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Polymeric tertiaryphosphine as a green and recyclable organocatalyst for stereoselective isomerization reaction

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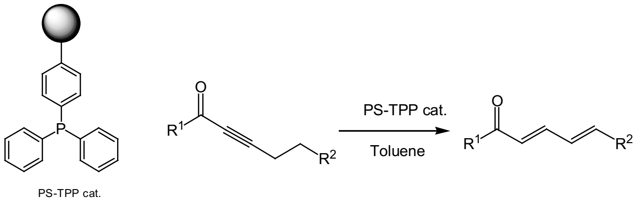
Abstract—A green, simple and effective polymeric organocatalytic system, polymer-supported triphenylphosphine (PS-TPP), for the stereoselective isomerization of α,β-ynones to (*E*,*E*)-α,β-γ,δ-dienones is reported here. The catalyst, PS-TPP could be recovered by simple filtration and reused several times with high activity.

Metal-free organocatalysts have drawn great attention because of their particular catalytic capability, and metal-free organocatalyzed reactions are of current interest and have become an intensively studied area in organic synthesis, especially in asymmetric synthesis in modern organic chemistry.[1] Compared with organometallic catalysts, most of the organocatalysts are easier to be prepared, more stable, cheaper and more environmental friendly. Unfortunately, separation of ordinary organocatalysts from the products is often rather tedious because they are composed of purely small organic molecules. Therefore it is important to design and prepare new but practical organocatalysts in organic synthesis and in industry as well.

Recent efforts have been focused on polymer-supported organocatalysts because they are superior to the small molecular organocatalysts with apparent characteristics: they can be separated, recovered and recycled with ease and thus they are environmental friendly.[2] While triphenylphosphine, as an organocatalyst, was successfully applied in the stereoselective isomerization reaction of yne–carbonyl compounds to conjugated diene–carbonyl compounds,[3] polymer-supported triphenylphosphine (PS-TPP) was often used as the reagent or ligand of transition metal catalysts for Mitsunobu reaction,[4] Wittig reaction,[5] aza-Baylis–Hillman reaction,[6] conversion of acids or alcohols to the corresponding acyl or alkyl chlorides in CCl_4[7] and Pauson–Khand reaction.[8] Herein, we wish to show the potential of using PS-TPP as polymeric organocatalyst to develop green organic reactions with atom economy (Scheme 1).

The isomerization of α,β-ynones to (*E*,*E*)-α,β-γ,δ-dienones was chosen as the model reaction to test the catalytic capability of PS-TPP. As depicted in Table 1, 1-(2-furyl)-oct-2-yn-1-one (**1a**, 1 mmol) was smoothly isomerized to the corresponding conjugated dienone in toluene solution (3 mL) with 20 mol% of PS-TPP (3 mmol/g resin, 2% DVB) at 80 °C. The conversion of **1a** was 90.8%, and **2a** was obtained in 78.9% yield. The precise structure of **2a** was confirmed by ^1H NMR, GC–MS and IR analyses. The experimental results showed that PS-TPP could be employed as the organocatalyst of the isomerization and its efficiency is as good as its homogeneous analogue of triphenylphosphine. Because PS-TPP contains nucleophilic



Scheme 1.

Keywords: Organocatalyst; Polymer-supported triphenylphosphine; Isomerization; Ynone.

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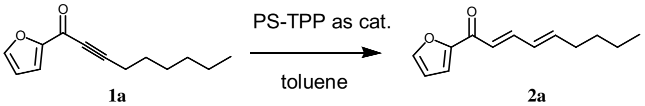
Table 1. Optimization of isomerization of ynone **1a** catalyzed by PS-TPP[a]



1a **2a**

Entry	Cat. (mol%)	Temperature (°C)	Time (h)	Yield[b]
1	10	25	8	0
2	10	80	14	Trace
3	20	80	8	47.3
4	20	80	14	63.5
5	20	80	18	78.9

[a] Typical procedure: reactions were carried out in a test tube (20 mL) under N_2 atmosphere with gentle magnetic stirring. 1-(2-Furyl)-oct-2-yn-1-one (1 mmol), PS-TPP (10–20 mol%), $PhCH_3$ (3 mL, dried) were added into the test tube in sequence. The reaction mixture was heated and stirred at 80 °C for 8–18 h. After the reaction mixture was cooled to room temperature, the catalyst was recovered by filtration under N_2 atmosphere and conserved in a vacuum desiccator after drying. The filtrate was concentrated by a rotary evaporator and the residue was purified by flash silica gel chromatography using petroleum ether–ethyl acetate = 30:0.8 or 30:1 as eluant. Then the products were analyzed using GC, GC–MS, ^{1}H NMR, ^{13}C NMR and IR.

[b] Isolated yield.

phosphorous functional groups, the triple bond in the substrates may be attacked by the catalysis centre of the polymeric catalyst. This led to the stoichiometric isomerization of ynones in excellent yields. Isomerization of other α,β-ynones was also carried out successfully under the optimized conditions (Table 2).

