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High-valent tin(IV) porphyrins: Efficient and selective catalysts for cyclopropanation of styrene derivatives with EDA under mild conditions

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ABSTRACT

An efficient and selective method for cyclopropanation of styrene derivatives with ethyl diazoacetate (EDA) catalyzed by tin(IV) tetraphenylporphyrinato trifluoromethanesulfonate, [Sn^{IV}(TPP)($OTf)_2$], and tin(IV)tetraphenylporphyrinato tetrafluoroborate, [Sn^{IV}(TPP)($BF_4)_2$] is reported. These electron-deficient catalysts catalyzed the cyclopropanation of styrene derivatives in high yields and short reaction times under mild conditions. The reactions were highly selective and only *trans*-isomers were produced. Electron-rich styrenes were reacted faster than electron-poor ones. The catalysts were reused several times without loss of their catalytic activity and diastereoselectivity.

1. Introduction

Since cyclopropanes are versatile molecules with many potential applications in organic chemistry, therefore, their preparation from olefins is an important reaction in synthetic organic chemistry. Frequently, cyclopropane rings can be found as biologically active compounds and have a key role in the biosynthesis of steroids, carotenoids and retinoid [1–3]. These compounds are also useful intermediates in the formation of new carbon–carbon bonds.

Metal complexes are used as catalyst in the cyclopropanation of olefins with readily available and cheap diazo compounds. This is a simple and straight method for production of cyclopropanes [4–10]. In 1965, Nozaki et al. used copper complexes as catalyst for cyclopropanation of olefins with EDA [11]. Aratani et al. improved this study by using a chiral copper complex [12–15]. Subsequently, a wide variety of catalytic systems has been applied for cyclopropanation of olefins but when metalloporphyrins are used as catalyst, the reaction shows excellent activity and selectivity [16–18]. Up to now, Co, Rh, Ru, Os and Fe porphyrins have been used as catalyst for cyclopropanation of olefins with diazo compounds [16,19–24].

Electron-deficient metalloporphyrins have been used as mild Lewis acid catalysts. Suda group has reported the use of chromium and iron porphyrins in organic synthesis. They used Cr(tpp)Cl for regioselective [3] rearrangement of aliphatic allyl vinyl ethers and for Claisen rearrangement of simple aliphatic allyl vinyl ethers, Fe(tpp)OTf for rearrangement of α,β-epoxy ketones into 1,2-diketones and Cr(tpp)OTf for highly regio- and stereoselective rearrangement of epoxides to aldehydes [25–30].

Recently, we have reported the use of [Sn^{IV}(TPP)($ClO_4)_2$], [Sn^{IV}(TPP)($OTf)_2$], [Sn^{IV}(TPP)($BF_4)_2$], [Sn^{IV}(TNH_2PP)($OTf)_2$] supported on polystyrene and also [V^{IV}(TPP)($OTf)_2$] in organic transformations [31–40].

In continuation of our investigation on the reactivity of tin porphyrins, here, we report the application of high-valent [Sn^{IV}(TPP)($OTf)_2$] and [Sn^{IV}(TPP)($BF_4)_2$] catalysts for efficient and selective cyclopropanation of styrene derivatives with ethyl diazoacetate (EDA) at room temperature (Scheme 1).

2. Experimental

All chemicals were purchased from Merck or Fluka chemical companies. All reactions were performed under nitrogen atmosphere using a glove box equipped with a M040H Dri-Train gas

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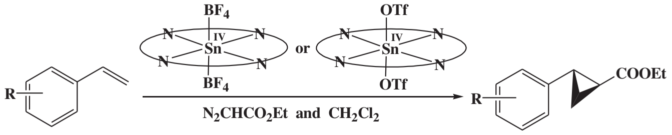

Scheme 1. Cyclopropanation of styrene derivatives with EDA catalyzed by [Sn^{IV}(TPP)(OTf)$_2$] or [Sn^{IV}(TPP)(BF$_4$)$_2$].

purification system. Toluene and THF were dried before use. NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer using CDCl$_3$ as solvent. Infrared spectra were run on a Philips PU9716 or a Shimadzu IR-435 spectrophotometer. All GC analyses were performed on an Agilent 6890 instrument equipped with a flame ionization detector (FID) using a 6FT3H OV-101 column. The GC yields were calculated by the "internal standard addition" method and in this manner ethyl hexanoate was used as internal standard (the same results were obtained using *n*-decane as internal standard). The styrene derivatives, EDA and diethyl fumarate were identified by comparison of their retention times by known samples. The corresponding cyclopropanes were isolated and identified. The tetraphenylporphyrin was prepared and metallated according to the literature [41]. The catalysts, [Sn^{IV}(TPP)(OTf)$_2$] [34] and [Sn^{IV}(TPP)(BF$_4$)$_2$] [35], were prepared as reported previously.

2.1. General procedure for the cyclopropanation of styrenes

A solution of ethyl diazoacetate (1.5 mmol) in dichloromethane (0.5 mL) was added dropwise to a solution of styrene derivative (1 mmol) and [Sn^{IV}(TPP)(OTf)$_2$] (10 mg, 0.01 mmol) or [Sn^{IV}(TPP)(BF$_4$)$_2$] (20 mg, 0.02 mmol) in dichloromethane (1 mL). The reaction mixture was stirred at room temperature under nitrogen atmosphere. The progress of the reaction was monitored by GC and TLC. After completion of the reaction, the solvent was evaporated, *n*-hexane (10 mL) was added and the catalyst was filtered. The filtrates were concentrated under reduced pressure and purified by chromatography on a short column of silica gel to afford the pure product.

