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Advances in Physical Organic Chemistry

Volume 36

Edited by

T. T. TIDWELL

Department of Chemistry
University of Toronto
Toronto
Ontario M5S 3H6, Canada

J. P. RICHARD

Department of Chemistry
University of Buffalo, SUNY
Buffalo NY 14260-3000, USA

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Advances in Physical Organic Chemistry

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Editor's preface

This year there is a new co-editor of the series, Professor John Richard of the State University of New York at Buffalo. With two editors, there is a wider range of expertise available, thus providing more opportunity for soliciting manuscripts that cover the full breadth of topics included within the field of Physical Organic Chemistry. It is planned to expand the Board of Editors as well, as these individuals help to ensure that the subject matter covered includes a wide range of topics. We intend to continue to solicit contributors not only from around the world, but from the increasingly diversified group of laboratories at which modern aspects of the subject are pursued.

In 2001 the new millennium officially begins, and the current volume includes a retrospective of one of the major topics in Physical Organic Chemistry in the 20th Century, namely free radical reactivity. There is a fascinating report by the late Lennart Eberson, who was a valued member of the Board of Editors, concerning the reasons that the many nominations of Moses Gomberg for the Nobel Prize in Chemistry were not successful. In 1900 Gomberg made the bold claim that he had prepared a stable free radical, namely triphenylmethyl, and this proposal was shown, after great discussion, to be correct, and sparked an outpouring of chemical creativity that continues unabated into the 21st Century. Eberson reveals why the Nobel Prize Committee on Chemistry missed the opportunity to recognize Gomberg's great insight, through a combination of a lack of appreciation on the part of the Committee, and unfortunate timing. This essay was Eberson's last major contribution, and was sent to the Editor shortly before his untimely death. We wish to acknowledge the assistance of Anne Wiktorsson at the Center for History of Science, The Royal Academy of Sciences, Stockholm, in the editing of this manuscript. The Nobel prizes exert a profound influence on the conduct of science, and it is helpful for the scientific community to be aware of how these are decided. Eberson was uniquely suited for this task, as he was Chair of the Nobel Committee on Chemistry, a free radical chemist himself who could easily read the Nobel archives in his native Swedish, and he possessed a lucid style of writing.

Accompanying this article, Tidwell has contributed a summary of the development of free radical chemistry from the work of Gomberg through the year 2000. Free radicals have been featured in *Advances in Physical Organic Chemistry* since Volume 1, and all of the chapters in the current volume deal with this topic to some degree.

The other chapters in Volume 36 include a report on the kinetics and mechanism of reductive bond dissociations, by Maran, Wayner, and

Workentin. This complements other chapters in Volume 35 that dealt with electron transfer processes, and also highlights the work of Eberson.

The two other Chapters deal with reactive intermediates, specifically N-arylnitrenium ions by Novak and Rajagopal, and phenylnitrenes by Gritsan and Platz. These species have long been known, and nitrenium ions and arylnitrenes are interconvertible by proton transfer. These nitrogen analogs of the more familiar carbocations and carbenes share the property of existing as singlets or triplets, but have not received the attention of their carbon-centered cousins. Particularly in the case of arylnitrenes, their study is a challenging problem, while arylnitrenium ions may be formed under surprisingly mild conditions. With the realization that nitrenium ions are active carcinogens, and that nitrenium ions can form from nitrenes, these species are receiving increasing attention. Because of the different spin states of nitrenes and the rapidity of their interconversion, it is only with the availability of very fast spectroscopic techniques that these species may be studied in detail. These chapters, by leading practitioners in the areas, provide an up-to-date summary of the investigations of these species.

The editors will continue to strive to highlight important areas of the field in a timely fashion at reasonable cost. Suggestions for further topics for coverage are always welcome.

