
Atlanta, Georgia

Albert Padwa
Consulting Editor

Preface

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
University of Alberta
Edmonton, Alberta

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Free Radical Chain Reactions Involving Saturated and Unsaturated Alkylmercurials

GLEN A. RUSSELL

1. INTRODUCTION

Alkylmercurials (RHgX, R_2Hg) are readily available organometallic reagents possessing moderate reactivity in electrophilic substitution, and low reactivity in nucleophilic attack at carbon.[1] Pyrolysis of organomercurials has been utilized as a method to generate alkyl radicals useful in homolytic aromatic substitution processes,[2] and in defining a set of σ-constants for substituent stabilization of benzylic radicals.[3] One of the most widely studied chain reactions of an organomercurial has been the

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alkaline $NaBH_4$ or $LiAlH_4$ reduction of alkylmercury halides or carboxylates to yield the alkane,[4–6] or products derived from alkyl radical attack upon a suitable coreactant.[7] The reaction is widely applied for solvomercuration products.[8–11]

During the past several years, we have developed a series of free radical reactions in which RHgX or R_2Hg participate in the propagation step of a chain process which does not usually involve $RHg\cdot$ as an intermediate, other than in the initiation step.[12] 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 R_2Hg or RHgX by molecular halogens.[13] 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.[14] Racemization of chiral alkyl groups in R_2Hg compounds is also recognized to occur by a radical chain mechanism in which the racemic $R\cdot$ displaces a chiral group from R_2Hg.[15] Another group of reactions involves electron transfer to RHgX from an electron donating free radical or radical ion and leads directly to the alkyl radical, mercury metal and X^-.[16] 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 Hg(I) INTERMEDIATES

Both the pyrolysis of R_2Hg and the alkaline $NaBH_4$ reduction of RHgCl are reactions which involve unstable mercury(I) intermediates ($RHg\cdot$) which readily dissociate into $R\cdot$ and $Hg\cdot$.[17] In the borohydride reduction of RHgX (X = halide, carboxylate), attack of $R\cdot$ upon RHgH,[18] or of an adduct radical $RCH_2\dot{C}H(EWG)$ upon RHgH,[19,20] occurs readily, Scheme 1.

Scheme 1

$$RHgX + NaBH_4 \xrightarrow{OH^-} RHgH \longrightarrow R\cdot$$

$$RHg\cdot \longrightarrow R\cdot + Hg^0$$

$$R\cdot + CH_2{=}CHCO_2Et \longrightarrow RCH_2\dot{C}HCO_2Et\ (R'\cdot)$$

$$R\cdot\ (\text{or } R'\cdot) + RHgH \longrightarrow RH\ (\text{or } R'H) + RHg\cdot$$

For such processes involving $RHg\cdot$, the structure of the alkyl group has little effect on the reactivity of its precursor; competitive reactions involving *tert*-butyl and *n*-butylmercury chlorides with $NaBH_4$ lead to approximately equal amounts of *tert*-butylation and *n*-butylation products, particularly when a reactive radicalphile (e.g., $CH_2{=}C(Cl)CN$) is present to trap $R\cdot$.[21,22]

Further evidence for the formation of $R\cdot$ in the $NaBH_4$ reduction of RHgCl involves the cyclization of $R\cdot$ = 5-hexenyl· and the formation of alcohols in the presence of oxygen via the reaction $R\cdot + O_2 \rightarrow ROO\cdot$; $ROO\cdot + RHgH \rightarrow RHg\cdot + ROOH$; $ROOH + NaBH_4 \rightarrow ROH$.[23,24] A common intermediate ($R\cdot$) is implicated by the similar distribution of products upon the reduction of *cis-exo*-2-acetoxynorbor-5-ene-3-mecuric bromide by Bu_3SnH, $NaBH_4$ or $HCuP(Bu)_3$, and in the Bu_3SnH reduction of *endo*-2-chloro-*exo*-3-acetoxynorborn-5-ene.[25]

Another route to $RHg\cdot$ intermediates involves a β-hydrogen abstraction from R_2Hg, Reaction 1.[26]

$$CCl_3\cdot + Me_2CHCH_2HgCH_2CMe_3 \longrightarrow HCCl_3 + Me_2C{=}CH_2 + Me_3CCH_2Hg\cdot \qquad (1)$$

Reaction of dialkylmercurials with CCl_4 with peroxide initiation is reported to involve Reaction 1 and the chain sequence of Scheme 2.

