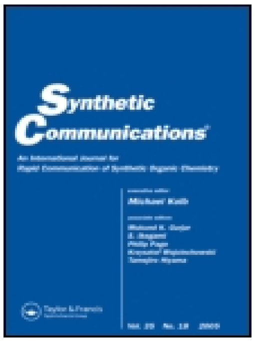

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Highly efficient TfOH-catalyzed head-to-tail dimerization of vinylarenes

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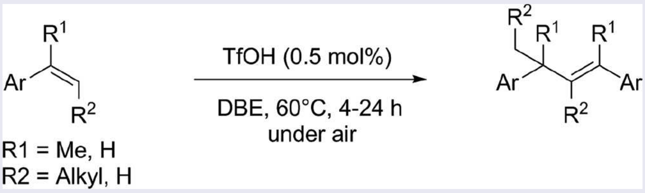
ABSTRACT
A convenient and efficient TfOH-catalyzed head-to-tail dimerization of vinylarenes has been realized under mild conditions. The present protocol provides an attractive approach to a diverse range of higher olefins in good to excellent yields.

GRAPHICAL ABSTRACT



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KEYWORDS
Brønsted acids; dimerization; metal free; vinylarenes

Introduction

Alkenes, some of the most useful substrates, play a central role in the organic reactions because they can be transformed into a wide range of important synthetic intermediates based on their rich chemistry.[1] Among the various alkene-participated reactions, the catalytic dimerization of alkenes is a 100% atom-economical reaction and an industrially important process for preparing higher alkenes from simple and small alkenes.[2] Compared with the head-to-head[3] and tail-to-tail[4] dimerization of alkenes, the head-to-tail dimerization of alkenes has been considered more attractive transformation because a new allylic carbon stereogenic center can be created (Scheme 1), which is an important part of various valuable biologically active compounds and pharmaceuticals, such as oral anticoagulants warfarin and phenprocoumone, antihyperlipidemic nafenopin, and antiallergic agent dimentindene.[5]

In past decades, many catalytic systems have successfully been developed for the head-to-tail dimerization of styrenes.[6–9] For example, cationic Ni complexes such as $[Ni(\pi\text{-}C_3H_5)(OCOCF_3)]_2$,[6a](ally)Ni-$Cl_2$,[6b] Ni(dppp)$Cl_2$/$Bu_3N$,[6c] and (ally)Ni-NHC[6d] have been used for styrene dimerization, leading to 1,3-diphenyl-1-butenes in moderate to good yields. Also, cationic Pd complexes $[(\eta^3\text{-}\ C_3H_5)\ Pd(CD_3NO_2)_2]^+BF_4^-$,[7a] $Pd(PPh_3)_2$

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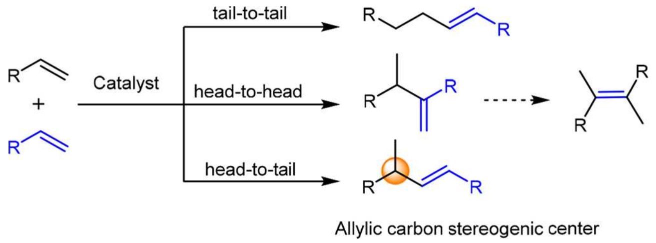


Scheme 1. Three possible reaction pathways for the dimerization of alkenes.

