



Digest Paper

Chemoselective reductions and iodinations using titanium tetraiodide



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ABSTRACT

Titanium(IV) halides are extensively used in carbon–carbon bond forming reactions as a Lewis acid and low valent titanium halides promote reductive coupling reactions of carbonyl compounds. In most of these reactions, ligands of titanium halides are chloride or bromide. On the other hand, titanium(IV) tetraiodide had been rarely used in organic synthesis until the late 1990s. Since 2000 several useful synthetic reactions have been developed utilizing a moderate Lewis acidity, reducing and iodination abilities of titanium(IV) tetraiodide. This digest summarizes examples of chemoselective reductions and iodinations using titanium(IV) tetraiodide (TiI₄).

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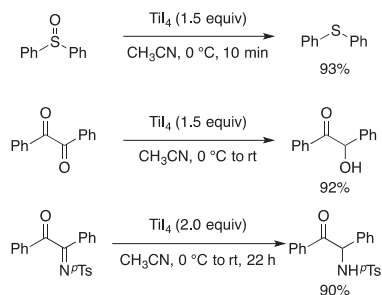
Introduction

Titanium(IV) halides are extensively used in carbon–carbon bond forming reactions; for examples, Mukaiyama aldol reactions of aldehydes with silyl enol ethers, Diels–Alder reactions, and carbonyl–ene reactions as a Lewis acid. Low valent titanium halides promote reductive coupling reactions of carbonyl compounds. In most of these reactions, ligands of titanium halides are chloride

or bromide.¹ Although titanium(IV) tetraiodide had been used for the production of high purity metal titanium, its use was rare in organic synthesis. Titanium(IV) tetraiodide has a moderate Lewis acidity and is used as a promoter and a catalyst in Mannich-type reactions,² and 1,4- and 1,2-double nucleophilic addition of ketene silyl acetals with α,β -unsaturated aldimines.³ On the other hand, titanium(IV) tetraiodide is different from titanium(IV) chloride or bromide in many reports and in particular shows reducing and iodination abilities in some useful organic reactions. Herein, this digest describes examples of chemoselective reductions and iodinations using titanium(IV) tetraiodide (TiI₄).

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Scheme 1.

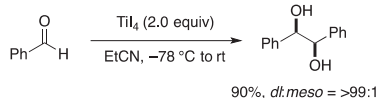
Reduction

Pinacol coupling reaction

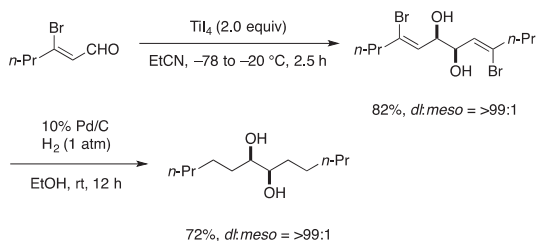
Reactions using reducing ability of iodide anion are well-known.⁴ Titanium(IV) tetraiodide is used as a chemoselective reducing agent; for examples, reduction of sulfoxides to sulfides,⁵ α -diketones to α -hydroxy ketones,⁶ and α -imino ketones to α -amino ketones (Scheme 1).⁷

Titanium(IV) tetraiodide promoted diastereoselective pinacol coupling reaction of aromatic aldehydes is reported; however, the reaction of aliphatic aldehydes does not proceed (Scheme 2).⁸

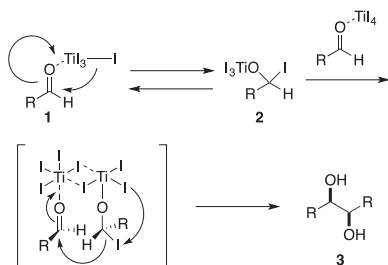
Nevertheless, the pinacol reaction of β -halogenated α,β -unsaturated aldehydes is promoted by titanium(IV) tetraiodide to give the coupling products in good yields with high *dl*-selectivities, and the subsequent reduction with $\text{H}_2/\text{Pd-C}$ gives saturated *vic*-diols in good yields (Scheme 3).⁹ Although two steps are needed, this pinacol-coupling/hydrogenation of β -halogenated α,β -unsaturated



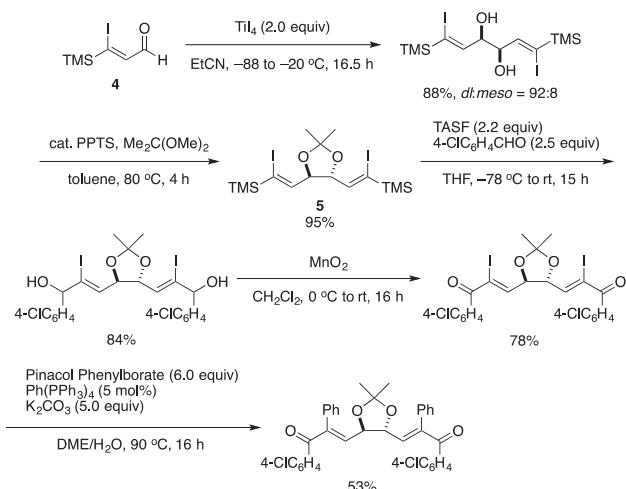
Scheme 2.



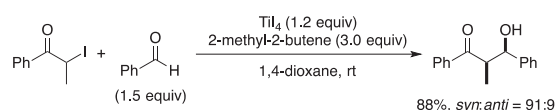
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

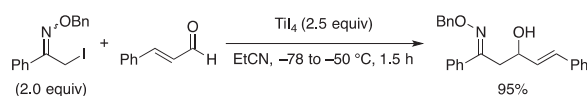
aldehydes can be regarded as the pinacol-coupling reaction of aliphatic aldehyde to afford the saturated *vic*-diol in high *dl*-selectivity. It is known that β -halo free enals do not always undergo the efficient pinacol coupling reaction.

A possible reaction pathway of titanium(IV) tetraiodide promoted pinacol coupling reaction is shown in Scheme 4. An initial iodination of the carbonyl group of the aldehyde 1 gives the iodinated intermediate 2, which is attacked by the iodide anion from titanium(IV) tetraiodide to form an anionic species. It has been reported that a similar halogenated intermediate was formed in the reaction of BCl_3 with aromatic aldehydes.¹⁰ The species generated from reductive dehalogenation in turn undergoes addition to another aldehyde to form a pinacol product 3. The formation of iodinated intermediate 2 appears to be easy in the case of aldehydes with an electron-withdrawing substituent; therefore, the pinacol coupling reaction proceeds readily with β -halogenated α,β -unsaturated aldehydes.

In 2008, titanium(IV) tetraiodide promoted pinacol coupling reaction of (*Z*)-3-iodo-3-trimethylsilylpropenal 4 was used for the preparation of *trans*-4,5-bis(*Z*)-2-(trimethylsilyl)vinyl]-2,2-dimethyl-1,3-dioxolane 5, which was utilized for the subsequent C–C bond forming reactions (Scheme 5).¹¹

Reformatsky-type reaction

Reformatsky reaction of α -haloesters with carbonyl compounds in the presence of zinc powder gives β -hydroxy carbonyl compounds and is well-known as one of the most important carbon–carbon bond forming reactions. Reformatsky-type reaction promoted by some metal iodides such as AlI_3 ,¹² CeI_3 ,¹³ and $\text{TiCl}_4/n\text{-Bu}_4\text{NI}$ ¹⁴ has been reported. Titanium enolates reductively



Scheme 7.

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