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Spotlight 85

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

Chemistry of Tetrathiomolybdate and Tetraselenotungstate: Applications in Carbohydrate and Peptide Chemistry

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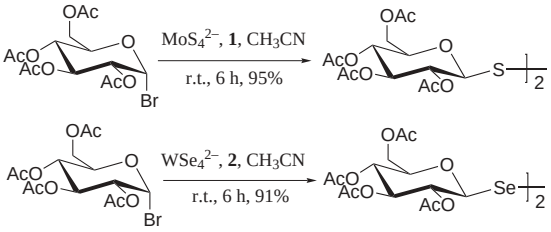
Introduction

The reagents, benzyltriethylammonium tetrathiomolybdate, $[BnNEt_3]_2MoS_4$ **1**[1] and tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$ **2** have been shown to be useful for sulfur and selenium transfer reactions respectively in organic synthesis. Preparation of disulfides from alkyl halides,[2] ring opening of epoxides,[3] tandem sulfur transfer-reduction-Michael addition[4] in one step, reduction of aryl azides to amines[5] and alkyl azides to imines[5] have been reported from our laboratory using the reagent tetrathiomolybdate **1**. Tetrathiomolybdate **1** is also used for the selective deprotection of propargyloxycarbonyl (**Poc**) protective group for amines[6] in peptides and for alcohols[7] in carbohydrate chemistry. Recently, regioselective reduction of anomeric azides[8] to amines using the reagent **1** has been reported. Reagent **1** has also been used, as a sulfur transfer reagent, for the synthesis of phosphorothioate oligonucleotides.[9] Large quantities of **1** can be prepared from ammonium tetrathiomolybdate and benzyltriethylammonium chloride.[2a]

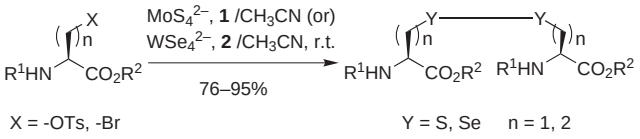
On the other hand tetraselenotungstate **2** has been used for the formation of diselenides[10] form alkyl halides and in the synthesis of diselenides of several amino acid deirvatives[11] from the corresponding halides or activated alcohols. The reagent **2** can be prepared from K_2Se_3 and $W(CO)_6$ in DMF.[10,12]

Abstracts

(A) The first report on the application of tetrathiomolybdate, MoS_4^{2-} **1** in carbohydrate chemistry appeared in 1997 towards the synthesis of sugar disulfides. More recently use of tetraselenotungstate, WSe_4^{2-} **2** towards the synthesis of sugar diselenides has been published. The reagents **1** or **2** work very well for the synthesis of disulfides and diselenides respectively from the corresponding sugar halides.



(B) The formation of disulfides and diselenides has been applied in the efficient synthesis of cystine, selenocystine, and their higher homologues like homo and bis-homo amino acid derivatives from natural amino acids. The generality of the reaction has been studied by capping various groups to amino and carboxyl components of canonical amino acids.[11]



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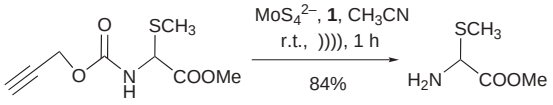
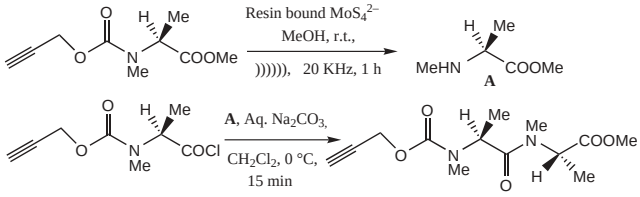
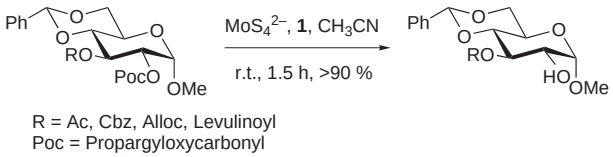
(C) Tetrathiomolybdate **1** deprotects propargyloxy carbonyl (Poc) group, a protective group for amines, which has been developed in our laboratory. The preliminary results on the highly selective deblocking of Poc group from sulfur containing amino acids and peptides using tetrathiomolybdate **1** has been reported recently.[6a]



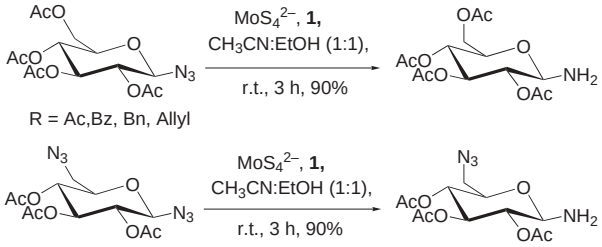
(D) Polymer supported tetrathiomolybdate has been used for the deprotection of propargyloxycarbonyl in the synthesis of small peptides and it has also been shown that the protective group is stable under peptide coupling reaction conditions using acid chlorides.[6b]



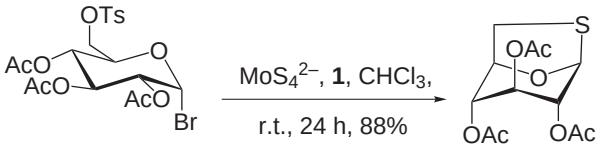
(E) Tetrathiomolybdate **1** selectively deprotects propargyloxycarbonyl (Poc) protective group in the case of alcohols in carbohydrate chemistry under neutral conditions at room temperature.[7]



(F) Tetrathiomolybdate **1** reduces the aryl azides to the corresponding amines and alkyl azides to the corresponding imines. Moreover it selectively reduces the anomeric azides to the corresponding anomeric amines with excellent regioselecitvity.[8]



(G) Tetrathiomolybdate **1** react with 1, 6 diactivated carbons in hexoses to give the corresponding epithio derivatives (1,6-anhydro derivatives) as the only products in excellent yield.[13]



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