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Highly Enantioselective Synthesis of 3,4-Dihydropyrans through a Phosphine-Catalyzed [4+2] Annulation of Allenones and β,γ-Unsaturated α-Keto Esters

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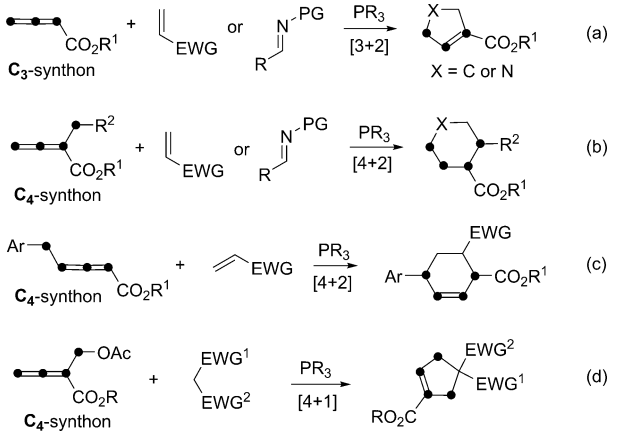
Supporting Information

ABSTRACT: A phosphine-catalyzed novel [4+2] annulation process was devised employing allene ketones as C_2 synthons and β,γ-unsaturated α-keto esters as C_4 synthons. In the presence of an L-threonine-derived bifunctional phosphine, 3,4-dihydropyrans were obtained in high yields and with virtually perfect enantioselectivities. The synthetic value of the dihydropyran motif was demonstrated by a concise preparation of an anti-hypercholesterolemic agent.

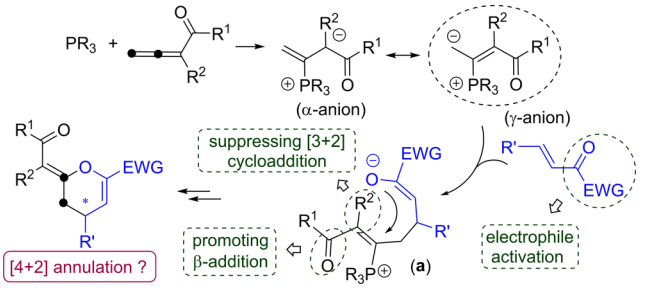
Over the past decade, asymmetric nucleophilic phosphine catalysis has been intensely investigated as a powerful tool for the preparation of structurally divergent chiral molecules.[1] The most common mode of activation involves nucleophilic addition of a tertiary phosphine to activated alkenes, allenes, or alkynes to form a zwitterion intermediate, which is then trapped by an electrophile. Due to their unique reactivity, electron-deficient allenes are widely employed in phosphine catalysis. In 1995, Lu[2a] discovered a phosphine-catalyzed [3+2] cyclization between allenoates and activated alkenes, in which allenoates were used as a three-carbon unit. Subsequently, [3+2] annulations received enormous attention and were widely explored for the synthesis of five-membered carbocyclic and heterocyclic compounds (Scheme 1a).[2] In 2003, Kwon[3a] disclosed a novel [4+2] annulation of α-substituted allenoates with *N*-sulfonylimines; it is noteworthy that allenoates were used as C_4 synthons in that study. Shortly after, Kwon also utilized activated alkenes in [4+2] annulation with α-substituted allenoates (Scheme 1b).[3] Very recently, Huang[4a] and Marinetti[4b] independently reported the utilization of γ-substituted allenoates in phosphine-catalyzed [4+2] annulation reactions with activated olefins to construct spirocyclic structures, and allenoates were used as C_4 synthons in those studies (Scheme 1c). In [4+1] annulation of α-substituted allenoates with a nucleophilic reaction partner, Tong and co-workers employed allenoates as electrophilic C_4 synthons (Scheme 1d).[5] As part of our interest in asymmetric phosphine catalysis,[6] we were particularly interested in designing novel reactions to access important structural motifs via unprecedented utilization of allenes as a reaction partner in annulation reactions.

