SILVER IN ORGANIC CHEMISTRY

Edited by

MICHAEL HARMATA

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SILVER IN ORGANIC CHEMISTRY
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MICHAEL HARMATA
This volume is dedicated to the memories of two outstanding chemists, Dr. Christopher R. Schmid and Dr. Anthony J. Shuker, both of whom succumbed to cancer at an all too early age. Their legacies live on not only in their science but also in those whom they loved, befriended, and inspired.
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In the last two centuries, the discipline of synthesis has profoundly transformed our world, enabling access to molecules that in former times would be only scarcely or unreliably available from natural sources. Increasingly, synthesis is also being used to access new molecules, designed for function (e.g., catalysts, smart materials, self replicating materials, molecular devices, energy generation and storage systems, diagnostics, drug delivery systems, therapeutics)—many with activities superior to or often different from what nature has produced. We are no longer exclusively reliant on nature for our molecular needs. This too brings new opportunities. Whereas once the challenge in synthesis was simply to make molecules, increasingly that challenge has given away to a more demanding goal: developing strategies that provide molecules in a step economical, and green, if not ideal way. Our ability to meet this goal rests heavily not only on the refinement of existing methodology, but also on the introduction of new reactions and reagents that enable or enhance new synthetic strategies—a focus of this book.

This book explores the use of silver in organic synthesis. Silver and its salts and complexes have figured significantly in the history of chemistry, recognized for their special conductive properties, use in photography, and even biological activities. Notwithstanding the importance of these areas the broader use of silver in chemistry, and more specifically in synthesis, has lagged behind that of other coinage metals. That is changing. One now finds silver as a key component of much that is “nano,” including nano-rods, spheres, sheets, clusters, prisms, membranes, plates, pillars, cubes, bowls, fibers, wires, gels, and sensors. Increasing interest is also being directed at its use and that of other coinage metals in improving synthetic procedures and in enabling new ones. This book provides an insightful overview of how silver figures in these new developments.
Professor Harmata is one of the gifted educators of our time. Through his research and books he has contributed significantly to the advancement of synthesis. For this book, he has assembled a remarkable team of thought leaders who have in their own research contributed significantly to the emerging interest in silver-based reaction science. The resultant product is a must read for those interested in synthesis. It spans impressively from the preparation and use of silver compounds to silver-catalyzed or mediated cycloadditions, rearrangements, isomerizations, group transfers, aldols, and coupling reactions to supramolecular chemistry and comparisons with other metals. It is both an educational and inspirational experience. It has impressive depth and breadth. This contribution to our community sprung in part from frustration with a rejected but clever manuscript title (“All that glitters is not gold”) and the resultant motivation “to do something on behalf of silver.” There is a silver lining to that cloud, as this book on silver in organic chemistry represents a brilliant contribution to the field and an educational experience that is expected to inspire new ideas and glitter for an emerging area of interest.

Paul A. Wender

Stanford University
April 2010
PREFACE

It was a dark and stormy night. . . .

Editors get to have some fun, don’t they? This book was born out of the recognition that there existed no compilation on the power of silver in organic chemistry, particularly synthesis. I recognized this, and within less than a year, while these reviews were being written, a very nice *Chemical Reviews* issue appeared dedicated to the coinage metals and their importance to organic chemistry. That’s life! Such is the pace of developments in the area of coinage metals that those reviews, and those contained herein, will need to be updated within the next few years, however. Have I just suggested that I might take on a second edition of this monograph? I must be nuts.

This book also came about because I am at times pigheaded and not the teddy bear that I am often perceived to be. Not too long ago, I tried to publish a paper that was partially entitled “All that glitters is not gold,” in an effort to do some cheerleading for the silver cation. A referee thought this was an abomination, and my response was less than that of a gentleman and scholar. Fortunately, cooler heads eventually prevailed, the situation was resolved, and the paper was published: I changed the title. However, I was left with the feeling that I needed to do something on behalf of silver, and this book is the result.

My thanks go out to the authors. Through their fine efforts, a very nice monograph has been produced. If this monograph teaches and inspires, even just a little, we will have accomplished our mission.

I must thank Wiley and all the fine folks there for their help and support. My thanks go in particular to Ms. Anita Lekhwan, whose confidence in me and the project never waivered. We all need people to believe in us.