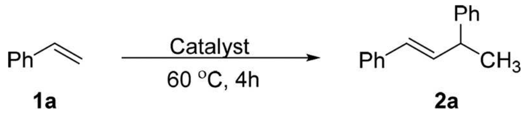
$(BF_4)_2$,[7b,7c] or $[(ally)Pd(PPh_3)]^+OTf^-$[7d] and some Pd-catalyzed systems including $Pd(OAc)_2/PPh_3/M(OTf)_3$,[8a,8d,8e] $Pd(OAc)_2/BmimPF_6$,[8b] $Pd(OAc)_2/PPh_3/BF_3\text{-}OEt_2$,[8c,8f] $Pd(OAc)_2/HFIP$,[8g] and $Pd(acac)_2/TFA$[8h] could catalyze the dimerization reaction of styrenes. Currently, other catalyzed systems such as $[(\eta^6\text{-}C_6H_6)(PCy_3)(CO)RuH]^+BF_4$,[9a,9b] and $FeCl_3/AgNTf_2$[9c] could be applied for the same dimerization reaction as well, generating various 1,3-diphenyl-1-butene derivatives in good yields. Nevertheless, most of these reactions are inevitably accompanied with the problems such as the need of expensive phosphorus ligands and additives and the preparation of metal complexes. Therefore, there is still a great demand for more technically feasible and especially environmentally friendly methods to conveniently realize the dimerization of alkenes.

Nowadays, using Brønsted acids as catalysts has attracted much attention for their advantages of low cost, nontoxicity, and operation simplicity.[10] During our study of Brønsted acid TfOH-catalyzed sp^3-sp^2 C-C bond formation via direct coupling of alcohols with simple alkenes,[11] a control experiment was performed in the absence of alcohol, which unexpectedly resulted in the dimerization product of styrene. To the best of our knowledge, few methods have been developed for the dimerization of styrene by using Brønsted acids as catalysts, and most of these reactions were limited to the generation of oligomers and polymers and/or needed stoichiometric amount of acids.[12] Herein, we present an efficient head-to-tail dimerization reaction of styrenes, requiring neither metal catalyst nor synthetic ligand or additive but only catalytic amounts of a simple Brønsted acid.

Results and discussion

To optimize the formation of **2a**, we examined the reaction under various conditions (Table 1). The screening of a range of solvents showed that the reaction performed in 1,2-dibromoethane (DBE)[13] was better than those in DCE, toluene, and $CHCl_3$(entries 1–4). No desired product was observed in solvents such as *n*-hexane and cyclohexane (entries 5 and 6). Subsequently, the catalytic activity of other catalysts was investigated in DBE. Besides, TfOH, $HClO_4$ could also efficiently catalyze this dimerization reaction (entry 7). Nevertheless, other Brønsted acids such as methylsulfonic acid (MSA), p-toluenesulfonic acid (PTSA), H_2SO_4, trifluoroacetic acid (TFA), CH_3COOH, HNO_3, and HCl did not catalyze or only sluggishly catalyzed this reaction (entries 8–14). Further optimization suggested that the best yield (87%) was obtained when the TfOH loading was decreased to 0.5 mol%, and the DBE was increased to 2 mL (entries 15–18). In addition, the effect of temperature on this reaction was also investigated and the results were shown in the

Table 1. Optimization of the reaction conditions.[a]



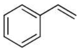
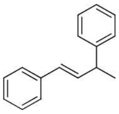
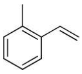
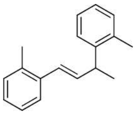
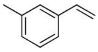
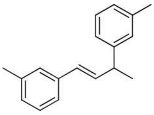
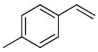
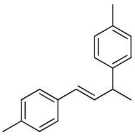
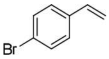
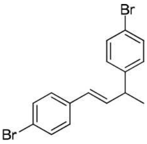
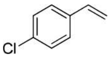
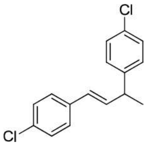
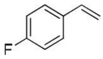
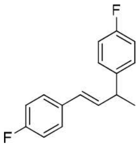
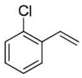
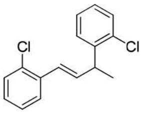
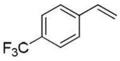
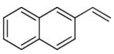
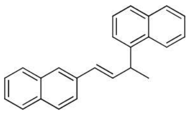
Entry	Catalyst (%)	Solvent (mL)	Yield (%)[b]
1	TfOH (2.5 mol%)	DBE	47
2	TfOH (2.5 mol%)	DCE	33
3	TfOH (2.5 mol%)	Toluene	37
4	TfOH (2.5 mol%)	$CHCl_3$	36
5	TfOH (2.5 mol%)	*n*-Hexane	0
6	TfOH (2.5 mol%)	Cyclohexane	0
7	$HClO_4$ (2.5 mol%)	DBE	42
8	MSA (2.5 mol%)	DBE	<5
9	PTSA (2.5 mol%)	DBE	<5
10	H_2SO_4 (2.5 mol%)	DBE	<5
11	TFA (2.5 mol%)	DBE	0
12	CH_3COOH (2.5 mol%)	DBE	0
13	HNO_3 (2.5 mol%)	DBE	0
14	HCl (2.5 mol%)	DBE	0
15	TfOH (1.25 mol%)	DBE	49
16	TfOH (1.25 mol%)	DBE[c]	56
17	TfOH (0.5 mol%)	DBE[c]	58
18	TfOH (**0.5 mol**%)	**DBE**[d]	**87**