Dihydropyrans represent an important structural motif featured in bioactive molecules and natural products,[7] and they are also versatile intermediates in organic synthesis.[8] Given their importance, a number of approaches have been developed to access these compounds, including asymmetric inverse-electron-demand Diels–Alder reactions[9] and amine-catalyzed cascade/cyclization reactions of α,β-unsaturated carbonyl compounds.[10] To the best of our knowledge, there is no report on the synthesis of chiral dihydropyran skeletons via asymmetric phosphine catalysis.[11] This is somewhat surprising, given the wide use of phosphine-catalyzed reactions in the formation of ring structures. We reasoned that a novel [4+2] annulation reaction may be developed by employing α-substituted allene ketones[12] and highly activated alkenes as C_2 and C_4 synthons, respectively (Scheme 2). When an α-

Scheme 1. Phosphine-Catalyzed Cycloaddition Reactions of Activated Allenes



Scheme 2. Working Hypothesis



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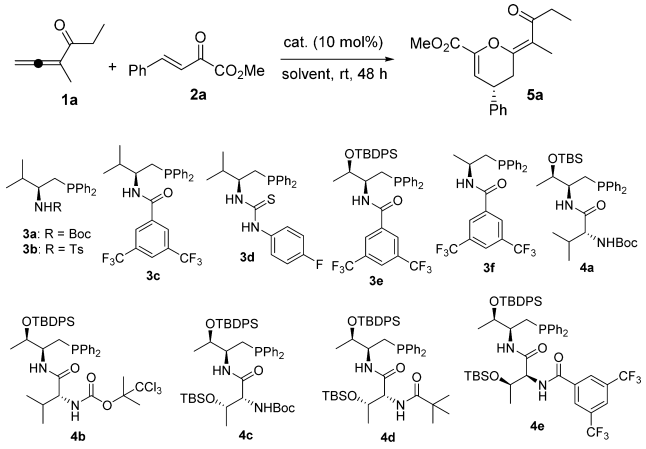
substituted allene ketone reacts with a highly activated alkene in the presence of a phosphine catalyst, formation of advanced intermediate **a** is well-anticipated. We envisage that the presence of an α-R^2 group will suppress [3+2] cycloaddition by preventing enolate C-attack at the carbonyl α-position. Moreover, the presence of the ketone function makes the β-position highly electrophilic and prone to nucleophilic attack. Should an enolate O-attack take place at the β-position, a dihydropyran can be formed. Herein, we document a phosphine-triggered novel [4+2] annulation reaction between allene ketones and β,γ-unsaturated α-keto esters,[13] leading to highly enantioselective construction of dihydropyran architectures.

We initiated our investigation by examining the reaction between allene ketone **1a** and β,γ-unsaturated α-keto ester **2a**, employing different phosphine catalysts (Table 1). In the presence of Ph_2PMe, the desired [4+2] annulation occurred smoothly to yield racemic 3,4-dihydropyran **5a** in 58% yield (entry 1). Our amino acid-based bifunctional phosphines were then examined for asymmetric induction. Testing of a number of valine-derived bifunctional phosphines revealed that amide function was superior to other functional groups (entries 2−5). L-Threonine-derived **3e** and L-alanine-based **3f** were found to be poor catalysts (entries 6,7). We next turned to dipeptidic phosphine catalysts, which were developed by us earlier and shown to be powerful. While the dipeptidic phosphines with an *N*-carbamate terminal gave only moderate enantioselectivities (entries 8−10), we were delighted to discover that bifunctional phosphines containing an amide terminal worked remarkably well for the annulation (entries 11,12). A quick solvent screening identified ether as the solvent of choice (entries 13−18). When reaction was performed in ether in the presence of **4e**, dihydropyran **5a** was obtained in 95% yield, and with 99% ee.

With the optimized reaction conditions in hand, we next examined the scope of this novel [4+2] annulation (Table 2).