My family has been very patient with me as I put in the extra effort to bring this book to life. My deepest thanks to Judy, Gail, Diana, and Alexander.
Finally, whenever I do a project like this, I like to remind the community that I can make time for this because I have a supported research program. When I began this project, I had both NIH and NSF funding. I will retain the latter for the next few years and hopefully regain the former. A synergistic activity like this allows me to produce a teaching and learning tool and affords me the chance to interact with leading colleagues of the day. Hopefully it adds something to the community; it certainly enriches me.

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1

SILVER ALKYLs, ALKENYLs, ARYLs, AND ALKYNYLs IN ORGANIC SYNTHESIS

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1.1 Introduction

1.2 \( C_{sp^3}\)-Ag

1.2.1 Synthesis, Stability, and Reactivity of Alkylsilver Compounds
1.2.2 Synthesis and Stability of Perfluoroalkylsilver Compounds
1.2.3 Reactivity of Perfluoroalkylsilver Compounds

1.3 \( C_{sp^2}\)-Ag

1.3.1 Synthesis and Stability of Arylsilver Compounds
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1.4.2.3 Reaction with Alkyl Halides
1.4.2.4 Coupling Reactions
1.4.2.5 Reactions with Non-carbon Electrophiles
1.1 INTRODUCTION

While the coordination and inorganic chemistry of silver compounds have been prolifically documented, the use of organosilver compounds to effect useful synthetic transformations is severely underrepresented in the synthetic organic chemistry literature. This has prompted us to present a review of literature reporting synthetically useful applications of organosilver compounds in the hope of inspiring further development in this field. The majority of the literature covered in this review concentrates on silver(I) organo-species as reagents, although on some occasions silver(II) and silver “ate” complexes will be discussed, in addition to organosilver intermediates. General reviews encompassing all classes of organosilver compounds have appeared previously.¹⁻³

1.2 \( C_{sp^3}\)-Ag

1.2.1 Synthesis, Stability, and Reactivity of Alkylsilver Compounds

As a result of extremely low thermal stability, alkylsilver compounds have found only a narrow range of use in organic synthesis. Procedures for the synthesis of alkylsilver compounds as anything but fleeting proposed intermediates are limited to a handful. Semerano and Riccoboni first reported the synthesis of methyl-, ethyl-, and propylsilver in 1941 (Scheme 1.1). Reaction of silver nitrate and the corresponding tetralkyllead in alcohol at \(-80^\circ\text{C}\) gave the compounds as brown precipitates that decomposed rapidly on warming to room temperature to give metallic silver and a mixture of hydrocarbons.⁴ This methodology has been utilized in a limited number of investigations into the mechanism of decomposition of alkylsilver compounds.⁵,⁶ In these cases, the presence of the alkylsilver compound, and its subsequent decomposition, is inferred from the isolation of alkyl dimers.

Two plausible mechanistic pathways have been proposed for the thermal decomposition of alkylsilver compounds: either a radically-mediated cleavage of the carbon–silver bond or a process by which the breaking of the silver–carbon bond and formation of the carbon–carbon bond are concerted. Mechanistic studies by Whitesides and coworkers in which the product ratios obtained for the thermal process

\[
\text{R}_4\text{Pb} + \text{AgNO}_3 \rightarrow \text{RAg} + \text{R}_3\text{PbNO}_3
\]

Scheme 1.1
were compared to those for known radically-mediated reactions have suggested that a concerted process is more likely, although this has not proved to be general.\textsuperscript{7–9}

The formation of methylsilver and dimethylargentate has been observed in the collision-induced dissociation MS\textsuperscript{3} spectrum of silver diacetate. Dimethylargentate is stable in the gas phase, and has been isolated for short periods (10 s) without significant decomposition.\textsuperscript{10}

Alkylsilver compounds have been prepared by treatment of Grignard reagents with silver salts,\textsuperscript{11–19} and similarly undergo oxidative homocoupling to give alkyl dimers.\textsuperscript{11–13,19,20} Exploitation of this finding has resulted in the development of general methodology for silver-catalyzed alkyl–alkyl homocoupling of Grignard reagents (Table 1.1).\textsuperscript{21} The catalytic cycle of this reaction is proposed to proceed via the oxidation of metallic silver with 1,2-dibromoethane to generate silver bromide (Scheme 1.2).