[a] Reaction conditions: styrene **1a** (1 mmol), 0.5 mL 1,2-dibromoethane (DBE), 60 °C, 4 h, under air.
[b] Isolated yields based on the styrene **1a**.
[c] 1 mL DBE.
[d] 2 mL DBE.

supporting information (Table S1). No product was detected when the reaction was performed in the absence of catalyst.

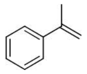
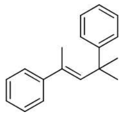
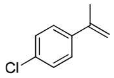
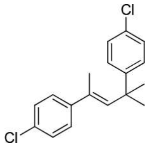
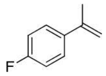
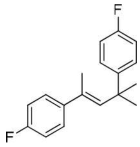
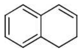
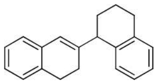
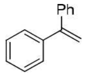
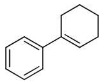
With the optimized conditions in hand, the scope and limitations of this reaction were investigated and some results are summarized in Table 2. In general, vinylarenes containing electron-withdrawing or electron-donating groups were all suitable substrates and generated the corresponding products in good to excellent yields. Thus, the dimerization reactions of *o*-Me, *m*-Me, and *p*-Me substituted styrenes proceeded efficiently and gave the desired 1,3-diaryl-1-butene derivatives **2b–d** in 88%, 59%, and 62% yields, respectively (entries 3 and 4). Halogen-substituted styrenes such as *p*-Br-, *p*-Cl-, and *p*-F-styrene were also tolerated and gave the dimerization products **2e–g** in excellent yields (entries 5–7). By contrast, *o*-Cl-styrene produced the desired product in a poor yield of 35%, and no conversion was observed with trifluoromethyl styrene as substrate, possibly because of an electronic effect (entries 8 and 9). Vinylnaphthalene could be transformed to the corresponding dimerization product in good yield (entry 10). In addition, the sterically hindered disubstituted aromatic olefins such as alpha-methyl styrene and substituted alpha-methyl styrenes were compatible with this reaction, leading to the desired products in good to excellent yields (entries 11–14). Notably, aromatic cyclic olefins such as 1,2-dihydronaphthalene could also be used in the reaction to give the expected products in 60% yields. Nevertheless, when disubstituted aromatic olefins with greater steric hindrance such as 1,1-diphenylethylene and 1-phenyl-1-cyclohexene were used as substrates, none of the desired products were detected (entries 15 and 16).