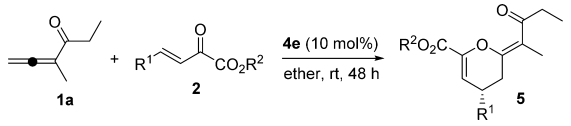
Table 1. Asymmetric [4+2] Cyclization Catalyzed by Amino Acid-Derived Phosphines[a]



entry	cat.	solvent	yield (%)[b]	ee (%)[c]
1	Ph_2PMe	$CHCl_3$	58	–
2	**3a**	$CHCl_3$	75	12
3	**3b**	$CHCl_3$	60	6
4	**3c**	$CHCl_3$	87	50
5	**3d**	$CHCl_3$	50	11
6	**3e**	$CHCl_3$	85	7
7	**3f**	$CHCl_3$	84	24
8	**4a**	$CHCl_3$	88	59
9	**4b**	$CHCl_3$	85	49
10	**4c**	$CHCl_3$	84	54
11	**4d**	$CHCl_3$	83	95
12	**4e**	$CHCl_3$	83	99
13	**4e**	toluene	84	99
14	**4e**	xylene	85	99
15	**4e**	THF	–	–
16	**4e**	**ether**	**95**	**99**
17	**4e**	CH_2Cl_2	73	98
18	**4e**	EtOAc	80	98

[a]Reactions were performed with **1a** (0.15 mmol), **2a** (0.1 mmol), and the catalyst (0.01 mmol) in the solvent specified (0.5 mL) at room temperature. [b]Yield of isolated product. [c]Determined by HPLC analysis on a chiral stationary phase.

Table 2. Dipeptide Phosphine 4e-Catalyzed [4+2] Annulation of Allene Ketone 1a with β,γ-Unsaturated α-Keto Esters[a]



entry	R^1/R^2 (**2**)	**5**	yield (%)[b]	ee (%)[c]
1	Ph/Me (**2a**)	**5a**	95	99
2	Ph/Et (**2b**)	**5b**	92	99
3	Ph/*i*-Pr (**2c**)	**5c**	71	99
4	Ph/Bn (**2d**)	**5d**	83	99
5	3-BrC_6H_4/Et (**2e**)	**5e**	95	99
6	4-ClC_6H_4/Et (**2f**)	**5f**	92	99
7	2-ClC_6H_4/Et (**2g**)	**5g**	87	99
8	2-MeC_6H_4/Et (**2h**)	**5h**	86	99.6
9	3-MeC_6H_4/Et (**2i**)	**5i**	87	99
10	4-MeC_6H_4/Et (**2j**)	**5j**	87	99.8
11	4-FCC_6H_4/Et (**2k**)	**5k**	94	99.5
12	4-$MeOC_6H_4$/Et (**2l**)	**5l**	89	99
13[d]	4-$NO_2C_6H_4$/Et (**2m**)	**5m**	87	99
14	3,4-$Cl_2C_6H_3$/Et (**2n**)	**5n**	92	99
15	3-CNC_6H_4/Et (**2o**)	**5o**	93	99
16	1-naphthyl/Et (**2p**)	**5p**	91	99
17	2-thiophenyl/Et (**2q**)	**5q**	91	99
18	styryl/Et (**2r**)	**5r**	76	98
19	Me/Et (**2s**)	**5s**	71	99
20	Et/Et (**2t**)	**5t**	79	99
21	*n*-C_5H_{11}/Et (**2u**)	**5u**	78	97
22	$PhCH_2CH_2$/Et (**2v**)	**5v**	83	99.6
23	*i*-Pr/Et (**2w**)	**5w**	84	97
24	cyclohexyl/Et (**2x**)	**5x**	87	99

[a]Reactions were performed with **1a** (0.15 mmol), **2** (0.1 mmol), and **4e** (0.01 mmol) in diethyl ether (0.5 mL) at room temperature. [b]Yield of isolated product. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The solvent used was $CHCl_3$.

