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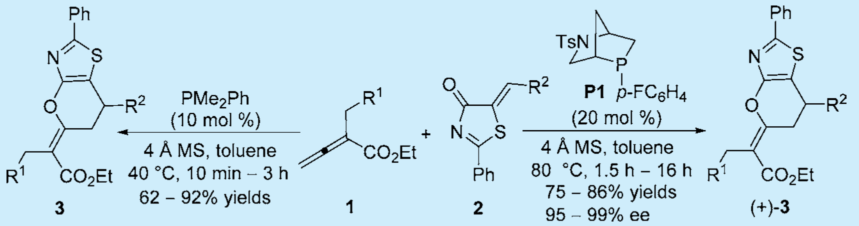
Phosphine-Catalyzed [2 + 4] Annulation of Allenoates with Thiazolone-Derived Alkenes: Synthesis of Functionalized 6,7-Dihydro-5*H*-pyrano[2,3-*d*]thiazoles

Chang Wang, Zhenzhen Gao, Leijie Zhou, Chunhao Yuan, Zhanhu Sun, Yumei Xiao,* and Hongchao Guo

Department of Applied Chemistry, China Agricultural University, Beijing 100193, P. R. China

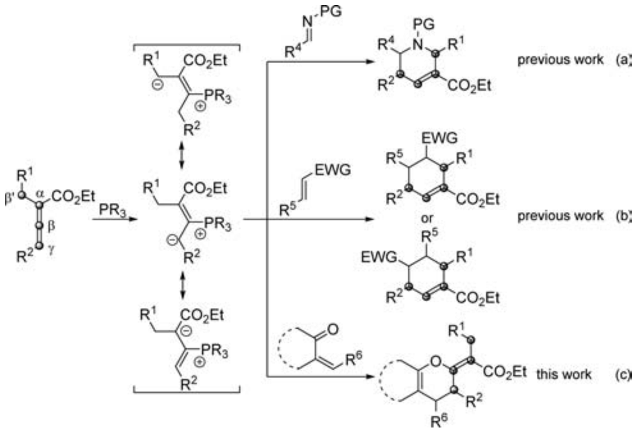
Supporting Information



ABSTRACT: Phosphine-catalyzed [2 + 4] annulation of allenoates with thiazolone-derived alkenes has been achieved under mild conditions, giving biologically important 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazole derivatives in high to excellent yields. With the use of Kwon's phosphine as the chiral catalyst, optically active products were obtained in good yields with excellent enantioselectivities.

Phosphine-catalyzed annulation reactions of allenaotes have emerged as a powerful tool for the synthesis of carbocyclic and heterocyclic compounds,[1] and serve as key steps in the total synthesis of some natural products.[2] Since the pioneering work from Lu on the phosphine-catalyzed [3 + 2] annulation reaction of unsubstituted allenoates,[3] numerous annulation reactions of allenoates involving using phosphine as the catalyst have been developed.[1] In the presence of a phosphine catalyst, the activated allenes exhibit diverse reactivity toward electrophilic reagents such as electron-deficient alkenes, imines, aldehydes, etc. Among several types of allenoates including unsubstituted, α- and γ-substituted allenoates, α-substituted allenoates have been applied in various annulation reactions[4] since Kwon reported the first phosphine-catalyzed [4 + 2] annulation of *N*-tosylaldimines with allenoates for the synthesis of highly functionalized tetrahydropyridines.[5] Generally, α-substituted allenoates behave as four-carbon synthons to react with imines or alkenes to furnish the [4 + 2] annulations, providing six-membered carbo- and heterocyclic compounds (Scheme 1a and 1b).[6,7] To the best of our knowledge, α-substituted allenoates functioning as two-carbon synthons for the phosphine-catalyzed [2 + 4] annulation have never been reported. In fact, the γ-substituted allenoates and allenones have been demonstrated to be able to work as two-carbon synthons for the [2 + 4] annulation. Huang achieved the phosphine-catalyzed [2 + 4] annulation reaction of γ-substituted allenoates functioning as C_2 synthons with α-cyano-α,β-unsaturated ketones, 1,3-bis(sulfonyl)butadiene, or salicyl *N*-thiophosphinylimines as C_4 synthons to afford dihydropyran, biaryl, or chroman derivatives.[8] Lu reported the chiral phosphine-catalyzed [2 + 4] annulation employing allene ketones as C_2 synthons and β,γ-unsaturated α-keto esters or α-cyano-α,β-unsaturated ketones as C_4 synthons to give functionalized dihydropyrans in high yields with excellent enantioselectivities.[9] Herein, we present the first phosphine-catalyzed [2 + 4] annulation of α-substituted allenoates behaving as C_2 synthons with thiazolone-derived alkenes as C_4 synthons to furnish biologically important functionalized 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazoles[10] and its asymmetric variant.