J. P. Richard, T. T. Tidwell

Contributors to Volume 36

Lennart Eberson Department of Chemistry, Lund University, Lund, Sweden

Nina Gritsan Institute of Chemical Kinetics and Combustion, 630090, Novosibirsk, Russia

Flavio Maran Dipartimento di Chimica Fisica, Universita di Padova, via Loredan 2, 35131, Padova, Italy

Michael Novak Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, USA

Matthew S. Platz Department of Chemistry, Newman & Wolfrom Lab. of Chemistry, Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210 1173, USA

Sridharan Rajagopal Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, USA

Thomas Tidwell Department of Chemistry, University of Toronto, Ontario, M5S 3H6, Canada

Daniel D.M. Wayner Molecular Interfaces Program, Steacie Institute for Molecular Sciences, National Research Council, Ottawa, Ontario, K1A 0R6, Canada

Mark S. Workentin Department of Chemistry, The University of Western Ontario, London, Ontario, N6A 5B7

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The Gomberg Century: Free Radicals 1900–2000

THOMAS T. TIDWELL

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada

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1 Introduction

MOSES GOMBERG AND THE TRIPHENYLMETHYL RADICAL

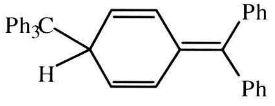
The proposal[1] by Moses Gomberg in 1900 of the formation of the stable and persistent free radical triphenylmethyl was a major landmark that set the stage for the rapid development of free radical chemistry in the 20th Century. Prior to Gomberg's proposal, the theory of free radicals had risen to prominence and then fallen into disrepute, but his work immediately attracted the attention of the world chemical community, and led to the ultimate acceptance of this once controversial concept.

Gomberg treated triphenylmethyl chloride with silver or zinc metal and obtained a colored solution which reacted with oxygen to yield a peroxide.[1] The species in solution was confidently identified by Gomberg as the triphenylmethyl radical **1**, and he published his discovery in both German and English, which ensured its wide exposure to chemists worldwide. Upon removal of the solvent, a solid dimer was formed, for which the symmetrical structure **2** and the unsymmetrical structure **3** were given serious consideration over the next decade, while the peroxide was assigned as **4**. Wilhelm Schlenk and co-workers in 1910 obtained tris(4-biphenylyl)methyl (**5**) as a deeply colored solid which was almost completely dissociated in solution, and thus removed all doubt as to the existence of **1**.[2] As recounted by McBride,[3] the wrong structure for the dimer, namely the head-to-head structure **2,** became accepted for half a century, before this was corrected to the unsymmetrical structure **3** based on spectroscopic data.[4] Techniques were widely available that would have permitted correction of this structure well before 1967.

$$Ph_3CCl \xrightarrow[-AgCl]{Ag} \underset{\mathbf{1}}{Ph_3C\,\bullet} \xrightarrow{O_2} \underset{\mathbf{4}}{Ph_3COOCPh_3} \qquad (1)$$

Ph_3CCPh_3

2



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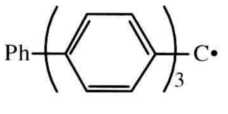

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OVERVIEW OF FREE RADICALS IN THE 20TH CENTURY

On the occasion of the centennial of Gomberg's discovery it is appropriate to look back over the subsequent development of the field, highlighting some of the advances that have been made. Such a survey must of necessity be cursory, as a comprehensive review would occupy many volumes. The goal of this essay is to note the more prominent original contributions, and for some examples to cite recent advances of these themes. It is also of interest to note missed opportunities, or errant interpretations. This is not to belittle the pioneers involved, but to illustrate that science is a human activity, and progress is based on individual decisions that may favor certain areas rather than others. The discussion is roughly chronological, and is intended to show the evolution of new ideas. Much has been excluded, either by design or oversight, and the author is responsible if important topics or contributors have been unfairly neglected.

The history of the radical concept prior to Gomberg in the 19th Century has been described by Ihde,[5,6] who recounted how the existence of free radicals had gained strong support from the work of Kolbe[7] in 1849, who reported the electrolytic decarboxylation of carboxylic acids which apparently gave free radicals such as $CH_3\cdot$. However, the development of valence theory shortly thereafter, particularly the concept of the tetravalency of carbon, led to the recognition that these "radicals" were dimers, and caused the general abandonment of free radicals as organic intermediates. However, in 1891 Walker and Crum Brown reintroduced the idea of electrolysis as involving radicals (equation 2),[8] and Nef in 1897[9] formulated a theory of organic reactivity with a major role for divalent carbon. Thus there were premonitions of the revival of the free radical concept.

$$\mathrm{RCO_2H} \xrightarrow{-e^-,\,-H^+} \mathrm{RCO_2}\bullet \xrightarrow{-CO_2} \mathrm{R}\bullet \longrightarrow \mathrm{RR} \qquad (2)$$

