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## Stereoselective synthesis of (*E*)- $\alpha,\beta$ -unsaturated esters: triethylamine-catalyzed allylic rearrangement of enol phosphates†

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$\alpha,\beta$ -Unsaturated esters are key structural motifs widely distributed in various biologically active molecules, and their *Z/E*-stereoselective synthesis has always been considered highly attractive in organic synthesis. Herein, we present a >99% (*E*)-stereoselective one-pot synthetic approach towards  $\beta$ -phosphorylated  $\alpha,\beta$ -unsaturated esters via a mild trimethylamine-catalyzed 1,3-hydrogen migration of the corresponding unconjugated intermediates derived from the solvent-free Perkow reaction between low-cost 4-chloroacetoacetates and phosphites. Versatile  $\beta,\beta$ -disubstituted (*E*)- $\alpha,\beta$ -unsaturated esters were thus afforded with full (*E*)-stereoretentivity by cleavage of the phosphoenol linkage *via* Negishi cross-coupling. Moreover, a stereoretentive (*E*)-rich mixture of a  $\alpha,\beta$ -unsaturated ester derived from 2-chloroacetoacetate was obtained and both isomers were easily afforded in one operation.

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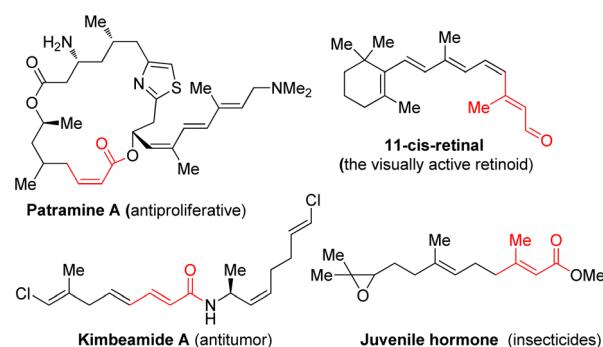
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$\alpha,\beta$ -Unsaturated carbonyl motifs, such as the relevant esters, amides, and aldehydes, are widely distributed in biologically active molecules as key structural components (Fig. 1).<sup>1–4</sup> Generally, the (*Z*) and (*E*)-isomers of those molecules possess very different living activities.<sup>5</sup> Moreover, ubiquitous  $\alpha,\beta$ -unsaturated esters are also widely employed as useful intermediates for enantioselective hydrogenation,<sup>6</sup> allylic substitution,<sup>7</sup> conjugate addition,<sup>8</sup> and especially for the stereoselective generation of acyclic substituted alkenes in either (*Z*) or (*E*)-isomeric forms.<sup>9</sup>

Whilst numerous methods have been developed towards  $\alpha,\beta$ -unsaturated esters,<sup>10–13</sup> configuration-retentive transition-metal catalyzed (TMC) cross-coupling of alkenyl (pseudo)halides is universally recognized as one of the most practical methodologies.<sup>14</sup> Among the known non-classical pseudohalides,<sup>15</sup> diethylphosphoroxyl (DEP) functionality has been proved as a good leaving group in many organic reactions and the corresponding enol phosphates (EPs), possessing high stability and accessibility, were found to participate in various organic transformations.<sup>16</sup> Particularly, EPs have been utilized in many types of TMC coupling reactions including Suzuki–Miyaura, Stille, Negishi, and Heck reactions *via* cleavage of the enol-linkage affording highly substituted alkenes.<sup>17</sup> However, the EPs-involved (*Z*) and (*E*)-stereocomplementary synthetic method towards  $\alpha,\beta$ -unsaturated esters with sufficient substrate

generality is still quite limited at present. The latest impressive approach was reported by Tanabe group, which employed *N*-methylimidazole (NMI)-promoted phosphorylation of  $\beta$ -ketoesters to obtain (*Z*) and (*E*)- $\alpha,\beta$ -unsaturated esters, but which suffers from pre-activation of the unstable diphenyl phosphorochloride (DPPCl) and usage of strong metallic *tert*-butoxide bases.<sup>18</sup> Based on our recent progress in regioselective solvent-free synthesis of EPs,<sup>19</sup> we envisioned that phosphorylated (*Z*) and/or (*E*)- $\alpha,\beta$ -unsaturated esters may act as the universal synthon of  $\alpha,\beta$ -unsaturated esters and should be facilely obtained from the commercially available and low-cost chloroacetoacetates and phosphites *via* a simple metal-free Perkow reaction. Herein, we wish to present a stereoselective one-pot synthetic approach towards  $\beta$ -phosphorylated (*E*)- $\alpha,\beta$ -unsaturated esters, which are subsequently converted into the corresponding disubstituted  $\alpha,\beta$ -unsaturated esters by Negishi cross-coupling (Scheme 1).

