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Short Communication

Dimerization of styrenes catalyzed by PhP(O)HOR/Mn(II)/Co(II)/O_2

Kaijian Liu [a,1], Ying Wang [b,1], Peng Li [a], Wenwen Cai [a], Jiannan Xiang [a,*]

[a] College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, PR China
[b] Institute of Cancer Research, Southern Medical University, Guangzhou, 510515, PR China

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ABSTRACT

A methodology for the dimerization of substituted styrenes is reported using a PhP(O)HOR/Mn(II)/Co(II)O_2 catalyst, in which the alkyl phenylphosphinate compound acted as a catalyst rather than a substrate as is generally observed. Mechanistic studies suggested the reaction most likely proceeded *via* addition–elimination.

1. Introduction

The dimerization of alkenes is a 100% atom-efficient reaction that provides useful intermediates [1], and has traditionally been performed in the presence of transition metal-catalyzed conditions [2–4]. Among the alkenes for use in catalytic dimerization, styrene derivatives have been extensively studied [5–8]. During the last decades, manifold transition-metal catalysts such as palladium, nickel, and zirconium have been proven to be efficient for the dimerization of styrenes [9–11]. Meanwhile, catalytic dimerization of styrenes generally produces a head-to-tail isomers [12–14], while there are a few reports on catalyst systems that can afford tail-to-tail [15,16] or head-to-head isomers [17,18] in a regioselective manner. Although previous transition-metal catalysts have showed high catalytic activity for the dimerization of styrenes, we hope to develop a novel and multiple catalyst system for such type of dimerization.

Organophosphonates, a useful class of compounds in synthetic applications and biological activity, can be prepared *via* hydrophosphorylation of alkenes in the presence of radical initiators such as benzoyl peroxide, AIBN, bases, acids and transition metals [19–25]. A widely studied example is the large scale synthesis of various dialkyl phosphonates *via* the hydrophosphorylation of alkenes catalyzed by Mn(II)/Co(II)/O_2 redox system [26–28]. Dialkyl phosphate undergoes a one-electron oxidation by Mn(III) (generated *in situ* from Mn(II) by Co(II) and O_2) to form phosphonyl radicals, which then add to alkenes leading to dialkyl phosphonates.

We are consequently attempt to synthesize a series of organophosphonates *via* addition of phosphates to styrene catalyzed by Mn(II)/Co(II)/O_2 redox system. However, during the course of our study we discovered a novel C–C bond forming product not the expected hydrophosphorylation products (**3a**) and (**3b**) when PhP(O)HOBu (**2a**) was employed for addition to 2,4,5-trimethoxy-1-propenylbenzene (**1a**). The structure of product (**4a**) was a dimer of 2,4,5-trimethoxy-1-propenylbenzene confirmed by single-crystal X-ray diffraction (supporting information). In addition, we conducted the reaction by using AIBN in place of PhP(O)HOBu in the presence of Mn(II)/Co(II)/O_2; however, no dimerization of styrenes occurred. Since PhP(O)HOBu was considered to be a substrate and to participate in the addition reaction of 2,4,5-trimethoxy-1-propenylbenzene (**1a**) (Scheme 1), PhP(O)HOBu works as a co-catalyst of Mn(II)/Co(II)/O_2 to give the corresponding dimer (**4a**). Herein, we disclosed the synthetic and mechanistic aspects of these phenomena.

2. Experimental

2.1. Chemicals and characterization

Reactions were carried out in a 25-mL three-necked flask under an oxygen atmosphere. Uncorrected melting points were measured using a Beijing Taike XT-4 microscopy melting point apparatus. Mass spectrometry was performed using an Agilent 1100 HPLC/MSD spectrometer. ^1H NMR spectra were recorded using an INOVA-400 spectrometer with a TMS internal standard. ^{13}C NMR spectra were recorded using an INOVA-125 spectrometer. $Mn(OAc)_2$ and $Co(OAc)_2$ were purchased from Acros Organics, and $PhPCl_2$ was purchased from Alfa Aesar, all of which were used as received. Alkyl phenylphosphinate was prepared according to the literature [29]. TLC

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[*] Corresponding author. Tel./fax.: +86 731 88821740.
E-mail address: Jnxiang@hnu.edu.cn (J. Xiang).

[1] Kaijian Liu and Ying Wang have equal contribution in this work and are both equally considered as first author.