Scheme 1. Phosphine-Catalyzed [4 + 2] Annulation of α-Substituted Allenoates



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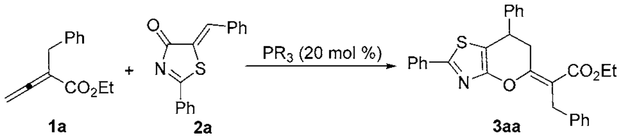
Initially, we carried out our study by examining the reaction of α-benzyl allenoate (**1a**) and 5-phenylmethylene substituted thiazolone (**2a**), employing different phosphine catalysts (Table 1, entries 1–4). In toluene, PMe_2Ph turned out to be the most efficient catalyst and the desired [2 + 4] cycloaddition product (**3aa**) was obtained in 56% yield at room temperature (entry 3). In the presence of $PMePh_2$ or PMe_2Ph, the substrate **2a** could completely be consumed in 1 h (entries 2–3). However, the isolated yields of the product **3aa** were only moderate. The unknown side product observed in the reaction process, which might be formed from the direct attack of phosphine to enone and thus causing a subsequent side reaction, eroded the yield of **3aa**. The solvent screening showed that toluene was the optimal choice in terms of the yield and reaction time (entries 5–7). To further improve the reaction efficiency, we next screened the effect of additives on this reaction. 4 Å MS displayed a favorable effect, leading to an increase of the yield of **3aa** to 72% (entry 8). To our delight, decreasing the catalyst loading of PMe_2Ph to 10 mol % slightly improved the results, furnishing the desired product in 75% yield (entry 9). This might be attributed to the suppression of the side reaction through a decrease of the catalyst loading. A higher temperature is favorable for the reaction, affording the product with 80% yield (entry 10). A further increase in the temperature did not offer better results (entries 11–12). Based on these experimental results, the best reaction conditions were confirmed to be PMe_2Ph (10 mol %), at 40 °C in toluene containing 4 Å MS.

Table 1. Screening of the Reaction Conditions[a]

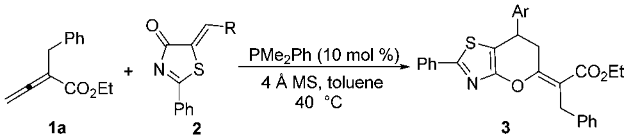


entry	PR_3	solvent	*t* (°C)	*t*	yield (%)[b]
1	PPh_3	toluene	25	3 d	18
2	$PMePh_2$	toluene	25	1 h	55
3	PMe_2Ph	toluene	25	1 h	56
4	PBu_3	toluene	25	3 d	36
5	PMe_2Ph	CH_2Cl_2	25	3 d	trace
6	PMe_2Ph	THF	25	1 h	25
7	PMe_2Ph	MeCN	25	1 h	22
8	PMe_2Ph	toluene	25	1 h	72
9[c,d]	PMe_2Ph	toluene	25	1 h	75
10[c,d]	PMe_2Ph	toluene	40	40 min	80
11[c,d]	PMe_2Ph	toluene	60	40 min	72
12[c,d]	PMe_2Ph	toluene	80	40 min	71

[a] Unless otherwise stated, all reactions were performed with **1a** (0.15 mmol), **2a** (0.1 mmol), and catalyst (0.02 mmol) in solvent (1 mL). [b] Isolated yield. [c] In the presence of 4 Å MS (100 mg). [d] Decreasing the catalyst loading to 10 mol %.

A variety of 5-argiomethylene substituted thiazolones **2** were next exposed to the optimal reaction conditions. As summarized in Table 2, various 5-argiomethylene thiazolones **2**, regardless of electronic properties of the substituents at aromatic ring, carried out [2 + 4] annulation to give the heterocyclic products in good to excellent yields (entries 1–11). The reactions were quite fast, requiring a <1 h reaction time. The thiazolone (**2m**) bearing 2-naphthyl and thiazolone (**2n**) having 2-thienyl also reacted with allenoate under current reaction conditions, giving bicyclic heterocyclic product **3am** in 77% yield and **3an** in 70% yield, respectively (entries 12 and 13).