The history of free radicals in the 20th Century may be conveniently divided into thirds, with the dividing points being the General Discussion of the Faraday Society held at the University of Cambridge from 28–30 September, 1933, and published in 1934,[10] and the 1966 International Free Radical Conference in Ann Arbor, Michigan.[11] At the close of the century, from 25–29 June, 2000, there was another conference in Ann Arbor marking the Centennial of Gomberg's original discovery, which was designated as an International Chemical Landmark.[12] Brief summaaries of this development have appeared.[13,14]

The Cambridge meeting had a distinctly physical orientation, and those in attendance included Gomberg and many pioneers of the subject and other prominent figures, including F. Paneth, K. Ziegler, M. Polanyi, E. Rabinowitch, C.P. Snow, E. Hückel, and C.K. Ingold. Besides the discovery of triphenylmethyl, other developments at that time included the elucidation of the free radical chain reaction of H_2 with Br_2, the demonstration of nitrogen, oxygen, and sulfur-centered organic radicals, the discovery of ketyl and nitroxyl radicals, the elucidation of free radical mechanisms for thermal and photochemical reactions of the halogens, the generation of free alkyl radicals by Paneth, free radical polymerization, and the formation of free radicals from azoalkane thermolysis and ketone photolysis. Later, Faraday Discussions on free radicals were held in London, in 1947,[15] on "The Labile Molecule", and then in Toronto in 1952.[16] The latter meeting was notable for the participation of five future Nobel laureates (R.G.W. Norrish, G. Porter, J. Polanyi, Linus Pauling, and Gerhard Herzberg).

At the Conference on Free Radicals in Ann Arbor in 1966, plenary lecturers included C. Walling, P.D. Bartlett, K.U. Ingold, S. Hunig, and Glen Russell.[12] Further advances up to this time included a thorough understanding of the reactivity of many free radical initiators, the examination of phenyl radicals and radical aromatic substitution, the study of free radical halogenation of alkanes which revealed the loss of stereochemistry of alkyl radicals, the widespread utilization of free radical polymerization, and the elucidation of polar effects in radical reactions. The epochal monograph on free radicals by Walling had appeared in 1957,[17] and while this was by no means the first book on free radicals it was the most influential. In the final third of the Century, advances have emphasized the utilization of ESR spectroscopy and CIDNP, spin trapping and spin labeling, further examination of the cage effect, rate measurements of free radical reactions including cyclizations and ring openings, the elucidation of the role of free radicals in biological systems, and the systematic utilization of radicals in organic synthesis.

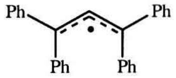
2 Free radicals: The first generation

DELOCALIZED PERSISTENT RADICALS

Following Gomberg's discovery, a variety of related persistent radicals were prepared. Schlenk and Hermann Mark reported the pentaphenylethyl radical **6**,[18] and Karl Ziegler and co-workers prepared the tetraphenylallyl radical (**7**)[19] and the pentaphenylcyclopentadienyl radical (**8**).[20] Ziegler did extensive work on free radicals and also in the 1920s began work on organometallic compounds, which led to his discovery of organoaluminum catalysts for ethylene polymerization, for which he won the Nobel Prize in Chemistry in 1963. However, even in 1931 the idea of stable radicals met some resistance, as Koelsch prepared and submitted for publication a report of the long-lived radical **9**, but the complete unreactivity of the radical towards oxygen seemed improbable, and the manuscript was rejected. In 1957, ESR spectroscopy of the same sample confirmed the identification, and the original manuscript was resubmitted and published.[21] The radical **10** was reported by Löwenbein: it reversibly forms a dimer, and reacts with oxygen to give the peroxide.[22] Ballester also prepared the perchlorotriphenylmethyl radical **10a**, which is almost completely inert.[23]

$Ph_3C\dot{C}Ph_2$

6



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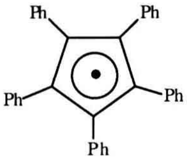

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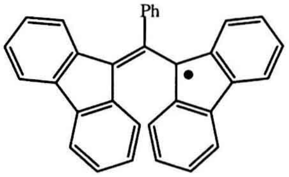