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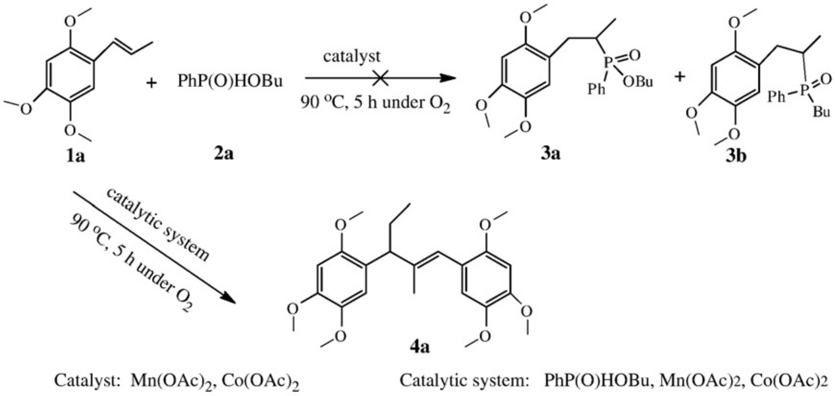


Scheme 1. Catalytic dimerization of **1a**.

analyses were performed using silica gel plates, and column chromatography was conducted using silica gel (mesh 200–300), both of which were obtained from Qingdao Ocean Chemicals.

*2.2. Synthesis of 3-ethyl-2-methyl-3-(2″,4″,5″-trimethoxy)phenyl-1-(2′,4′,5′- trimethoxy)phenyl-1-propene (**4a**)*

A typical dimerization reaction was carried out as follows. Butyl phenylphosphinate (3.0 mmol), $Mn(OAc)_2$ (0.05 mmol) and $Co(OAc)_2$ (0.05 mmol) were added to a solution of 2,4,5-trimethoxy-1-propenylbenzene (1.0 mmol) in ethyl acetate (15 mL), and the mixture was heated at 90 °C for 5 h. After cooling, the mixture was extracted with ethyl acetate, and the organic layer was washed with saturated NaCl until the pH was neutral. The resulting oil was purified by column chromatography and eluted with 1:6 ethyl acetate/petroleum ether to afford the title product as a white solid (0.158 g, 76%).

3. Results and discussion

Due to the hypothesis that alkyl phenylphosphinate compound acts as a catalyst rather than a substrate we first examined influence of substrate structure on dimerization reaction. It was found the dimerization reaction failed when substrate was replaced by a linear alkene (amylene) instead of a styrene-based compound, indicating that the alkene structure was a significant factor in this reaction, and is discussed later. We then aimed to test the effects of individual catalytic factor on the mentioned reaction. As shown in Table 1, the corresponding results were not obtained in the absence of PhP(O)HOBu (Table 1, entry 1). Similarly, no products were detected in the absence of $Mn(OAc)_2$ or $Co(OAc)_2$ (Table 1, entries 2 and 3). When the same catalyst system was used, the dimerization did not proceed under a pure nitrogen atmosphere (Table 1, entry 4). In contrast, the dimer **4a** was obtained in 76% yield under an oxygen atmosphere (Table 1, entry 5). This result demonstrated that the dimerization requires a synergistic relationship between the styrene-based compounds, alkyl phenylphosphinate and Mn(II)/Co(II)/O_2 redox system. In addition, by changing the ratio of **1a** and **2a** from 1:3 to 1:0.5, the dimerization also proceeded; however, the yield of **4a** decreased to 30% (Table 1, entry 6). The radical mechanism for alkene hydrophosphorylation using Mn(II)/Co(II)/O_2 is well known, so a free radical inhibitor, *p*-hydroquinone, was selected to further confirm the mechanism (Table 1, entry 7). It demonstrated that the dimerization was inhibited completely by addition of *p*-hydroquinone.

Table 1
Dimerization of **1a** by **2a** using Mn(II)/Co(II)/O_2[a].

