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

**Introduction**

The Petasis reagent (dimethyl titanocene, Cp$_2$TiMe$_2$) is readily prepared by the reaction of methylmagnesium chloride or methyllithium with titanocene dichloride. It is used for transforming carbonyl groups to terminal alkenes, like the Tebbe reagent or Wittig reaction. Unlike the Wittig reaction, the Petasis reagent can react with a wide range of carbonyls, such as aldehydes, ketones, esters, and lactones including enolizable and acid-labile substrates. The Petasis reagent is also non-pyrophoric, relatively air- and water-stable, and can be used directly as a solution in toluene–THF.

The active olefinating reagent, Cp$_2$TiCH$_2$, can be prepared by heating the Petasis reagent in toluene or THF to 60–75 °C. The Petasis reaction can also be promoted by microwave irradiation.

**Scheme 1**

### Abstracts

(A) Aldehydes and ketones can be selectively methylenated in the presence of less electrophilic carbonyls groups such as esters and amides.

(B) Reaction of dimethyl titanocene with heteroatom-substituted carbonyls, such as silylesters, lactones, thioesters, selenoesters, and acylsilanes gives the corresponding heteroatom-substituted alkenes.

(C) Petasis methylation can be accomplished in the presence of many protecting groups, like silyl ethers, benzyl ethers, and acetals. The reaction in the presence of an unprotected hydroxyl group can also be efficient when an excess of the reagent is used.

(D) The selectivity of this reaction has been extended to unsymmetrical oxalates and oxalate monoesters or monosulfides. Improvement of the methyleneation can be promoted by microwave irradiation.

(E) The reaction of β-lactams with Cp$_2$TiMe$_2$ can be realized in good yields as long as the lactams are properly activated by N-protection.

**SYNLETT** 2009, No. 19, pp 3221–3222

Advanced online publication: 13.11.2009


© Georg Thieme Verlag Stuttgart · New York
(F) Homologue dialkyltitanocene derivatives of the Petasis reagent can be prepared from titanocene dichloride and alkylolithium or Grignard reagents, with the exception of compounds that undergo facile β-hydride elimination.

(G) The Petasis reagent has been utilized in a tandem methylenation–Claisen rearrangement to give ring extension or contraction. The Petasis reagent has been utilized as an exceptional powerful tool for the total synthesis of complex natural products.

(H) One application of the Petasis reagent is the Petasis–Ferrier rearrangement, which involves methylenation of a 1,3-dioxan-4-one followed by acid hydrolysis. A one-carbon homologation was achieved using Petasis methylreagent as both methylenation reagent and RCM catalyst. A one-pot methylenation–RCM procedure has been developed by Nicolaou using Petasis reagent as both methylenation reagent and RCM catalyst.

(I) A one-carbon homologation was achieved using Petasis methylenation followed by acid hydrolysis.

References