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COMMUNICATION

Manganese(III)-mediated phosphinoyl radical reactions for stereoselective synthesis of phosphinoylated tetrahydronaphthalenes[†]

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Reactions of diphenylphosphinoyl radicals with 5-aryl-2pentenoates or β -phenylethylene styrenes generate *trans*-substituted tetrahydronaphthalenes through a cascade reaction sequence.

Reaction of phosphorous-centred radicals with unsaturated compounds to generate phosphorous-carbon bonds is a subject of current interest.¹ Hydrogen transfer of compounds containing a labile P–H bond is an efficient way to form phosphonyl radicals $[(RO)_2P(O)^{\bullet}]$ and phosphinoyl radicals $[R_2P(O)^{\bullet}]$. These radicals add to alkenes at the rates of around $10^6-10^7 \text{ M}^{-1} \text{ s}^{-1}$, which are 1 to 2 orders faster than the addition of carbon-centred radicals.^{2,3} The greater *s*-contribution and pyramidalization of the phosphorous atom makes phosphonyl radicals more reactive than phosphinoyl radicals.⁴

A significant amount of effort has been spent on the study of physical and chemical properties of phosphonyl and phosphinoyl radicals.^{5–9} However, the synthetic application of phosphinoyl radicals is far behind the phosphonyl radicals.^{1a} A literature search indicated that only the Taillades¹⁰ and Parsons¹¹ groups have reported the addition of diphenylphosphinoyl radicals to alkenes for the synthesis of alkylphosphine oxides. In those two cases, Et₃B and AIBN were used to promote the formation of phosphinoyl radicals, respectively. Introduced in this communication is Mn(OAc)₃-promoted formation of a diphenylphosphinoyl radical and its application for cascade addition and cyclization reactions.

We recently reported the Mn(OAc)₃-mediated reactions of phosphonyl radicals for direct phosphonylation of arenes,¹² heteroarenes,¹³ and arylalkenes.¹⁴ A reaction of methyl cinnamate **1** with dimethyl phosphonate **2** to form *trans* phosphonylated product (*E*)-**3** is shown in Scheme 1.¹⁴ To study the role of the phenyl group in this regio- and stereoselective reaction, acrylates containing non-conjugated phenyl such as **4a**, **5a** and **5b** were reacted with dimethyl phosphonate **2** in acetic acid at 50 °C. All reactions afforded complicated mixtures containing

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regioisomers, E/Z isomers, and polymers. When diphenylphosphine oxide 7 was used to replace dimethyl phosphonate 2, reactions of 5a and 5b both gave complicated mixtures. However, the reaction of 4a gave a major product 8a. Under the optimization conditions of using 1 equiv. of 4a, 2 equiv. of 7, and 2 equiv. of Mn(OAc)₃ in acetic acid at 50 °C for 30 min, 8a was prepared in 60% isolated yield (Scheme 2). By-products generated by hydrophosphinoylation and direct phosphinovlation on the acrylate and on the phenyl ring were not observed. X-Ray crystal structure analysis confirmed the structure of 8a to be a trans-disubstituted tetrahydronaphthalene (Fig. 1).¹⁵ In this reaction, the less reactive phosphinovl radical and the ethylene group in 4a provide a right combination to control the reactivity and selectivity in the formation of phosphinoylated tetrahydronaphthalene 8a. Similar substrates 6a-c bearing electron-withdrawing groups such as COPh, CN, and NO₂ gave complicated mixtures. It is known that phosphinoyl radicals are moderately nucleophilic.1a Addition of a phosphinoyl radical to electron-poor alkenes could be too fast to give selective products.

A mechanism for the reaction of 5-aryl-2-pentenoate 4a is proposed in Scheme 3. Phosphinoyl radical 9 adds to the β -position of the acrylate to form radical 10. This carbon-centered

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Fig. 1 X-Ray crystal structure of 8a.



radical cyclizes to the phenyl ring to yield *trans*-substituted **11**. It is oxidized with $Mn(OAc)_3$ to give carbocation **12** followed by deprotonation to afford product **8a**.

Reactions of a series of 5-aryl-2-pentenoates **4** indicated that a methyl at 2-, 4- and 5-positions of acrylate had no significant effect on the reactivity and afforded *trans* products in 50-62%yields (Table 1, entries 2, 4, and 5). X-Ray crystal structure analysis confirmed the structure of **8d** (see ESI†). If the methyl is at the 3-position, no reaction is observed because of the steric hindrance at the reaction site (Table 1, entry 3). The effect of the substituent on the phenyl was also investigated. It was found that both electron-donating and electronwithdrawing groups are tolerated (Table 1, entries 6–8).

In a recent paper we reported that the reactions of dimethyl phosphonate 2 with 1-phenylalkenes 13a-c afforded mixtures of regio- and E/Z isomers of alkenylphosphonates.¹⁴ We wondered if β -phenylethylene styrene 14a could react with diphenylphosphine oxide 7 to afford phosphinoylated tetra-hydronaphthalene product 15a. Indeed, reaction of 1 equiv. of 14a, 2 equiv. of 7, and 2 equiv. of Mn(OAc)₃ in acetic acid at 50 °C for 30 min afforded 15a in 55% yield together with by-product 16a in 21% yield (Scheme 4). A mechanism for the formation of 15a and 16a is proposed. Radical 17 undergoes cyclization by following the pathway presented in Scheme 3 to form 18 and then acetylated to yield by-product 16a.

Styrene 14a prepared by the Wittig reaction was a mixture of 7:3 E/Z isomers. To understand if isomers could have different outcomes, (Z)- β -phenylethylene styrene (Z)-14a was synthesized by hydrogenation of 1,4-diphenyl-1-butyne with the Lindlar catalyst. Reaction of (Z)-14a with a phosphinoyl radical gave a very similar result as that for 14a

Fable 1 Reactions of β -phenylethylene acrylat



Scheme 4

(Table 2, entries 1 and 2). It is concluded that E/Z isomers of **14a** have no significant impact on product yield and stereochemistry.

Reactions of a series of β -phenylethylene styrenes with diphenylphosphine oxide 7 are shown in Table 2. The results indicate that electron-donating and withdrawing groups on the phenyl ring of styrene are tolerated (Table 2, entries 3 and 4). The methyl groups at 1-, 2-, 3- and 4-positions of the styrene were also studied. Except the methyl at the 2-position (Table 2, entry 6), all other methyl-substituted substrates afforded the expected phosphinoylated tetrahydronaphthalenes **15** as a major product together with a small amount of noncyclized byproducts **16** (Table 2, entries 5, 7, and 8). The reaction of **14h** afforded a complicated mixture (Table 2, entry 9).

In summary, we have developed a $Mn(OAc)_3$ -mediated regio- and stereoselective reaction for the preparation of



2-phosphinoylated tetrahydronaphthalenes. 5-Aryl-2-pentenoates and 5-phenylethylene styrenes are good substrates to form phosphinoylated tetrahydronaphthalenes through a phosphinoyl radical addition and cyclization process. This straightforward reaction represents a new application of phosphinoyl radicals in stereoselective synthesis.

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