Catalysis Communications 107 (2018) 5–8

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

FeCl$_2$/DTBP: An efficient and highly E-selective cross - coupling of silanes with styrene and its derivatives

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ARTICLE INFO

Keywords:
Silyl radical
Cross-coupling
Stereoselectivity
Vinylsilanes

ABSTRACT

An efficient FeCl$_2$-catalyzed cross-coupling of silanes with styrene and its derivatives using DTBP as oxidant for selective synthesis of vinylsilanes was developed. This method presented an inexpensive, non-toxic and environmentally benign catalytic system with an appropriate substrate scope. This approach is E-specific and produced important classes of vinylsilanes in good yields. Control experiments indicated that the reaction may proceed via a radical pathway.

1. Introduction

Organosilicon compounds play a critical role in organic synthesis as valuable synthetic intermediates [1] and have a plethora of applications in materials science [2]. Among them, vinylsilanes become important building blocks or starting materials in organic synthesis, which rely on their unique reactivity profile and low environmental impact [3]. Thus, the construction of vinylsilanes C—Si bonds has attracted great attention from the synthetic community in the past decade. Great progress has been achieved in this area [4,5], including metathesis between vinylsilanes and olefins [6], hydrosilylation of alkynes [7,8] and dehydrogenative silylation of alkenes [9,10]. Compared to these conventional methods, synthesis of vinylsilanes through direct C—H bond functionalization is attractive from the viewpoints of atom economy, efficiency, and environmental benignity. Several concerned methods has been reported in this field using noble metals such as Ru [11], Pt [12], Ir [13], and Rh [14] as catalysts (Scheme 1, a). However, exorbitant price and high toxicity of those catalysts limit their large scale application.

Unlike other transition metals, iron is the most abundant metal in the earth's crust after aluminum [15], and therefore is much cheaper than the precious metals [16,17]. On the other hand, various iron species are incorporated in biological systems [18]. Some relatively low toxic iron species have already been extensively used in pharmaceutical industry, the food industry, and cosmetics [19]. Over the past few decades, iron catalysts have been reported in various reactions, such as oxidation, addition, substitution, and cyclization, etc. [20,21] Nevertheless, the iron-catalyzed C—Si bond-forming reactions are underdeveloped. The synthesis of vinylsilanes catalyzed by Fe (CO)$_5$ have already been reported by Nesmeyanov in 1962 (Scheme 1, b) [22], afterwards, some similar reactions catalyzed by Fe species have turned up gradually [23,24]. Plietker's group reported hydrosilylation of internal alkynes catalyzed by Fe complexes [25], and in the same year, subsequently, Thomas and co-workers discovered an iron-catalyzed hydrosilylation of alkenes and alkynes with extra ligand [26]. In addition, Marciniec's group researched the addition of HSiR$_3$ with styrene by Fe(0) catalysts [27,28]. Recently, Huang's group summarized the advances in base-metal-catalyzed alkene hydrosilylation [29]. Oestreich and co-workers proposed a Fe-catalyzed silylation of electron-rich arenes by an electrophilic aromatic substitution [30]. However, disadvantages exist with the above protocols, which usually use iron complexes that are difficult to synthesis and unstable as catalysts, or need extra additives.

Recently, our group reported an efficient synthesis of vinylsilanes via combining silicon-centered radicals with styrenes which catalyzed by copper (Scheme 1, c) [31]. We consider that the single electron transfer between copper salt and oxidant could initiate a radical, which then promoted the formation of the silyl radical by a hydrogen abstraction process. In addition, those already reported transformations indicated that iron salts could also trigger radical generation with some specific oxidants, such as DTBP [32,33], DDQ [34], TBHP [35], etc. Based on those reports, we wondered whether silyl radical could be formed in the presence of iron salt and certain oxidant. Herein we present a direct FeCl$_2$-catalyzed C—H silylation process of styrene and its derivatives (Scheme 1, d). Our protocol possesses several advantages such as low cost and low toxicity, environmental friendliness and high stereoselectivity.

