SYNLETT
Spotlight 321

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

Vanadium Oxytrihalide (VOX_3)

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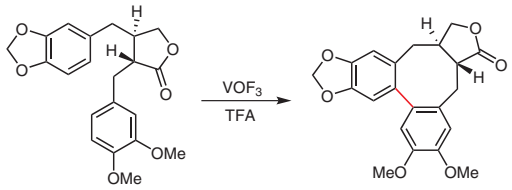
Introduction

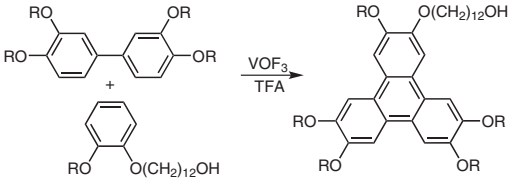
Applications of VOX_3 (X = F or Cl) in organic synthesis have gained significant importance in recent years. VOX_3 are well-known as strong oxidizing agents promoting both intra- and intermolecular oxidative biaryl coupling. This property has been used for synthesis of natural products,[1,2] phenanthridine,[3] phenanthrene[4] and phenanthrene-9,10-dione[5] derivatives. It were also used for the synthesis of discotic liquid crystalline triphenylene[6] and heteroanalogues.[7] VOX_3 also acted as regio- and stereoselective dimerization agents of stilbene derivatives,[8] and as hydroxylation[9] and aromatization[10] agents. Other applications of VOX_3 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

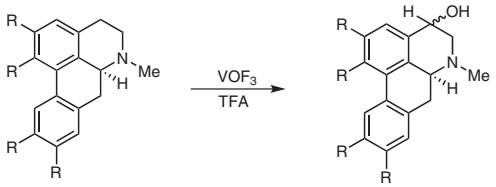
(A) The intramolecular oxidative biaryl coupling is one of the most significant applications of VOX_3 in organic synthesis. Numerous important natural products containing the biaryl segments have been synthesized.[1,2] As example, the oxidative cyclization with VOF_3 of bursehernin resulted in a new deoxy isosteganone.[2]



(B) VOX_3 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 VOF_3 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 VOF_3 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.



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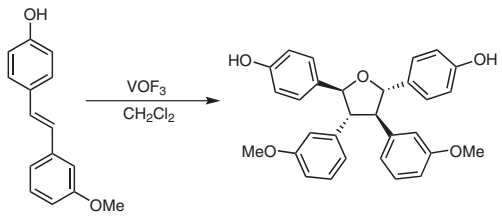
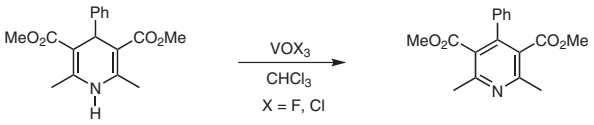
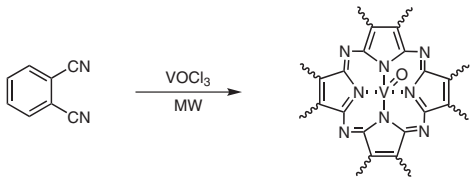
(D) VOX_3 can be used as metal oxidant in the regio- and stereoselective dimerization of stilbene derivatives. Velu et al.[8] reported that the treatment of 12-hydroxy-3-methoxystilbene with VOF_3 gave the tricuspidatol A analogue.



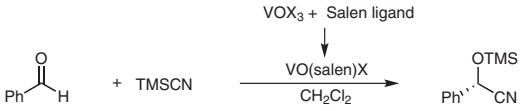
(E) Filipan-Litvic et al. and Gradillas et al. reported that vanadium oxytrihalide could be also used as metallic oxidant aromatization agent.[10] An example of the rapid, efficient, room-temperature aromatization of Hantzsch 1,4-dihydropyridines with vanadium(V) salts is given.



(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 VO(salen)(X) complexes, which are powerful catalysts for the asymmetric addition of the cyanide nucleophile to benzaldehyde.[13]



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