Table 2. TfOH-catalyzed head-to-tail dimerization of vinylarenes.[a]

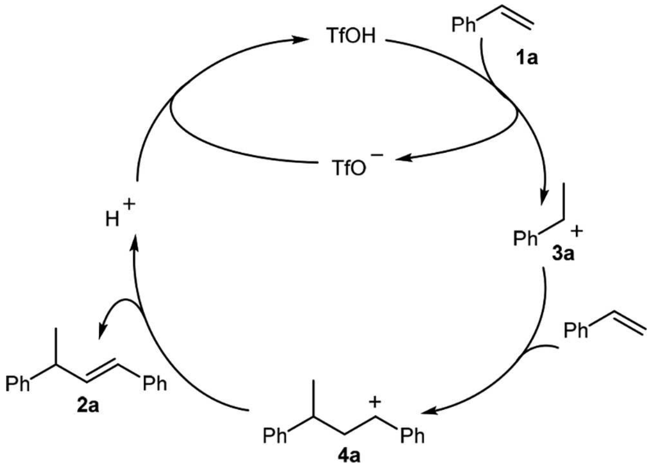
Entry	Vinylarene	Product	Yield (%)[b]
1	 **1a**	 **2a**	87
2	 **1b**	 **2b**	88
3	 **1c**	 **2c**	59
4	 **1d**	 **2d**	62
5	 **1e**	 **2e**	86
6	 **1f**	 **2f**	84
7	 **1g**	 **2g**	83
8	 **1h**	 **2h**	35
9	 **1i**	ND —	—
10	 **1j**	 **2j**	43

(*Continued*)

Table 2. Continued.

Entry	Vinylarene		Product		Yield (%)[b]
11		**1k**		**2k**	83
12		**1l**		**2l**	76
13		**1m**		**2m**	81
14		**1n**		**2n**	60
15		**1o**	N.D.	—	—
16		**1p**	N.D	—	—

[a]Reaction conditions: vinylarenes (1 mmol), TfOH (0.5 mol%), DBE (2 mL), 60 °C, 4–24 h, under air.
[b]Isolated yields based on vinylarenes **1**.



Scheme 2. Plausible mechanism.

Based on experimental observation and previous studies,[11–14] a possible mechanism for the TfOH-catalyzed head-to-tail dimerization of vinylarenes is proposed in Scheme 2. It involves the generation of benzylic cation **3** from the vinylarene in the presence of TfOH. Then, electrophilic addition of styrene with **3** provides corresponding alkylarylcarbenium ion **4**, which undergoes deprotonation to provide the desire product **2**.

Conclusions

In summary, we have successfully developed a convenient and efficient method for head-to-tail dimerization of vinylarenes by employing simple Brønsted acid TfOH as catalyst under mild conditions. The present protocol provides an attractive approach to a diverse range of higher olefins in good to excellent yields with high selectivity. Further studies of the detailed reaction mechanism and the enantioselective induction on the product by using a chiral acid are ongoing.

Experimental

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, and Alfa Aesar Chemical Company. All reagents and solvents were used as received without further purification unless otherwise stated. NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 400 spectrometer with tetramethylsilane (TMS) as internal standard (400 MHz ^{1}H, 100 MHz ^{13}C) at room temperature; the chemical shifts (δ) were expressed in parts per million (ppm); and J values were given in hertz (Hz). The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Splitting patterns that could not be easily interpreted were designated as multiplet (m) or broad (br). High-resolution mass spectrometry (HRMS) data were obtained on a Waters Micromass GCT Premier mass spectrometer by the EI method. Column chromatography was performed on silica gel (200–300 mesh).

General procedure for the dimerization of vinylarenes

The vinylarene (1 mmol) in DBE (2 mL) in a round-bottomed flask was stirred at 60°C under air. Then, TfOH (0.5 mol%) was added. The mixture was magnetically stirred at 60°C for 4–24 h until the complete consumption of vinylarene (observed by thin-layer chromatography, TLC). The mixture was filtered through silica gel and washed with ethyl acetate (10 mL) to give a brown solution. After filtration, the solvent was removed by vacuum evaporation. The residue was purified by silica-gel flash column chromatography by using petroleum ether / ethyl acetate (400:1 in volume) as the eluent. The desired product was isolated as viscous oil, which was suitable for analytical purposes.

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