Table 2. Scope of Thiazolone-Derived Alkenes 2[a]

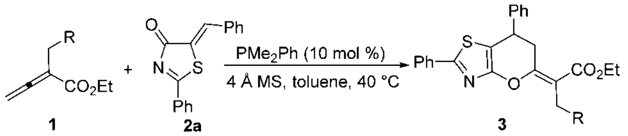


entry	R in 2	*t*/min	3	yield (%)[b]
1	$2\text{-}MeC_6H_4$ (**2b**)	30	**3ab**	78
2	$3\text{-}MeC_6H_4$ (**2c**)	30	**3ac**	83
3	$4\text{-}MeC_6H_4$ (**2d**)	30	**3ad**	85
4	$2\text{-}OMeC_6H_4$ (**2e**)	15	**3ae**	78
5	$4\text{-}OMeC_6H_4$ (**2f**)	40	**3af**	81
6	$4\text{-}FC_6H_4$ (**2g**)	10	**3ag**	85
7	$2\text{-}ClC_6H_4$ (**2h**)	15	**3ah**	90
8	$4\text{-}ClC_6H_4$ (**2i**)	10	**3ai**	92
9	$4\text{-}BrC_6H_4$ (**2j**)	15	**3aj**	92
10	$4\text{-}CNC_6H_4$ (**2k**)	10	**3ak**	82
11	$3,4\text{-}Cl_2C_6H_3$ (**2l**)	40	**3al**	75
12	2-naphthyl (**2m**)	30	**3am**	77
13	2-thienyl (**2n**)	20	**3an**	70

[a] All reactions were performed with **1a** (0.15 mmol), **2** (0.1 mmol), 4 Å MS (100 mg), and PMe_2Ph (0.01 mmol) in toluene (1 mL) at 40 °C. [b] Isolated yield.

With the optimal conditions in hand, we then investigated the substrate scope of the allenoates **1** in the [2 + 4] annulation. As shown in Table 3, the reaction shows good tolerance to a wide range of aryl groups with either electron-poor or -rich substituents in allenoates **1**, providing various

Table 3. Scope of Allenoates 1[a]



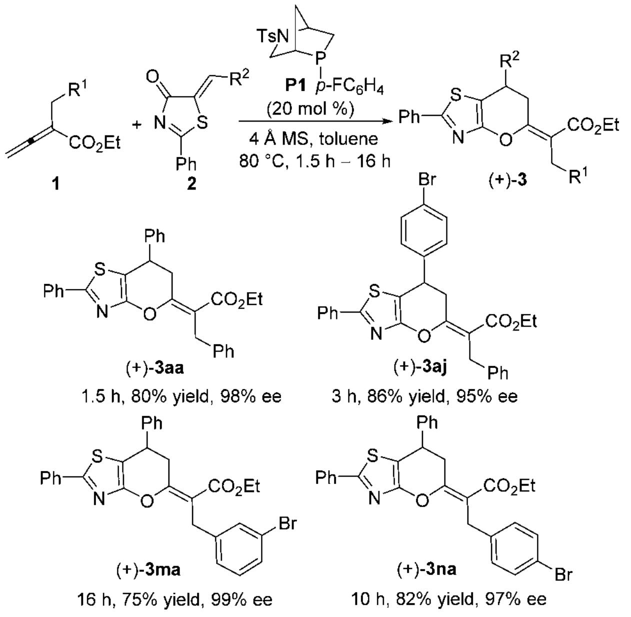
entry	R in 1	*t*	3	yield (%)[b]
1	$3\text{-}MeC_6H_4$ (**1b**)	1.5 h	**3ba**	62
2	$4\text{-}MeC_6H_4$ (**1c**)	1 h	**3ca**	67
3	$4\text{-}t\text{-}BuC_6H_4$ (**1d**)	1 h	**3da**	71
4	$3,5\text{-}OMe_2C_6H_3$ (**1e**)	1.5 h	**3ea**	70
5	$2\text{-}FC_6H_4$ (**1f**)	1 h	**3fa**	71
6	$3\text{-}FC_6H_4$ (**1g**)	1 h	**3ga**	72
7	$4\text{-}FC_6H_4$ (**1h**)	1 h	**3ha**	75
8	$2\text{-}ClC_6H_4$ (**1i**)	30 min	**3ia**	70
9	$3\text{-}ClC_6H_4$ (**1j**)	1 h	**3ja**	72
10	$4\text{-}ClC_6H_4$ (**1k**)	30 min	**3ka**	72
11	$2\text{-}BrC_6H_4$ (**1l**)	1 h	**3la**	70
12	$3\text{-}BrC_6H_4$ (**1m**)	50 min	**3ma**	71
13	$4\text{-}BrC_6H_4$ (**1n**)	30 min	**3na**	72
14	$3\text{-}CF_3C_6H_4$ (**1o**)	1 h	**3oa**	70
15	$4\text{-}CF_3C_6H_4$ (**1p**)	1 h	**3pa**	70
16	$4\text{-}CO_2MeC_6H_4$ (**1q**)	3 h	**3qa**	69
17	2-naphthyl (**1r**)	2 h	**3ra**	63
18	H (**1s**)	24 h	**3sa**	trace