\textbf{TABLE 1.1. Silver-Catalyzed Dimerization of Alkylmagesium Halides}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{MgBr} )</td>
<td>( \text{BrCH}_2\text{CH}_2\text{Br} )</td>
<td>97</td>
</tr>
<tr>
<td>2</td>
<td>( \text{O} - \text{O} )</td>
<td>( \text{O} - \text{O} )</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>( \text{BrCH}_2\text{CH}_2\text{Br} )</td>
<td>( \text{Ph} )</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>( \text{R} - \text{MgX} )</td>
<td>( \text{AgOTs} )</td>
<td>95</td>
</tr>
</tbody>
</table>

\textbf{Scheme 1.2}
Of particular note is the use of this reactivity to form small carbocycles. Whitesides and coworkers have shown that the treatment of primary bis(alkylmagnesium halides) with tributylphosphinesilver iodide produces carbocycles in a range of yields, with a strong dependence on ring size (Table 1.2). The best results were obtained for four-, five-, and six-membered rings. Although it was hoped that the aggregated nature of alkylsilver compounds would facilitate the formation of medium to large rings, compounds of this type were produced with only low yields.

It has also been shown that treatment of primary bis(alkylmagnesium halides) with silver trifluoromethanesulfonate effects ring closure under mild conditions for a range of substrates, thus highlighting the generality of this reaction for producing small carbocycles (Table 1.3).

An equivalent reaction has been achieved via the treatment of hydroborated bisalkenes with alkaline silver nitrate solution (Table 1.4). This method has been used to synthesize a number of small and medium-size carbocyclic rings in moderate to good yield. The selectivity for terminal cyclization observed for 1,6-heptadiene and 1,7-octadiene indicates that, in these cases, hydroboration of each of the alkenes occurs independently to yield acyclic boranes. It has, however, been found that both cyclic and acyclic boranes react under these conditions to yield the ring-closed products (Scheme 1.3).

### Table 1.2. Silver-Mediated Ring-Closing Reaction of Bis(Alkylmagnesium Halides)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Concentration $N \times 10^2$</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,4-Dibromobutane</td>
<td>5.0</td>
<td>Cyclobutane</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>1,5-Dibromopentane</td>
<td>2.5</td>
<td>Cyclopentane</td>
<td>83</td>
</tr>
<tr>
<td>3</td>
<td>1,6-Dichlorohexane</td>
<td>2.5</td>
<td>Cyclohexane</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>1,7-Dibromoheptane</td>
<td>2.5</td>
<td>Cycloheptane</td>
<td>23</td>
</tr>
<tr>
<td>5</td>
<td>1,8-Dibromooctane</td>
<td>2.5</td>
<td>Cyclooctane</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>1,9-Dichlorononane</td>
<td>2.5</td>
<td>Cyclononane</td>
<td>&lt;1</td>
</tr>
<tr>
<td>7</td>
<td>1,10-Dibromodecane</td>
<td>0.77</td>
<td>Cyclodecane</td>
<td>10–15</td>
</tr>
<tr>
<td>8</td>
<td>1,12-Dibromododecane</td>
<td>0.77</td>
<td>Cyclodecane</td>
<td>10–15</td>
</tr>
</tbody>
</table>

Of particular note is the use of this reactivity to form small carbocycles. Whitesides and coworkers have shown that the treatment of primary bis(alkylmagnesium halides) with tributylphosphinesilver iodide produces carbocycles in a range of yields, with a strong dependence on ring size (Table 1.2). The best results were obtained for four-, five-, and six-membered rings. Although it was hoped that the aggregated nature of alkylsilver compounds would facilitate the formation of medium to large rings, compounds of this type were produced with only low yields.

It has also been shown that treatment of primary bis(alkylmagnesium halides) with silver trifluoromethanesulfonate effects ring closure under mild conditions for a range of substrates, thus highlighting the generality of this reaction for producing small carbocycles (Table 1.3).

An equivalent reaction has been achieved via the treatment of hydroborated bisalkenes with alkaline silver nitrate solution (Table 1.4). This method has been used to synthesize a number of small and medium-size carbocyclic rings in moderate to good yield. The selectivity for terminal cyclization observed for 1,6-heptadiene and 1,7-octadiene indicates that, in these cases, hydroboration of each of the alkenes occurs independently to yield acyclic boranes. It has, however, been found that both cyclic and acyclic boranes react under these conditions to yield the ring-closed products (Scheme 1.3).
Intermolecular dimerization has also been effected by a comparable protocol. Treatment of triethylborane with silver nitrate and sodium hydroxide in water at 25°C led to the rapid evolution of n-butane (72%), ethylene (9%), and ethane (9%). Reaction of two different alkylboranes led to statistical mixtures of dimerized and cross-coupled products. Furthermore, this strategy has been used successfully in the synthesis of olefins from dihydroborated internal acetylenes, and in polymerizations of bifunctional organoboron compounds.

