SYNLETT Spotlight 321

Vanadium Oxytrihalide (VOX₃)

Compiled by Thanh-Tuan Bui

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

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Introduction

Applications of VOX₃ (X = F or Cl) in organic synthesis have gained significant importance in recent years. VOX₃ are well-known as strong oxidizing agents promoting both intra- and intermolecular oxidative biaryl coupling. This property has been used for synthesis of natural products,^{1,2} phenanthridine,³ phenanthrene⁴ and phenanthrene-9,10-dione⁵ derivatives. It were also used for the synthesis of

discotic liquid crystalline triphenylene⁶ and heteroanalogues.⁷ VOX₃ also acted as regio- and stereoselective dimerization agents of stilbene derivatives,⁸ and as hydroxylation⁹ and aromatization¹⁰ agents. Other applications of VOX₃ are the synthesis of near-infrared absorbent organic semiconductor vanadyl phthalocyanine for organic electronic applications^{11,12} and the use as catalysts in asymmetric synthesis.¹³

Abstracts

(A) The intramolecular oxidative biaryl coupling is one of the most significant applications of VOX₃ in organic synthesis. Numerous important natural products containing the biaryl segments have been synthesized.^{1,2} As example, the oxidative cyclization with VOF₃ of burschernin resulted in a new deoxy isostegane.²

(B) VOX₃ also promotes the intermolecular oxidative biaryl coupling. Weck et al.⁶ synthesized the triphenylene grafting functional alkyl chain by oxidative aryl-aryl coupling of the tetraalkoxy-substituted biphenyls with the bisalkylated catechols using VOF₃ in the presence of boron trifluoride diethyl ether.

(C) Hartenstein et al.⁹ studied the diastereoselective synthesis of the aporphine alkaloid (+)-cataline and they found that the reaction of (±)-glaucine with VOF₃ gave (±)-cataline, respectively. Carefully chromatographic separation of the reaction product yields to small amounts of the respective diastereomeric *cis*-4-hydroxyaporphine. Its antipode could also be isolated.

(D) VOX_3 can be used as metal oxidant in the regio- and stereoselective dimerization of stilbene derivatives. Velu et al.⁸ reported that the treatment of 12-hydroxy-3-methoxystilbene with VOF_3 gave the tricuspidatol A analogue.

(E) Filipan-Litvic et al. and Gradillas et al. reported that vanadium oxytrihalide could be also used as metallic oxidant aromatization agent.¹⁰ An example of the rapid, efficient, room-temperature aromatization of Hantzsch 1,4-dihydropyridines with vanadium(V) salts is given.

(F) Villemin et al.¹¹ developed a microwave-assisted, dry reaction (solvent-free) for the one-step synthesis of metallophthalocyanines. The strong near-infrared absorbent vanadyl phthalocyanine complex was obtained from phthalonitrile and VOCl_3 as blue-green solid in high yield (81%).

(G) VOX_3 were also used in the synthesis of $\text{VO}(\text{salen})(\text{X})$ complexes, which are powerful catalysts for the asymmetric addition of the cyanide nucleophile to benzaldehyde.¹³

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