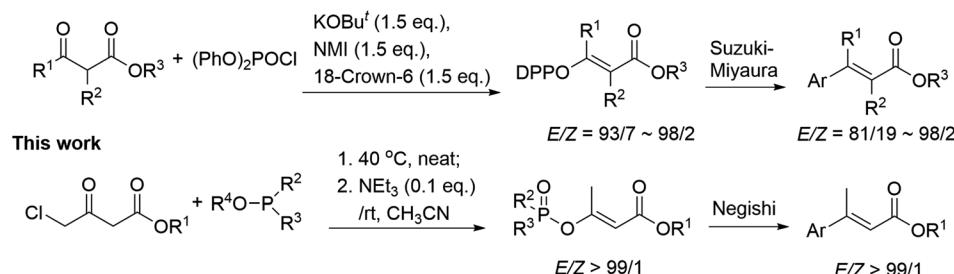
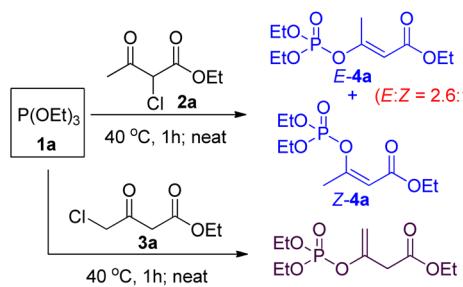

 Fig. 1 Selected bioactive  $\alpha,\beta$ -unsaturated carbonyl motifs.

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## Tanabe's work

Scheme 1 *E*-Stereoselective synthesis of  $\alpha,\beta$ -unsaturated esters from enol phosphates.

Scheme 2 Perkow reaction of phosphite with chloroacetoacetate.

Since both 2-chloroacetoacetates and 4-chloroacetoacetates are capable of undergoing Perkow reaction with phosphites, we then took them together for comparison. Solvent-free Perkow reaction conditions were initially selected in view of high

regioselectivity.<sup>19</sup> As shown in Scheme 2, reaction between  $(\text{EtO})_3\text{P}$  and 2-chloroacetoacetate **2a** gave a mixture of (*E*) and (*Z*)-isomers of  $\beta$ -phosphorylated  $\alpha,\beta$ -unsaturated ester **4a** in ratio of 2.6 : 1, whereas reaction between  $(\text{EtO})_3\text{P}$  and 4-chloroacetoacetate **3a** gave the  $\beta$ -phosphorylated allylic ester **5a** as the only product. In other words, only moderate *E/Z*-stereoselectivity can be achieved if using 2-chloroacetoacetate, while no conjugated EP product can be obtained if using 4-chloroacetoacetate. However, according to Seeman's report that bases, such as NaH, are supposed to be able to promote 1,3-hydrogen relocation of allyl compounds, we then suspect that the unconjugated EP product **5a** may be able to be transformed into the conjugated one in a stereoselective way.<sup>20</sup>

Inspired by the above idea, we then turned to examine the possibility of the base-promoted 1,3-hydrogen rearrangement of **5a**. As shown in Table 1, among the eight kinds of bases examined, including inorganic *t*-BuOK,  $\text{CH}_3\text{ONa}$ ,  $\text{NaOH}$ ,  $\text{NaH}$ ,

Table 1 Optimization of base-promoted 1,3-hydrogen rearrangement of unconjugated  $\beta$ -phosphorylated allylic ester **5a**<sup>a</sup>