The addition of lithium bromide significantly increases the thermal stability of alkylsilver compounds. Westmijze and coworkers found that the reaction of n-butylmagnesium bromide, for example, with AgBr·2LiBr gave a solution of butylsilver that was stable up to −10°C, which is in stark contrast to the species obtained from the reaction with silver bromide alone, which decomposes at −60°C. This marked stabilization of the alkylsilver compounds allowed for the first meaningful use of these reagents in intermolecular reactions.

The Grignard-derived alkylsilver–lithium bromide complexes have been added to conjugated enynes and enynenitriles to give allenes via the intermediacy of allenylsilver reagents (Scheme 1.4). The alkylsilver reagents generally reacted with the enynenitriles to give 2,3-alkadienenitriles on protolysis, while homoargentates (R₂AgMgCl) tended to give 2,4-alkadienenitriles. The homoargentates underwent selective trans addition to the enynenitriles, which is in contrast to the selective cis addition observed for alkylcopper reagents.

**TABLE 1.3. Silver-Mediated Ring-Closing Reaction of Bis(Alkylmagnesium Halides)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td></td>
<td>94</td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td></td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>82</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
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<td>61</td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

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A number of simple alkylsilver compounds have been found to react with enynylsulfinites via a 1,5 addition to give substituted butatrienes in excellent yield (Scheme 1.5).\textsuperscript{15} Interestingly, a different outcome was obtained for alkylcopper compounds, which underwent 1,3 addition to the enynylsulfinites.

Kauffmann and coworkers have described the reaction of alkylsilver compounds with cyclohexenone (Scheme 1.6).\textsuperscript{29} It was found that the alkylsilver derivatives reacted preferentially, and in some cases exclusively, in the $\beta$ position. A significant amount of 3-methylcyclohex-2-enol was observed for the reaction of Me$_2$AgMgBr, which has been attributed to the elimination and subsequent reaction of silver(I) hydride. Silver(I) hydride has been observed in the gas-phase fragmentation of other organosilver compounds.\textsuperscript{30}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td></td>
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<tr>
<td>3</td>
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<td></td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>19</td>
</tr>
</tbody>
</table>

TABLE 1.4. Silver-Mediated Ring Closing of Hydroborated Bisalkenes

A number of simple alkylsilver compounds have been found to react with enynylsulfinites via a 1,5 addition to give substituted butatrienes in excellent yield (Scheme 1.5).\textsuperscript{15} Interestingly, a different outcome was obtained for alkylcopper compounds, which underwent 1,3 addition to the enynylsulfinites.

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Silver trinitromethane undergoes addition to adamantyl (Ad) halides, methyl iodide, and trinitromethyl iodide (Scheme 1.7).

1.2.2 Synthesis and Stability of Perfluoroalkysilver Compounds

In comparison to the corresponding alkylsilver compounds, the perfluoroalkysilver derivatives are significantly more stable and are able to participate in chemistry not
known for the alkylsilver derivatives. The perfluoroalkyl silver compounds were first synthesized by Miller and coworkers through the nucleophilic addition of silver fluoride to perfluoroalkenes (Scheme 1.8). In an attempt to avoid the use of silver fluoride, Dyatkin and coworkers developed the reaction of perfluoroalkenes with silver trifluoroacetate in the presence of cesium or potassium fluoride to produce a variety of perfluoroalkyl silver derivatives. Perfluoroalkylsilver compounds have also been synthesized by transmetallation of the corresponding cadmium reagents with silver nitrate.

An interesting synthetic route to the perfluoroalkylsilver derivatives has been reported by Knunyants and coworkers with the production of perfluoroisopropylsilver in excellent yield via the decarboxylation of the silver salt of \(\alpha\)-hydroperfluoroisobutyric acid in pyridine (Scheme 1.9).

Tyrra has described the preparation of trifluoromethylsilver from Me$_3$SiCF$_3$ and silver fluoride in propionitrile (Scheme 1.10). On treatment with PNPCI ([PNP]$^+ = \text{Ph}_3\text{P} = \text{N} - \text{PPh}_3$) trifluoromethylsilver was trapped as a mixture of argentates,