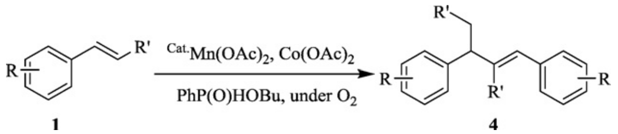
Entry	**2a** (mmol)	$Mn(OAc)_2$ (mmol%)	$Co(OAc)_2$ (mmol%)	Inhibitor[b] (mmol%)	Isolated yield[c] (%)
1	–	5	5	–	0
2	3	–	5	–	0
3	3	5	–	–	0
4[d]	3	5	5	–	0
5	3	5	5	–	76
6	0.5	5	5	–	30
7	3	5	5	10	0

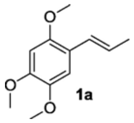
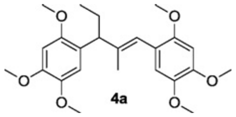
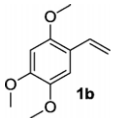
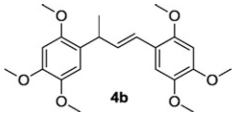
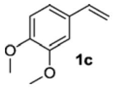
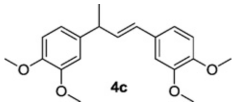
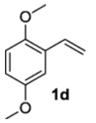
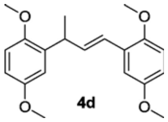
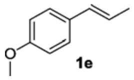
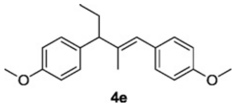
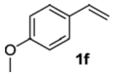
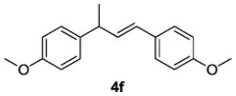
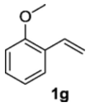
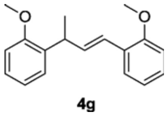
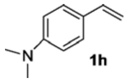
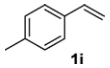
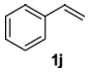
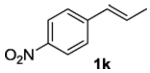
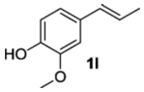
[a] **1a** (1 mmol) was catalyzed by **2a**, $Mn(OAc)_2$ and $Co(OAc)_2$ under O_2 at 90 °C for 5 h.
[b] *p*-Hydroquinone.
[c] Based on the amount of **1a** used.
[d] O_2 was replaced by N_2.

Having optimized the catalytic conditions, the corresponding dimers were obtained conveniently in the presence of several alkyl phenylphosphinates (Me, Et, and Bu). This suggested that alkyl groups of alkyl phenylphosphinate had little effect on the dimerization of styrenes. We further investigated the influence of styrene-based compounds with different substituents on the scope and limitations of dimerization. As shown in Table 2, styrene-based compounds bearing methoxy substituents on a phenyl ring gave good results (Table 2, entries 1–7). The yield of the dimers increased upon increasing the number of methoxy groups, while there was no obvious difference to the reaction when using monomethoxy and dimethoxy substituents. No dimer was obtained from styrene bearing an electron-withdrawing substituent such as NO_2 (Table 2, entries 11). These results indicate that the electronic effect of the substituents played an important role in the present dimerization reaction. However, it was worth noting the dimerization could not proceed for styrenes with other electron-donating substituents such as dimethylamino and methyl substituents (Table 2, entries 8 and 9). A likely explanation is that methoxy groups have higher donating efficiency compared with those of dimethylamino and methyl groups, which facilitate to form the strong *p*–*π* conjugation. These results demonstrated that sufficient donating efficiency in substrate preferred the dimerization of styrenes. When the substrate was a terminal alkene, the ^1H NMR spectrum exhibited a doublet of doublets from the two vinylic protons with a coupling constant of 16 Hz, typical for the coupling between vicinal vinylic protons at trans-position (Table 2, entries 2–4 and 6–7). Previously reported procedures for preparing alkene dimers catalyzed by transition metals are generally limited to terminal alkenes [3–6], while the present reaction could be applied to dimerization of non-terminal alkenes (Table 2, entries 1 and 5). In addition, this electronic effect did not account for the substrate with a phenolic hydroxyl group, for which no reaction took place (Table 2, entry 12). Presumably the reason was due to quinone formation of oxidized phenol under the oxygen conditions.

While a detailed reaction mechanism is not clear, the results can be well explained by a radical mechanism as depicted in Scheme 2. For the initiating step, the reaction is known to proceed by the

Table 2
Dimerization of styrene-based compounds catalyzed by **2a** with Mn(II)/Co(II)/O_2[a].