Entry	Base	Load (x eq.)	Solvent	T (°C)	Time (h)	Yield <sup>b</sup> (%)	<i>E/Z</i> ( <b>4a</b> ) <sup>c</sup>
1	<i>t</i> -BuOK	1.2	THF	rt	24	0	—
2	$\text{CH}_3\text{ONa}$	1.2	THF	rt	24	0	—
3	$\text{NaOH}$	1.2	THF	rt	24	0	—
4	$\text{NaH}$	1.2	THF	rt	24	0	—
5	$\text{K}_2\text{CO}_3$	1.2	THF	rt	24	0	—
6	$\text{Et}_3\text{N}$	1.2	THF	rt	24	90	>99 : 1
7	Pyridine	1.2	THF	rt	24	0	—
8	$(i\text{-Pr})_2\text{NEt}$	1.2	THF	rt	24	20	>99 : 1
9	$\text{Et}_3\text{N}$	1.2	$\text{CH}_3\text{CN}$	rt	4	92	>99 : 1
10	$\text{Et}_3\text{N}$	1.2	DCM	rt	20	90	>99 : 1
11	$\text{Et}_3\text{N}$	1.2	$\text{CH}_3\text{OH}$	rt	22	83	>99 : 1
12	$\text{Et}_3\text{N}$	1.2	DMF	rt	24	75	>99 : 1
13	$\text{Et}_3\text{N}$	0.5	$\text{CH}_3\text{CN}$	rt	7	92	>99 : 1
14	<b>Et<sub>3</sub>N</b>	<b>0.1</b>	<b>CH<sub>3</sub>CN</b>	<b>rt</b>	<b>12</b>	<b>92</b>	<b>&gt;99 : 1</b>
15	$\text{Et}_3\text{N}$	0.05	$\text{CH}_3\text{CN}$	rt	20	93	>99 : 1
16	$\text{Et}_3\text{N}$	0.1	$\text{CH}_3\text{CN}$	0	24	95	>99 : 1
17	$\text{Et}_3\text{N}$	0.1	$\text{CH}_3\text{CN}$	80	4	90	>99 : 1

<sup>a</sup> Reaction conditions: **5a** (1.0 equiv.), base (x equiv.), solvent (3 ml). <sup>b</sup> Isolated yields. <sup>c</sup> Determined by NMR.



$\text{K}_2\text{CO}_3$ , and organic  $\text{Et}_3\text{N}$ , Pyridine ( $i\text{-Pr}$ )<sub>2</sub>NET, only  $\text{Et}_3\text{N}$  and ( $i\text{-Pr}$ )<sub>2</sub>NET exhibited the supposed promoting abilities, affording the desired product **4a**, but encouragingly both in >99% (*E*)-stereoselectivity. Though only 20% yield was obtained by 1.2 equivalent ( $i\text{-Pr}$ )<sub>2</sub>NET after 24 h reaction in THF at room temperature (Table 1, entry 8), while up to 90% yield was acquired by using  $\text{Et}_3\text{N}$  (Table 1, entry 6). The following screening of solvents demonstrated that acetonitrile seemed to be the best choice that the reaction could be accomplished in only 4 h and gave a higher yield of 92% (Table 1, entry 10). Further investigation about the loadage of  $\text{Et}_3\text{N}$  showed that only 0.1 equivalent  $\text{Et}_3\text{N}$  was sufficient to promote the rearrangement effectively, affording the comparative yield though with a few longer time of 12 h (Table 1, entry 14). Less loadage of  $\text{Et}_3\text{N}$  and lower temperature both led to much longer reaction times (Table 1, entry 15&16). Though the reaction time could be shortened to 4 h at a higher temperature of 80 °C (Table 1, entry 17), we finally preferred the more benign room temperature for the following preparations.

Considering the convenience of experimental operation, we then turned into the possibility of one-pot manipulation. It was found that product **4a** was afforded in 92% yield if using the crude intermediate **5a** directly for the subsequent rearrangement reaction. Therefore, a mild *E*-stereoselective one-pot synthetic approach of  $\beta$ -phosphoroxylated  $\alpha,\beta$ -unsaturated esters was thus established: **3** (1.0 eq.) and P(III)-reagents (1.0 eq.) react 1 h at 40 °C neatly, then added triethylamine (0.1 eq.) and acetonitrile (3 mL), and further react about 12 h at room temperature.