Scheme 2

$$Me_2CHCH_2\cdot + CCl_4 \longrightarrow Me_2CHCH_2Cl + CCl_3\cdot$$

$$CCl_3\cdot + (Me_2CHCH_2)_2Hg \longrightarrow HCCl_3 + Me_2C{=}CH_2 + Me_2CHCH_2Hg\cdot$$

$$Me_2CHCH_2Hg\cdot \longrightarrow Me_2CHCH_2\cdot + Hg^0$$

$$CCl_4 + (Me_2CHCH_2)_2Hg \longrightarrow HCCl_3 + Me_2C{=}CH_2 + Hg^0 + Me_2CHCH_2Cl$$

Radicals do not usually attack halogen atoms in RHgX because of the strong mercury–halogen bond. However, photolysis of RHgYPh (Y = S, Se) in benzene does yield RYPh and Hg^0 by the steps of Scheme 3.[27]

Scheme 3 (R = alkyl)

$$R\cdot + RHgYPh \longrightarrow RHg\cdot + RYPh$$

$$RHg\cdot \longrightarrow R\cdot + Hg^0$$

Benzylmercurials $(PhCH_2)_2Hg$, $PhCH_2HgYPh$ (with Y = S, Se), or $PhCH_2HgCl$ also undergo a photostimulated free radical chain decomposition whose rate is decreased by the presence of radical traps such as $Ph_2C{=}CH_2$ or $(t\text{-Bu})_2NO\cdot$.[28] Attack of a benzyl radical in a S_H2 fashion at the benzyl–mercury bond leads to bibenzyl and a Hg(I) intermediate (Reaction 2).

$$PhCH_2\cdot + PhCH_2HgZ \longrightarrow PhCH_2CH_2Ph + \cdot HgZ \qquad (2)$$

With Z = $PhCH_2$ or YPh (Y = S, Se) the Hg(I) intermediate decomposes to Hg^0 and $PhCH_2\cdot$ or $PhY\cdot$. In the case of Z = $PhS\cdot$, the decomposition of $PhCH_2HgSPh$ follows the steps of Scheme 4.

Scheme 4

$$PhS\cdot + PhCH_2HgSPh \longrightarrow PhCH_2\cdot + (PhS)_2Hg$$

$$PhCH_2\cdot + PhCH_2HgSPh \longrightarrow PhCH_2CH_2Ph + PhSHg\cdot$$

$$PhSHg\cdot \longrightarrow PhS\cdot + Hg^0$$

In the presence of a very reactive PhYYPh (Y = Se or Te), the benzyl radical can be trapped to yield $PhCH_2YPh$ but PhSSPh is too unreactive to compete with $PhCH_2HgSPh$ in Scheme 4.[28] In the presence of $BrCCl_3$, $(PhCH_2)_2Hg$ reacts by a chain mechanism to form $PhCH_2Br$ and $PhCH_2CCl_3$ in a nearly 1:1 ratio. Here, $CCl_3\cdot$ takes the place of $PhCH_2\cdot$ in Reaction 2 to yield $PhCH_2CCl_3$ and $PhCH_2\cdot$ which attacks $BrCCl_3$ to give $PhCH_2Br$ and $CCl_3\cdot$.

Mercury(I) halide intermediates will continue chain reactions by S_H2 reaction with reagents such as RY–YR (Y = S, Se, Te), Cl–SO_2Ph, PhSe–SO_2Ph, or Br–CCl_3. The monomeric $\cdot HgCl$ also reacts with RHgCl according to Reaction 3. Reaction 3 is a process where rate is controlled by the stability of the incipient alkyl radical.

$$RHgCl + \cdot HgCl \longrightarrow R\cdot + HgCl_2 + Hg^0 \qquad (3)$$

Thus, in competitive experiments with mixtures of two alkyl mercury halides, the relative reactivities of R = t-Bu(1.0):c-C_6H_{11}(0.01):n-Bu(0.0001) are observed in PhH at 40°C.[29]

Hg(I) intermediates can also be formed by a free radical addition–elimination sequence from $R'CH{=}C(H)HgZ$ (R' = t-Bu, Ph, Cl).[30–33] In the case where Z = halogen, the $XHg\cdot$ intermediate will undergo electron transfer with anions such as $PhSO_2^-$, $(EtO)_2PO^-$, or $PhPO(Bu)O^-$ to yield Hg^0, X^-, and the radical derived from the anion (Reaction 4).

$$A^- + \cdot HgX \longrightarrow A\cdot + Hg^0 + X^- \qquad (4)$$

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