**SYNLETT Spotlight**

**Silver(I) Oxide**

Compiled by Clémentine Gibard

Clémentine Gibard was born in 1988 in Albertville, France. She obtained her M.Sc. in 2011 in bio-organic and bio-inorganic chemistry from Université Joseph Fourier, Grenoble, France. She is currently working towards her Ph.D. in Clermont-Ferrand under the supervision of Dr. Arnaud Gautier and Dr. Federico Cisnetti. Her research focuses on the development of new strategies for the functionalization of metal N-heterocyclic carbenes and the study of their applications.

Clermont Université, Université Blaise Pascal, CNRS, Institut de Chimie de Clermont-Ferrand, UMR 6296, BP 10448, F-63000 Clermont-Ferrand, France

E-mail: clementine.gibard@univ-bpclermont.fr

**Introduction**

Silver(I) oxide (Ag$_2$O) has been known for several centuries, and it is still widely used in synthetic chemistry, including in novel strategies. Ag$_2$O is a black powder that is prepared by the reaction of aqueous silver nitrate and hydroxide salts (eq. 1, Scheme 1). However, thanks to its stability and low cost, organic chemists most frequently purchase it from commercial suppliers. This reagent has many applications: it can act as a base — due to the presence of oxide —, as an oxidant — due to its easy reduction to metallic silver —, as a halogen scavenger — due to the precipitation of silver halides —, or as a source of silver ion, particularly useful for organometallics preparation.

**Abstracts**

(A) **Selective Protection of Hydroxyl Groups**

Hydroxyl groups can be selectively protected in the presence of catalytic amounts of potassium iodide under neutral conditions. The high selectivity for the monofunctionalization is due to hydrogen-bonding interactions, resulting in an increased acidity for a specific hydroxyl group and selective deprotonation by Ag$_2$O. The starting methyl 4,6-O-benzylidene-D-pyranoside is converted in good yield (70–98% yield), and the method can be applied to several protecting groups.

(B) **Free-Radical-Mediated Intramolecular C(sp$^3$)–C(sp$^2$) Coupling**

β-Ketoanilides are of synthetic interest as precursors for heterocyclic compounds which may display pharmaceutical activity. After numerous tests, the authors found that the product is obtained only in the presence of silver oxide. However, an external base is also required, the optimal one being cesium carbonate.

Ag$_2$O is poorly soluble in all common solvents including water. It is however readily soluble in ammonia, leading the Tollens’ reagent (eq. 2, Scheme 1) which possesses a historical importance in the development of organic chemistry. This also illustrates the fact that (as for other metal-based reagents), properties of Ag$_2$O may depend on the formation of complexes in the reaction medium.

**Scheme 1** Preparation of silver oxide and Tollens’ reagent

\[
\begin{align*}
2 \text{AgNO}_3(\text{aq}) + \text{NaOH}(\text{aq}) & \rightarrow 2 \text{Ag}_2\text{O}(\text{s}) + 2 \text{NaNO}_3(\text{aq}) \\
\text{Ag}_2\text{O}(\text{s}) + 4 \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightarrow 2(\text{Ag(NH}_3)_2)^+ + 2 \text{OH}^- (\text{aq})
\end{align*}
\]
C. Gibard

References