Silver(I) Oxide

Compiled by Clémentine Gibard

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Introduction

Silver(I) oxide (Ag₂O) has been known for several centuries, and it is still widely used in synthetic chemistry, including in novel strategies. Ag₂O 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.

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\begin{align*}
\text{AgNO}_3(aq) + \text{NaOH}(aq) &\rightarrow \text{Ag}_2\text{O}(s) + 2 \text{NaNO}_3(aq) + 2 \text{H}_2\text{O}(l) \quad (1) \\
\text{Ag}_2\text{O}(s) + 4 \text{NH}_3(aq) + \text{H}_2\text{O}(l) &\rightarrow 2\text{[Ag(NH}_3)_2]^{2+}(aq) + 2 \text{OH}^- (aq) \quad (2)
\end{align*}
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Scheme 1 Preparation of silver oxide and Tollens’ reagent

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 Ag₂O. The starting methyl 4,6-O-benzylidene-β-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(sp³)–C(sp²) 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.
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References

(5) Yu, Z.; Ma, L.; Yu, W. *Synlett* 2010, 2607.