Having identified the optimal reaction conditions, we next set out to examine the scope of this new mild one-pot enol phosphorylation procedure (Table 2). As for the different *O*-alkyl

Table 2 Scope of  $\beta$ -phosphoroxylated (*E*)- $\alpha,\beta$ -unsaturated esters<sup>a,b</sup>

1	1. 3 (1 eq) / 40 °C, neat;		E-stereospecific High yields Mild conditions Metal-free Gram scale Group tolerance		
	2. $\text{Et}_3\text{N}$ (0.1 eq) / rt, $\text{CH}_3\text{CN}$	one-pot			
$\text{R}^4\text{O}-\text{P}(\text{R}^2\text{R}^3)-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	$\text{R}^2\text{R}^3\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	<b>4</b>			
<b>4a</b> , 92% yield	<b>4b</b> , 96% yield	<b>4c</b> , 90% yield			
$\text{Et}_2\text{N}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	$\text{i-Pr}_2\text{O}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	$\text{Ph}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	<b>4d</b> , 90% yield	<b>4e</b> , 96% yield	<b>4f</b> , 90% yield
$\text{MeO}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOEt})-\text{OEt}$	$\text{EtO}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOMe})-\text{OEt}$		<b>4g</b> , 90% yield	<b>4h</b> , 92% yield	<b>4i</b> , 95% yield
$\text{EtO}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOPr}-i)-\text{OEt}$	$\text{EtO}-\text{P}(\text{OEt})_2-\text{O}-\text{C}(\text{CH}_2\text{CH}_2\text{COOBu}-t)-\text{OEt}$		<b>4j</b> , 93% yield	<b>4k</b> , 94% yield	

<sup>a</sup> Reaction conditions: **1** (1.0 mmol), **3** (1.0 mmol),  $\text{Et}_3\text{N}$  (0.1 mmol),  $\text{CH}_3\text{CN}$  (3.0 mL). <sup>b</sup> Isolated yields.

4-chloroacetoacetate substrates, all the common P(III)-reagents possessing P–O, P–C, and/or P–N bonds gave the corresponding EPs in high yields. During the preparation of compounds **4e** and **4f**, the rearrangement reactions were found much accelerated probably due to the higher reactivities of phosphonite and phosphinite compared to phosphites. To demonstrate the practical utility, the reaction towards product **4a** was performed at the 50 mmol scale and 92% yield was obtained. The stereoscopic (*E*-configuration of solid product **4f** was further confirmed by single crystal X-ray analysis.

With the *E*-stereospecific  $\beta$ -phosphoroxylated  $\alpha,\beta$ -unsaturated esters in hand, we then investigated their stereoretentive Negishi cross-coupling to prepare the corresponding *E*-stereodefined disubstituted  $\alpha,\beta$ -unsaturated esters. Among the typical catalysts screened including  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{Ni}(\text{acac})_2$  and  $\text{Pd}(\text{dppb})\text{Cl}_2$ , the latter demonstrated the best performance in this Negishi reaction with only 0.02 equivalent loading by refluxing in acetonitrile. Various aromatic  $\text{ArZnCl}$  nucleophiles containing electron-donating and/or electron-withdrawing substituents at *ortho*, *meta*, and/or *para* positions were all tolerated well, affording the desired products in good to excellent yields (80–

Table 3 Scope of (*E*)- $\alpha,\beta$ -unsaturated esters via a stereoretentive Negishi cross-coupling reaction of **4a**<sup>a,b</sup>

<b>4a</b>	$\text{ArMgBr}$	$\text{ZnCl}_2, \text{Pd}(\text{dppb})\text{Cl}_2$	<b>6</b>
92% yield; 50 mmol scale		reflux in $\text{MeCN}$	100% <i>E</i> -stereoretentive
<b>6a</b> , 84%	<b>6b</b> , 80%	<b>6c</b> , 93%	
<b>6d</b> , 88%	<b>6e</b> , 94%	<b>6f</b> , 92%	
<b>6g</b> , 88%	<b>6h</b> , 95%	<b>6i</b> , 90%	
<b>6j</b> , 96%	<b>6k</b> , 82%	<b>6l</b> , 87%	
<b>6m</b> , 94%	<b>6n</b> , 85%	<b>6o</b> , 90%	
<b>6p</b> , 92%	<b>6q</b> , 89%	<b>6r</b> , 85%	