3. Results and discussion

3.1. Cyclopropanation of olefins catalyzed by [Sn^{IV}(TPP)(OTf)$_2$]

Initially, we investigated the effect of OTf groups on the electron deficiency of tin(IV) porphyrin. In this manner, the cyclopropanation of styrene with EDA was performed in the presence of 1 mol% of [Sn^{IV}(TPP)(OTf)$_2$] or [Sn^{IV}(TPP)Cl$_2$] catalysts at room temperature. The results showed that only 35% of the corresponding cyclopropane was produced in the presence of [Sn^{IV}(TPP)Cl$_2$] after 3 h, while in the presence of [Sn^{IV}(TPP)(OTf)$_2$], the corresponding cyclopropane was obtained in 95% after 20 min. Then, the effect of catalyst amount, EDA and kind of solvent in the model reaction were also investigated (Table 1). The results showed that the highest yield of the corresponding cyclopropane was obtained in the presence of 1 mol% of [Sn^{IV}(TPP)(OTf)$_2$] (Table 1, entry 4). Moreover, the best results were obtained with 1.5 mmol of EDA. The excess amount of EDA was converted to diethyl fumarate (the side product was removed in the purification steps). The production of only fumarate ester can be attributed to the formation of carbene dimer-tin(IV) porphyrin complex which is blocked in a conformation favourable for the producing of thermodynamically stable fumarate ester [42]. Under these conditions, the highest yield of the corresponding cyclopropane was produced. In addition, the reaction was carried out in several solvents and the best results were observed in dichloromethane (Table 1, entry 4). It is noteworthy that when the reaction was carried out under air, the yield was dramatically decreased; therefore, all reactions were performed under N$_2$ atmosphere.

Table 1
Optimization of reaction conditions in the cyclopropanation of styrene with tin porphyrins.[a]

Entry	EDA (mmol)	Solvent	[Sn^{IV}(TPP)(OTf)$_2$] after 20 min		[Sn^{IV}(TPP)(BF$_4$)$_2$] after 30 min	
			Catalyst amount (mmol)	Yield (%)[b]	Catalyst amount (mmol)	Yield (%)[b]
1	1.5	CH$_2$Cl$_2$	0.003	20	0.005	18
2	1.5	CH$_2$Cl$_2$	0.005	42	0.007	25
3	1.5	CH$_2$Cl$_2$	0.007	59	0.01	43
4	1.5	CH$_2$Cl$_2$	0.01	95	0.02	95
5	1.5	CH$_2$Cl$_2$	0.02	95	0.03	95
6	1	CH$_2$Cl$_2$	0.01	80	0.02	70
7	2	CH$_2$Cl$_2$	0.01	95	0.02	95
8	1.5	*n*-Hexane	0.01	10	0.02	8
9	1.5	THF	0.01	60	0.02	40
10	1.5	DMSO	0.01	70	0.02	54

[a] Reaction conditions: styrene (1 mmol), EDA, solvent (1.5 mL) and [Sn^{IV}(TPP)(OTf)$_2$] or [Sn^{IV}(TPP)(BF$_4$)$_2$].
[b] GC yield.

The optimized conditions, which obtained for cyclopropanation of styrene were styrene, EDA and catalyst in a molar ratio of 100: 150: 1. Under these optimized reaction conditions, a variety of styrene derivatives was reacted with EDA in the presence of electron-deficient [Sn^{IV}(TPP)(OTf)$_2$], and the corresponding cyclopropanes were obtained in high yields and short reaction times (Table 2). These results showed that the electron-poor styrenes reacted in longer reaction times. On the other hand, electron-rich styrenes, such as 4-methoxystyrene and 4-methylstyrene were converted to their corresponding cyclopropanes in higher yields and shorter reaction times. After separation of the catalyst, the *E*/*Z* ratio of cyclopropanes was determined by their ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra of *trans*-cyclopropanes, the ethyl group hydrogens appear in 4.17 and 1.28 ppm; whereas for *cis*-cyclopropane these signals present at 3.88 and 0.98 ppm. Also in ^{13}C NMR spectra, the CH$_2$ group of cyclopropyl ring presents at 17–20 ppm for the *trans*-isomer while the same signal appears around 11 ppm for the *cis*-isomer [43]. As can be seen from NMR spectra, only *trans*-products have been produced and surprisingly no *cis*-isomer was detected in the presence of electron-deficient [Sn^{IV}(TPP)(OTf)$_2$].

As reported in the literature [44,45], Rh, Ru, Co, Os and Fe porphyrins have been used as efficient and selective catalysts for cyclopropanation of olefins. In all cases, a high *trans*/*cis* ratio has been reported in the presence of these catalysts. The investigations have revealed that the appropriate selection of the ligand and metal, and the nature of the diazo compound and the olefin have some influence on the *cis*/*trans* ratio [45]. For example, in the cyclopropanation of styrene with EDA catalyzed by different metal complexes of tetraphenylporphyrin, since the nature of olefin, EDA and ligand is the same, therefore, the variation in the *cis*/*trans* ratio can be attributed to the nature of the metal.

In order to check that GC values are completely true, some of products were quantitatively isolated. These results were in accordance to GC yields (Table 2).

It is important to note that no side product corresponds to insertion of carbene into OH bond was detected in the reaction mixture.

The Sn═C double bond is now well established, some of them structurally characterized and the Sn═C bond length and the environment of the respective tin atoms. An example of these tin-carbene complexes is formed by the reaction of imidazole-2-ylidene with SnR$_2$Cl$_2$ in which a square pyramidal or a trigonal