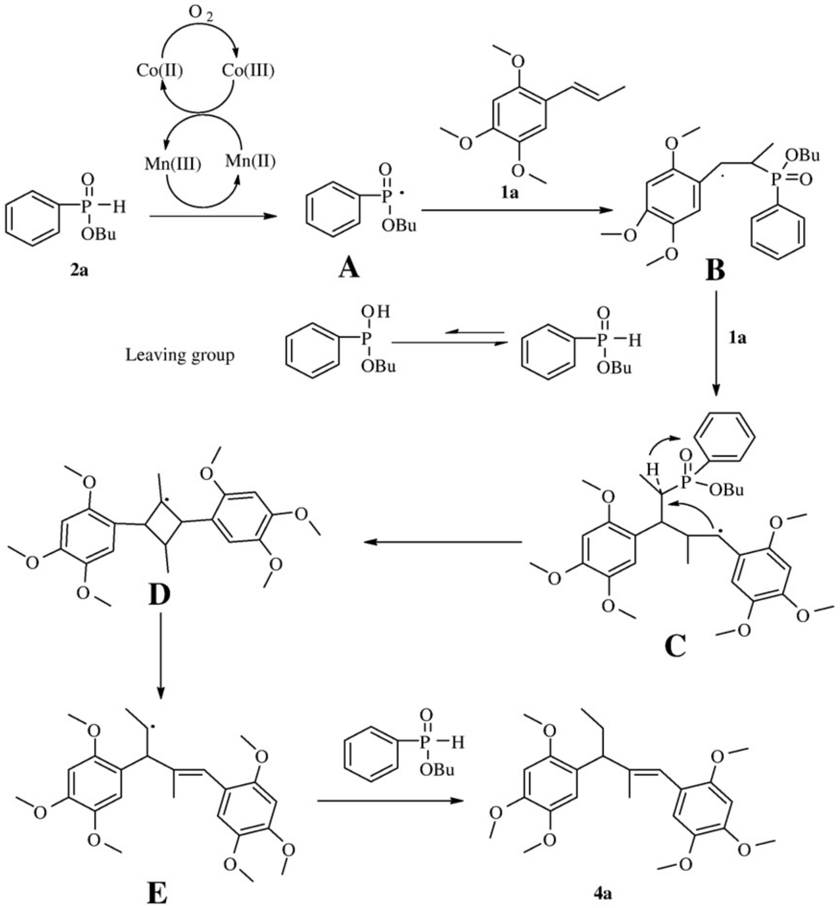
Entry	Substrate	Product	Isolated yield (%)
1	 1a	 4a	76
2	 1b	 4b	64
3	 1c	 4c	51
4	 1d	 4d	45
5	 1e	 4e	50
6	 1f	 4f	46
7	 1g	 4g	48
8	 1h	–	0
9	 1i	–	0
10	 1j	–	0
11	 1k	–	0
12	 1l	–	0

[a] Reaction carried out under the same conditions as in Table 1, entry 5.

generation of Co(III)-dioxygen complexes from Co(II) and O_2, and Mn(II) is then oxidized to Mn(III) by the Co(III)-dioxygen complexes. Subsequently, **2a** undergoes a one-electron oxidation by Mn(III) to give the phosphinyl radical (**A**) [26]. Owing to the strong *p*–*π* conjugation, the addition of phosphinyl radical (**A**) to alkene **1a** facilitates to the formation of radical (**B**). Radical **B** induces a similar reaction to form another radical (**C**), followed by an addition–elimination pathway to result in the formation of a four-membered ring radical (**D**) [30]. The intermediate radical (**E**) produced from the unstable four-membered radical (**D**) extracts a hydrogen atom from **2a** to yield the final styrene dimer (**4a**). Based on the knowledge of PhP(O)HOBu (or its tautomer PhP(OH)OBu) [31] acting as a leaving group, alkyl phenylphosphinate served as a catalyst in this reaction. Although the reaction as compared with classical hydrophosphorylation of alkenes is most likely associated with the addition–elimination process, the driving force of the formation of a four-membered ring radical (**D**) remains unclear.

4. Conclusions

We have found that dimerization of styrenes proceeded by a novel catalyst system of Mn(II)/Co(II)/O2 combined with alkyl phenylphosphinate, PhP(O)HOR, in which PhP(O)HOR acts as a co-catalyst rather than a substrate for hydrophosphorylation of styrenes. We believe that the present dimerization reaction of styrenes would proceed *via* a radical mechanism involving an addition–elimination sequence.



Scheme 2. Possible mechanism.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2012.01.010.

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