SYNLETT
Spotlight 414

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

Mercury(II) Acetate

Compiled by Milan Dejmek

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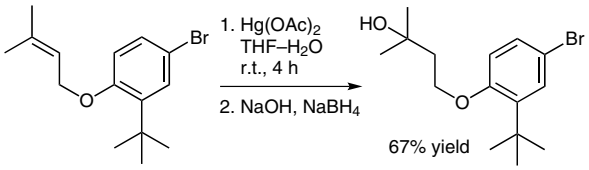
Introduction

Mercury(II) acetate is a commercially available reagent which can be prepared by the reaction of elemental mercury with peroxyacetic acid.[1] The standard use of this reagent is the textbook oxymercuration–demercuration reaction, an electrophilic addition in which mercury(II) acetate attacks a double bond forming a mercury–olefin complex, followed by nucleophilic ring opening with water and subsequent reductive demercuration with sodium borohydride.[2] The reaction proceeds in accordance with Markovnikov's rule, since the nucleophilic reagent attacks the higher substituted carbon atom to form the more stable carbocation intermediate. This reaction is also an *anti*-addition: the nucleophilic reagent attacks the double bond–mercury complex from the side opposite to the molecule.

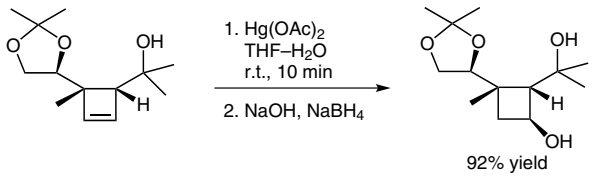
Not only water, but also other nucleophiles may be used to attack this complex, which opens up an arena for other potential uses of mercury(II) acetate including azidomercuration or formation of ethers and secondary amines. Although mercury(II) salts are generally considered to be very toxic (ingestion of as little as 1 g can be fatal),[3] the non-volatile, crystalline nature of mercury(II) acetate, together with its insolubility in lipids, assures safe manipulations with the reagent when handled in a fume-hood using standard safety precautions.



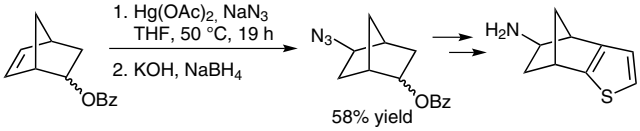
Scheme 1 Standard oxymercuration–demercuration procedure

Abstracts

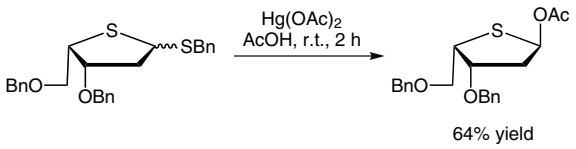
Examples of stereoselective oxymercuration have been found in cases of neighboring group participation (hydroxyl[4a] or carboxy groups[4b] in appropriate positions). These reactions are reported to offer very good yields with excellent stereoselectivity (only one product is isolated from the reaction mixture).[4]



Work of Hřebabecký et al.[5a] is a nice example of using a different nucleophile (azide) to open the olefin–HgOAc complex. Azidomercuratio[5] followed by reduction serves as a convenient way of introducing an amino group into the molecule.



In the chemistry of thiosugars, the anomeric benzyl-protected thio group is often the result of a sulfur atom introduction into the furanose molecule. It may be conveniently acetolysed using mercury(II) acetate in glacial acetic acid with good to near quantitative yields.[6] This reaction is widely used in the preparation of thionucleoside analogues.



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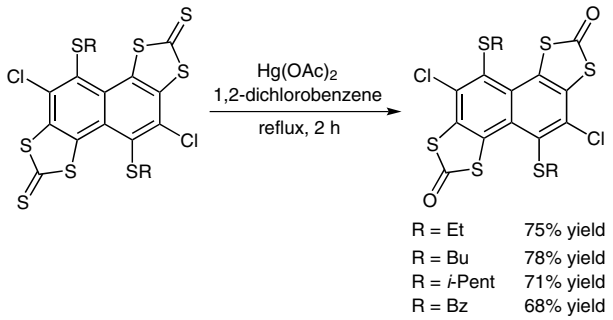
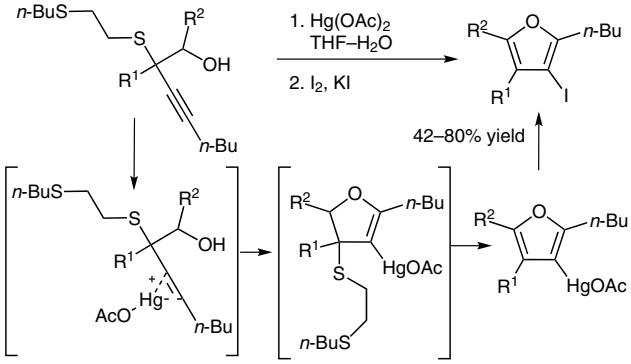
Mercury(II) salts have a strong affinity towards sulfur, which can be exploited in a number of desulfurization procedures.[7]

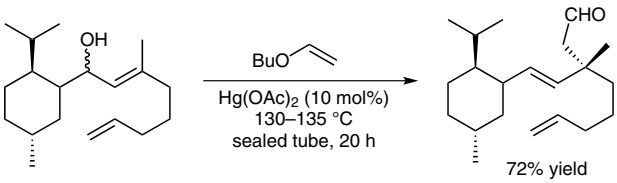


Very interesting procedures for the preparation of variously substituted furans were reported recently.[8] Reacting mercury(II) acetate with homopropargyl or allenyl thiolate leads to the formation of tetrasubstituted furans. This procedure is facilitated by the thiophilicity of the mercuric species, which allows an easy elimination of the sulfur moiety.



Various cyclization protocols including multiple[9a] and sequential[9b] cyclizations yielding structures based on tetrahydrofuran have been reported employing mercury(II) acetate. The depicted bis-tetrahydrofurane system represents a core part in several biologically active natural products (e.g., asimitrin, salzmanolin).

Mercury(II) acetate-catalyzed vinylation of allylic alcohols followed by Claisen rearrangement was used in the syntheses of various natural products. Arbour and coworkers used it in the synthesis of (+)-euphococcinine and (–)-adaline, two alkaloids with opposite configuration.[10]



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