<sup>a</sup> Reaction conditions: **4a** (1.0 mmol),  $\text{ArMgBr}$  (1.5 mmol),  $\text{ZnCl}_2$  (1.5 mmol),  $\text{Pd}(\text{dppb})\text{Cl}_2$  (0.02 mmol),  $\text{CH}_3\text{CN}$  (5.0 mL), reflux about 3 h.

<sup>b</sup> Isolated yields.



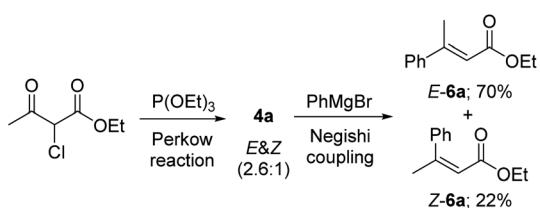
96%) without generating any stereochemical integrity (Table 3, **6a–6m**). Disubstituted, condensed and hetero aromatic organometallic substrates also gave 85–92% yields of the products (Table 3, **6n–6r**). However, it's regrettable that alkyl organozinc reagents was found unreactive under such conditions.

Furthermore, under the above optimal Negishi cross-coupling reaction conditions, both (*Z*) and (*E*) isomers of  $\alpha,\beta$ -unsaturated esters **6a** could be easily achieved, just by one operation, directly from the (*Z*) and (*E*) mixture of **4a** in 22% and 70% yields respectively (Scheme 3).

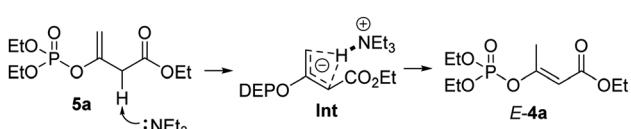
According to the Cram's mechanistic interpretation for the allylic rearrangements, an intra-molecular pathway of the  $\text{Et}_3\text{N}^+$ -promoted stereoselective 1,3-hydrogen rearrangement of the EPs **5a** was proposed because that the degree of the observed intramoleculararity depended strongly on the base and solvent used.<sup>21</sup> As shown in Scheme 4, triethylamine firstly removes the proton from the  $\alpha$ -carbon position of ester **5a**, resulting in a coplanar anionic allylic system by three carbon atoms. The hydrogen atom of the  $\text{H}-\text{Et}_3\text{N}^+$  ammonium then bonds to both terminal carbon atoms to form the intermediate **Int**, collapse of which would then give the thermodynamically favourable conjugated  $\alpha,\beta$ -unsaturated ester product *E*-**4a**.

In summary, a mild and environmental trimethylamine-catalyzed *E*-stereoselective 1,3-hydrogen allylic rearrangement of enol phosphates was firstly developed to afford versatile  $\beta$ -phosphoroxylated (*E*)- $\alpha,\beta$ -unsaturated esters which can be then efficiently converted into the corresponding  $\beta,\beta$ -disubstituted (*E*)- $\alpha,\beta$ -unsaturated esters in high yields by a 100% stereo-retentive Negishi cross-coupling reaction. Moreover, both (*Z*) and (*E*)- $\alpha,\beta$ -unsaturated esters were able to be achieved in one manipulation when just employing 2-chloroacetoacetate instead of 4-chloroacetoacetate for the solvent and metal-free Perkow reaction.

It is interesting to note that more structure-diverse  $\alpha,\beta$ -unsaturated esters should be easily obtained by derivation reactions at the allylic position of  $\alpha,\beta$ -unsaturated esters and/or by utilizing 2-substituted 4-chloroacetoacetates as the starting materials.



Scheme 3 Preparation of (*Z*) and (*E*) isomers of **6a** in one operation.



Scheme 4 Proposed (*E*)-stereospecific allylic rearrangement mechanism.

## Conflicts of interest

There are no conflicts to declare.

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