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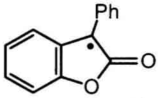


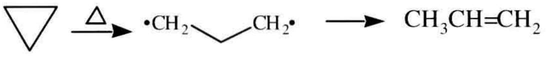
10

$(C_6Cl_5)_3C\cdot$

10a

DIRADICALS

Even before the report of the stable triphenylmethyl radical, Tanatar discovered in 1896 the cyclopropane to propene rearrangement (equation 3),[24] which eventually led to the recognition of diradicals and radical rearrangements in aliphatic systems. Chambers and Kistiakowsky[25] measured the kinetics of this reaction in 1934, and suggested the diradical pathway (equation 3) that is now generally accepted. The study of this reaction is still being pursued, and the suggestion has been made that a concerted path is almost competitive with the diradical route.[26,27] The stable diradical **11** analogous to triphenylmethyl was reported by Schlenk in 1915 (Schlenk diradical),[28] and the analogous trisradical by Leo in 1937.[29] This marked the beginning of the study of "high-spin" molecules, and these are gaining increasing attention.[30]



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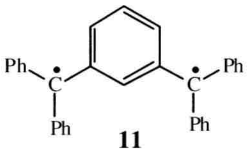

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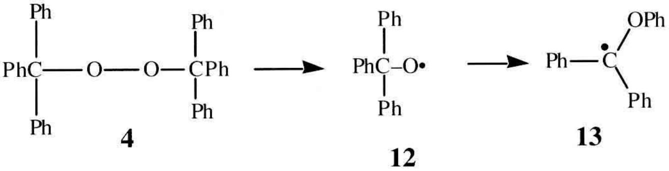
FREE RADICAL REARRANGEMENTS

Wieland observed, in 1911, that the Gomberg peroxide **4** rearranged upon heating to the pinacol ether **14** and attributed this to initial dissociation forming an intermediate alkoxy radical **12**. This rearranged forming the radical **13** (equation 4), which dimerized forming **14** (equation 5).[31] The kinetics of this rearrangement were later measured by Schuster *et al.*[32] In 1944 Urry and Kharasch reported the analogous rearrangement of phenyl to carbon, the neophyl rearrangement (equation 6),[33] and phenyl migration in $PhCOCH_2\cdot$ was discovered by McBay *et al.*[34,35]



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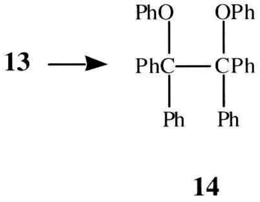

(5)

$$\mathrm{Ph_3CCH_2Br} \xrightarrow{\mathrm{Mg}} \mathrm{Ph_3C\dot{C}H_2} \longrightarrow \mathrm{Ph_2\dot{C}CH_2Ph} \qquad (6)$$

NITROGEN-CENTERED RADICALS.

The reversible dissociation of colorless tetraphenylhydrazine into the green diphenylaminyl (**15**) at 100°C was discovered by Wieland in 1911 (equation 7), and extended the free radical concept to nitrogen.[36–38] These radicals are trapped by nitric oxide to give diphenylnitrosoamine (**16**), and the rate of this reaction was used to show the rate of dissociation of the hydrazine.[39]

$$\mathrm{Ph_2NNPh_2} \rightleftharpoons \underset{\mathbf{15}}{2\mathrm{Ph_2N\cdot}} \xrightarrow{\mathrm{NO}} \underset{\mathbf{16}}{\mathrm{Ph_2NN{=}O}} \qquad (7)$$

NITROXYL RADICALS

Nitric oxide, NO, may be represented as either a nitrogen- or oxygen-centered radical, as can aminoxyl, H_2NO. Arylaminoxyls $Ar_2NO\cdot$ were reported by Wieland *et al.*,[40–42] and others of these have been prepared. The electronic structure as represented by **17** was proposed by Banfield and Kenyon in 1926.[43] Aminoxyls substituted with aliphatic groups bearing alpha hydrogens are subject to disproportionation and are often not isolable. In 1959, preparation of tetramethylpiperidinyloxy (TEMPO, **18**) was reported as a material that is quite stable, but this was initially in a provincial journal that was little noticed.[44,45] Then in 1961 the preparation of di-*tert*-butylnitroxyl **19**