The ester moiety of β,γ-unsaturated α-keto esters could be varied, and excellent ee values were maintained (entries 1−4). The reaction was applicable to a wide range of β,γ-unsaturated α-keto esters bearing different aromatic groups, regardless of the steric and electronic properties of the substituents on the aromatic ring (entries 5−15). 1-Naphthyl- and 2-thiophenyl-containing substrates could also be used (entries 16,17). Different vinyl- and linear/branched alkyl-substituted β,γ-

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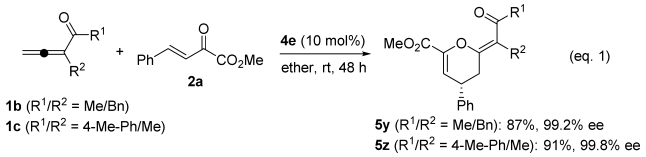
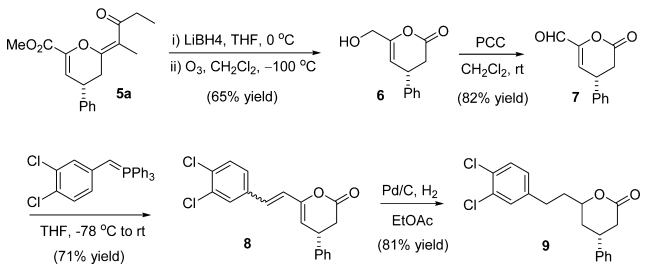
unsaturated α-keto esters were also tested, and the desired [4+2] annulation products were obtained in good yields and with nearly perfect enantioselectivities (entries 18−24). Moreover, when different allene ketones were used in the reaction, equally excellent results were obtained (eq 1). The absolute configurations of the annulation products were assigned on the basis of X-ray crystal structural analysis of **5a** and **5s**.

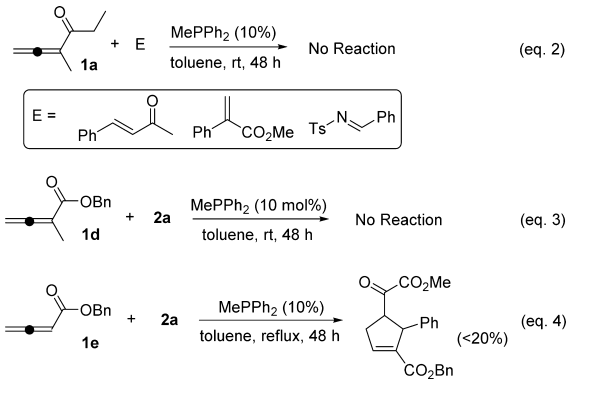


The optically enriched functionalized dihydropyrans are both biologically and synthetically valuable due to their wide presence in natural products and medicinal chemistry.[7,8] We envisioned that the [4+2] cycloaddition products, with the presence of an exocyclic alkene function, can be readily derived into chiral dihydropyranones. As illustrated in Scheme 3, selective cleavage of the exocyclic double bond gave pyranone **6**, which was easily transformed into anti-hypercholesterolemic agent[14] **9** through a few trivial reaction steps.

Scheme 3. Synthetic Manipulations of [4+2] Annulation Product



We next preformed further experiments to gain a better understanding of our reaction. A few common electrophiles were examined in their reactions with allene ketone **1a**, but no reaction took place (eq 2). While α-methyl allenoate **1d** failed



to react with keto ester **2a** (eq 3), allenoate **1e** reacted with **2a** to yield the [3+2] annulation product in low yield (eq 4). We believe the observed reactivity difference may be due to the different level of alkene activation in allene ketone and allenoate substrates, and theoretical studies are ongoing to fully understand the reaction mechanism.

In summary, we have developed a novel phosphine-catalyzed [4+2] annulation between allene ketones and β,γ-unsaturated α-keto esters. By utilizing dipeptide-based bifunctional phosphines, highly optically enriched 3,4-dihydropyrans (≥99% ee in most cases) were readily prepared in excellent yields. Notably, this is the first asymmetric synthesis of chiral pyran derivatives via a phosphine-catalyzed annulation reaction. We are currently investigating asymmetric synthesis of other heteroatom-containing ring systems by extending the strategy developed here.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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