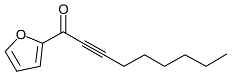
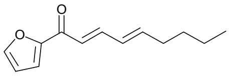
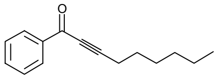
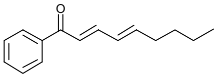
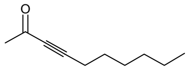
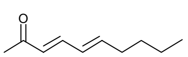
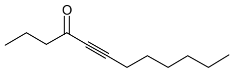
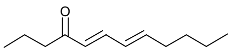
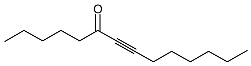
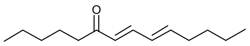
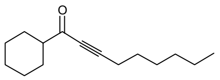
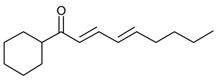
The results in Table 1 revealed that the reaction temperature and the amount of PS-TPP were critical to the isomerization. When 10 mol% PS-TPP was employed in the model reaction, no expected isomerization product was obtained after 8 h at 25 °C (Table 1, entry 1). When the temperature was raised to 80 °C and the reaction time prolonged to 14 h, a small quantity of the desired single isomeric product was obtained (Table 1, entry 2). Considering the reaction mixture was a liquid–solid biphase catalytic system and the quantity of catalyst might have a great effect on the transformation, the dosage of the PS-TPP was increased to 20 mol%. Under that condition, the reaction was accomplished smoothly and the (*E*,*E*)-dienone **2a** was obtained in moderate to good yields as the reaction time was changed from 8 h to 18 h (Table 1, entries 3–5).

Under the optimized conditions, the scope of the PS-TPP catalyzed stereoselective isomerization of ynones was extended. Investigation of representative ynones demonstrated that the transformation was feasible for aromatic, heteroaromatic and aliphatic ynones (Table 2, entries 1–6). Among the six ynones, the aromatic and heteroaromatic substitutional ynones could be isomerized to the corresponding π-conjugated products with high conversions (Table 2, entries 1 and 2), but the aliphatic substitutional ynones showed a relatively low conversion and yields especially for **1e** and **f** (Table 2, entries 5 and 6) because of the electronic and steric factors.

Lastly, we investigated the reusability of PS-TPP. PS-TPP could be recovered easily through simple filtration and reused after concise treatment. The results in Table 3 showed that the reused PS-TPP still retained its catalytic activity after multiple trials, but its catalytic capacity decreased along with the increase of reuse times. It was suspected that the decline of the catalytic capacity of reused PS-TPP was due to the oxidation of tertiary-phosphine, which reduced the nucleophilicity of phosphorous functional group in PS-TPP. In addition, physical destruction of the polymer matrix by stirring might be a co-factor for this decline.

In summary, the application of PS-TPP as a mild catalytic organocatalyst for isomerization of ynones has

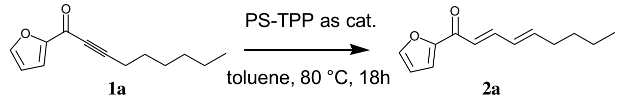
Table 2. Isomerization of ynones catalyzed by PS-TPP[a]

Entry	Substrate (ynones)	Product (dienones)	Conv. (%)	Yield[b]
1	 **1a**	 **2a**	90.8	78.9
2	 **1b**	 **2b**	93.3	81.3
3	 **1c**	 **2c**	92.5	79.6
4	 **1d**	 **2d**	87.9	64.2
5	 **1e**	 **2e**	84.2	51.3
6	 **1f**	 **1f**	82.1	47.4

[a] Reaction condition: ynones (1 mmol), PS-TPP (20 mol%, ≈0.067 g), $PhCH_3$ (dried, 3 mL), at the temperature of 80 °C for 18 h.

[b] Isolated yield, %.

Table 3. Regeneration and reuse of PS-TPP[a]



1a **2a**

Run time	Yield (%)[b]	Recovery of PS-TPP (%)
1st	78.9	98
2nd	71.6	98
3rd	63.2	97
4th	55.4	95

[a] Reaction condition: ynone **1a** (1 mmol), PS-TPP (20 mol%, ≈0.067 g), $PhCH_3$ (dried, 3 mL), at the temperature of 80 °C for 18 h.

[b] Isolated yield.

been demonstrated. Catalyzed by PS-TPP, the isomerization reaction afforded the conjugated dienone in good yield with high stereoselectivity and the polymeric organocatalyst, PS-TPP, was easy to be recovered and reused with high catalytic capability. More remarkably, the product could be separated easily from the system and continuous reactions might be achieved. All these virtues helped to extend the utility of PS-TPP across the spectra of both organic chemistry and biphase catalyst strategies.

Further investigation of PS-TPP as the recoverable organocatalyst in other reactions and as a more effective organocatalyst for the stereoselective isomerization of yne–carbonyl compounds in $scCO_2$ medium is in progress.

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