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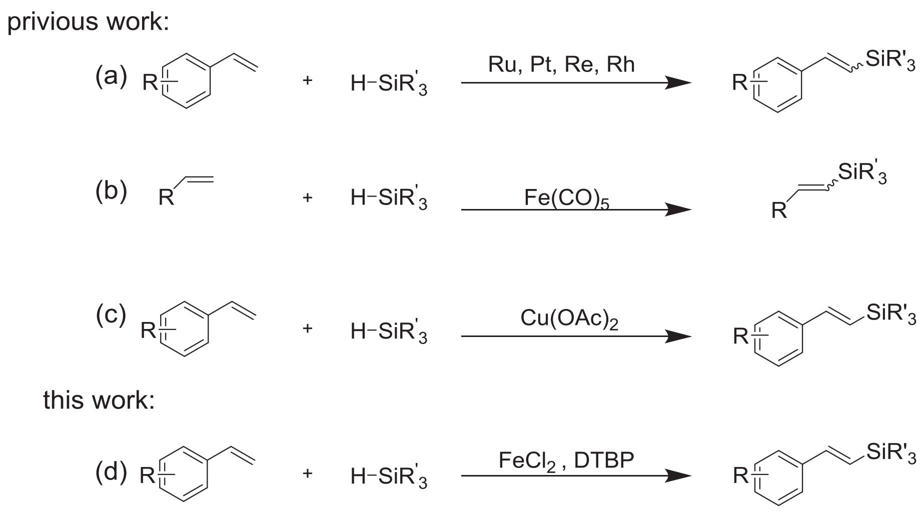
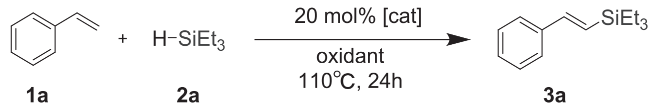
https://doi.org/10.1016/j.catcom.2017.12.023
Received 20 October 2017; Received in revised form 10 December 2017; Accepted 30 December 2017



Scheme 1. Strategies for transition-metal catalyzed silylation.

Table 1

Optimization of the reaction conditions.[a]



Entry	Catalyst	Oxidant	Solvent	Yield [b]/%
1	$FeCl_2$	DTBP	*t*-BuOH	78
2	$Fe(OAc)_2$	DTBP	*t*-BuOH	45
3	$FeCl_3$	DTBP	*t*-BuOH	–
4	$Fe(OTf)_3$	DTBP	*t*-BuOH	–
5	$Fe(acac)_3$	DTBP	*t*-BuOH	–
6	$FeCl_2$	TBHP	*t*-BuOH	11
7	$FeCl_2$	DCP	*t*-BuOH	8
8	$FeCl_2$	DDQ	*t*-BuOH	–
9	$FeCl_2$	DTBP	MeCN	11
10	$FeCl_2$	DTBP	DMSO	50
11	$FeCl_2$	DTBP	DMF	25
12	$FeCl_2$	DTBP	CH_2Cl_2	–
13[c]	**$FeCl_2$**	**DTBP**	***t*-BuOH**	**80 (75)**[f]
14[d]	$FeCl_2$	DTBP	*t*-BuOH	72
15[e]	$FeCl_2$	DTBP	*t*-BuOH	45
16	–	DTBP	*t*-BuOH	0
17	$FeCl_2$	–	*t*-BuOH	0

The significance of bold is the optimum conditions.

[a] Reaction conditions: catalyst (0.1 mmol), styrene (0.5 mmol), $HSiEt_3$ (2.5 mmol), oxidant (1.0 mmol), solvent (3 mL), at 110 °C for 24 h under Ar.

[b] Determined by GC.

[c] Temperature was 100 °C.

[d] Temperature was 90 °C.

[e] 10 mol% $FeCl_2$ was used.

[f] Isolated yield.

2. Results and discussion

The reaction of styrene (**1a**) and triethylsilane (**2a**) was chosen as a model reaction to optimize the reaction conditions (Table 1). With DTBP as the oxidant, triethylstyrylsilane (**3a**) was obtained in 78% yield, when $FeCl_2$ was used as the catalyst (Table 1, entry 1). A 45% yield of product 3a was achieved in the presence of $Fe(OAc)_2$ (Table 1, entry 2). $FeCl_3$, $Fe(OTf)_3$ and $Fe(acac)_3$ were not effective for the formation of **3a** (Table 1, entries 3–5). Different oxidants were also screened, less product was formed when other oxidant, such as TBHP, DCP and DDQ were used instead of DTBP (Table 1, entries 6–8). Further screening of solvents and temperatures revealed that *t*-BuOH was superior as a suitable solvent (Table 1, entries 9–12) and 100 °C was the optimum temperature (Table 1, entries 13 and 14). The amount of the catalyst was also explored, and the best yield could be obtained in the presence of a 20 mol% of catalyst (Table 1, entry 15). The conversion of the reaction in the optimum conditions is 98%. Finally, the starting materials remained unreacted when the reaction was carried out in the absence of $FeCl_2$ or DTBP (Table 1, entries 16 and 17). Moreover, the GC–MS spectrum shows there are no byproducts such as products of hydrogen addition and Z - products in the reaction mixture.

With the optimized conditions in hand, we turn to explore the