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Preparation and Reactions of Titanium(III) Chloride Solubilized in Inert Organic Solvents

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Titanium(IV) chloride reacts with dialkyl telluride in inert solvents such as dichloromethane or benzene to form a stable homogeneous solution of titanium(III) species. Reduction of several organic functionalities has been carried out using the low valent titanium solution thus obtained.

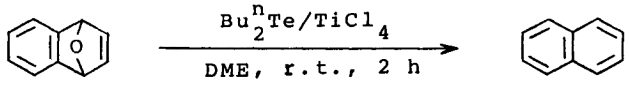
In the last decade the chemistry of titanium(III) has attracted considerable attention and numbers of synthetic methodologies based on its reducing ability have been developed.[1] Titanium(III) reagent of common laboratory uses is titanium(III) chloride, which is commercially available as anhydrous solid or 15-20% aqueous solution. This compound is insoluble in nonhydroxylic solvents and, although it combines with a variety of donor molecules to form stable complexes, most of them are practically insoluble in organic solvents. Thus, the reduction with titanium(III) chloride is usually carried out under heterogeneous conditions either with aqueous titanium(III) solution/organic phase or with solid titanium(III) reagent/organic phase.

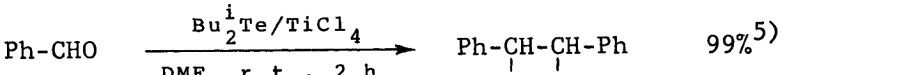
We wish to report herein that titanium(III) chloride solubilized in organic solvent can be easily obtained by the interaction of titanium(IV) chloride with dialkyl telluride. Thus, when titanium(IV) chloride is added to a solution of diisobutyl telluride in an inert solvent such as dichloromethane or benzene under nitrogen, a deep blue color of the titanium(III) species immediately developed and there resulted a homogeneous solution. This colored solution is stable and can be kept without appreciable change for many hours under a nitrogen atmosphere, although it slowly turns dark brown and leads to a decrease of reducing power on prolonged standing at room temperature.

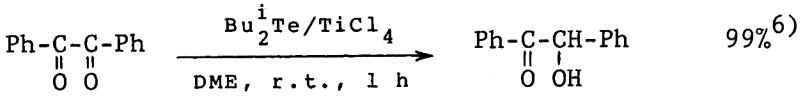
The above reagent allows to conduct a variety of functional group transformations under nonaqueous conditions and the presence of titanium(III) species is well evidenced by several characteristic reactions as shown below:

$$\mathrm{Ph\text{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\text{-}Ph} \xrightarrow[\mathrm{CH_2Cl_2,\ r.t.,\ 1\ h}]{\mathrm{Bu^i_2Te/TiCl_4}} \mathrm{Ph\text{-}S\text{-}Ph} \quad 94\%^{2)}$$

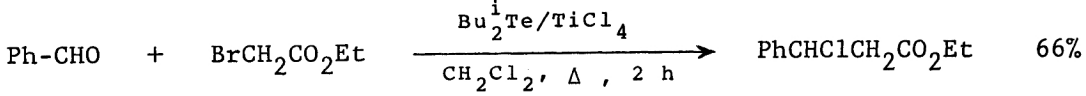
$$\mathrm{Ph\text{-}NO_2} \xrightarrow[\mathrm{CH_2Cl_2,\ r.t.,\ 0.5\ h}]{\mathrm{Bu^i_2Te/TiCl_4}} \mathrm{Ph\text{-}NH_2} \quad 74\%^{3)}$$



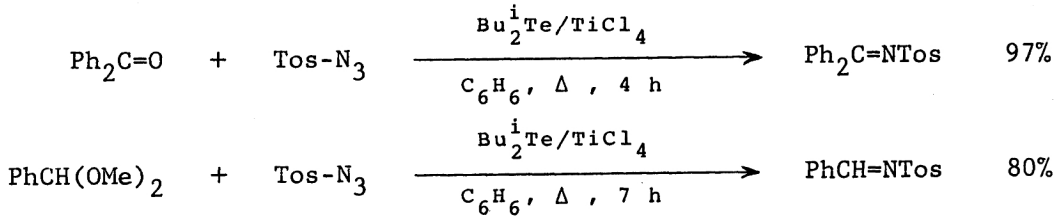




An interesting feature of this homogeneous solution of low valent titanium can be seen in the coupling reaction of benzaldehyde with ethyl bromoacetate, where β-chlorohydrocinnamic acid ester is obtained in a moderate yield.



In this solution, tosyl azide couples with aldehydes, ketones, and acetals to give the corresponding N-tosylimines.



Since titanium(III) chloride exhibits no tendency to dissolve into dichloromethane or benzene even in the presence of dialkyl telluride or telluronium salt, the low valent titanium generated by our method is supposed to exist in solution as a complexed species of some sort, probably stabilized through coordination to tellurium compound. We are now examining the possibility of applying the present procedure to the preparation of other low valent transition metals solubilized in inert organic solvents.[7]

References

1) For reviews, see T.-L. Ho, Synthesis, 1979, 1; J.E. McMurry, Acc. Chem. Res., 7, 281 (1974).
2) T.-L. Ho and C.W. Wong, Synth. Commun., 3, 37 (1973).
3) T.-L. Ho and C.M. Wong, Synthesis, 1974, 45.
4) H.N.C. Wong, Y.D. Xing, Y.F. Zhou, Q.Q. Gong, and C. Zhang, Synthesis, 1984, 787.
5) A. Clerici and O. Porta, Tetrahedron Lett., 1982, 3517. Isomeric ratio *dl*/*meso* of the product obtained with aqueous titanium(III) chloride is 1.3.
6) T.-L. Ho and G.A. Olah, Synthesis, 1976, 815.
7) Molybdenum(V) chloride reacts with dialkyl telluride to form a low valent molybdenum species soluble in inert organic solvents.

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