**SPOTLIGHT**

**SYNLETT Spotlight 322**

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

**Ytterbium Trifluoromethansulfonate**

Compiled by Tran Anh Tuan

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**Introduction**

Ytterbium trifluoromethansulfonate [Yb(OTf)$_3$] has been widely used in organic syntheses in the last few years.$^1$ Yb(OTf)$_3$ is a strong Lewis acid$^2$ due to the hard character of Yb$^{3+}$ ion and the presence of electron-deficient triflate in its coordination sphere. In contrast to traditional Lewis acids, such as AlCl$_3$, BF$_3$, TiCl$_4$, and SnCl$_4$, which are often used in stoichiometric amounts, only catalytic amounts of Yb(OTf)$_3$ are necessary. Moreover it can be easily recovered and reused without loss of activity. Interestingly, Yb(OTf)$_3$ remains catalytically active in the presence of many Lewis bases containing nitrogen, oxygen, phosphorus or sulfur atoms. The resulting water-compatibility of Yb(OTf)$_3$$^3$ is one of its well-known advantages, with respect to traditional Lewis acids that are very sensitive and easily decomposed or deactivated in the presence of small amounts of water. The most interesting point from a synthetic point of view is that Yb(OTf)$_3$-catalyzed reactions are clean, while Yb(OTf)$_3$ is regarded as environmentally friendly catalyst. Ytterbium triflate is prepared by heating ytterbium(III) oxide or chloride in an aqueous trifluoromethansulfonic acid solution (Scheme 1).$^4,5$

**Yb$_2$O$_3$ + 6 TfOH 2 Yb(OTf)$_3$ + 3 H$_2$O**

**YbCl$_3$ + 3 TfOH Yb(OTf)$_3$ + 3 HCl**

Scheme 1

This reagent has been used in numerous organic transformations,$^1$ e.g. in aldol reactions,$^6$ Kharasch-type additions,$^7$ glycosylations,$^8$ Friedel–Crafts acylations,$^9$ dealkoxyacetylations,$^{10}$ syntheses of β-enaminones,$^{11}$ etc. This article describes some major applications in organic synthesis in the recent years.

**Abstracts**

(A) **Friedel–Crafts Acylation:**

The acylation of 1-methylpyrrole has been reported recently.$^{12}$ The reaction is carried out in [bpy][BF$_4$] with a catalytic amount of Yb(OTf)$_3$ (10 mol%) at room temperature. Good yields were obtained (80–93%), but the reaction fails without catalyst. Moreover, the catalyst can be recycled three times without loss of activity.

(B) **Crotonation:**

3-Acrylic acids possess a high potential in the synthesis of biologically or pharmaceutically active compounds, such as 4.$^{13}$ 5.$^{14}$ and 6.$^{15}$ Recently, Gorobets and co-workers described a new facile protocol for the synthesis of aromatic and heteroaromatic 3-acryl-acrylic acids 9 in good yields (54–78%).$^{16}$ Aromatic ketones 7, glyoxylic acid monohydrate 8, and Yb(OTf)$_3$ (2.5 mol%) are reacted under microwave irradiation.

**SYNLETT** 2010, No. 12, pp 1880–1881
Advanced online publication: 30.06.2010
DOI: 10.1055/s-0030-1258101; Art ID: V33110ST
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(C) Tosylation:
Most tosylations use triethylamine or pyridine as a base in the reaction of appropriate alcohols with the tosylating agent. In 2004, Schirmacher and Comagic reported the low-yielding tosylation of \( \text{TsCl} \) and pyridine. Gratifyingly, when \( \text{Yb(OTf)}_3 \) is used, the tosylolation with \( \text{Ts}_2\text{O} \) proceeded in excellent yield (85%). These conditions were also applied for several primary and secondary alcohols and provided the tosylates in good yields (75–89%).

(D) TEMPO-Mediated Oxidation:
Vatèle described a new method for the oxidation of alcohols with iodobenzene peracetylation using the TEMPO/PhiO system as an oxidizing source. However, when 4-phenyl-butan-1-ol was treated with PhiO and TEMPO, only 5% of 4-phenyl-butan-1-ol was obtained. In the presence of \( \text{Yb(OTf)}_3 \) (2 mol%), the expected aldehyde was obtained in good yield (83%). The triflate can also catalyze the oxidation of several primary or secondary alcohols into the corresponding aldehydes or ketones in good to excellent yields (76–94%).

(E) One-Pot Multicomponent Synthesis of Substituted Imidazoles:
\( \text{Yb(OTf)}_3 \) has been used for the synthesis of substituted imidazoles through three-component condensation of benzil, carboxylate, and primary amine with different aromatic aldehydes in good yields (73–97%).

(F) Selective Anomeric Deacetylation:
Selective anomeric deacetylation is a key step in the oligosaccharide synthesis. \( \text{Yb(OTf)}_3 \) can promote the selective anomeric deacetylation of compound 14 (an important synthon involved in the synthesis of heparin sulphate fragments). The reaction is carried out using catalytic amounts of \( \text{Yb(OTf)}_3 \) (5 mol%) and gave compound 15 in good yield (75%). However, \( \text{Nd(OTf)}_3 \) proved to be a superior catalyst. This protocol also gave good yields (61–85%) when applied to other sugar peracetates, such as \( \text{AlCl}_3 \) and \( \text{FeCl}_3 \), gave low yields (45–60%) despite using 20 mol%.

References


Synlett 2010, No. 12, 1880–1881 © Thieme Stuttgart · New York