[a] All reactions were performed with **1** (0.15 mmol), **2a** (0.1 mmol), 4 Å MS (100 mg), and PMe_2Ph (0.01 mmol) in toluene (1 mL) at 40 °C. [b] Isolated yield.

biologically important 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazole derivatives in 62−75% yields (entries 1−16). It is worth noting that the reaction worked very efficiently under the standard conditions and completed in around 1 h in most cases. The allenoate **1r** bearing a 2-naphthyl group was also compatible with the reaction to give the product **3ra** in 63% yield (entry 17). Unfortunately, the α-alkyl substituted allenoate **1s** was not compatible with the reaction conditions and gave only a trace of the annulation product (entry 18). In addition, the allenoate without an α-substituent, namely ethyl buta-2,3-dienoate, and a γ-substituted allenoate did not succumb to the current reaction and provided no [2 + 4] annulation product. The structure of the annulation products was confirmed by single crystal X-ray analysis of the product **3ma**.[11]

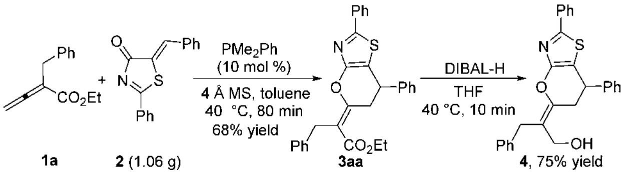
We then attempted to develop the asymmetric variant of this phosphine-catalyzed [2 + 4] annulation of α-substituted allenoates with 5-argiomethylene substituted thiazolones. In the initial exploration, the asymmetric reaction of allenoate **1a** and thiazolone **2a** was selected as a model reaction for screening several chiral phosphine catalysts (see details in Supporting Information). The commercially available Kwon's phosphine **P1**[12] was found to be an excellent chiral catalyst for this reaction, affording the chiral product (+)-**3** in good yields with excellent 95−99% ee (Scheme 2). Unfortunately, a qualified single crystal for X-ray crystallographic analysis could not be obtained; thus, the absolute configuration of the product (+)-**3** had not been assigned.

Scheme 2. Asymmetric [2 + 4] Annulation Reaction



As shown in Scheme 3, on the gram scale, the reaction still worked very efficiently and completed in 80 min to provide the product **3aa** in 68% yield, demonstrating the reaction to be a practical tool for the synthesis of 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazole derivatives. Further reduction of the current product with DIBAL-H gave the alcohol product **4** in 75% yield.

Scheme 3. Reaction on the Gram Scale and Further Transformation of the Product



Many compounds bearing a thiazole unit have been developed as the fluorescent probes for staining and imaging in live cells.[13] Therefore, the design and synthesis of novel thiazole-based fluorescent dyes have become an important research topic. Interestingly, the 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazoles **3aa** and **3ra** synthesized by our methodology (Figure 1) displayed satisfactory fluorescence absorption and might find potential application in the field of fluorescent material.

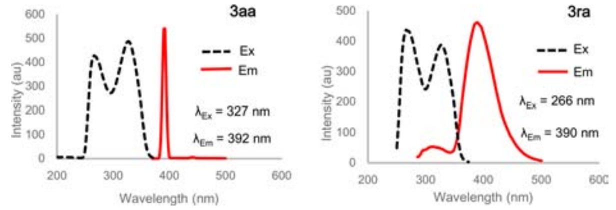
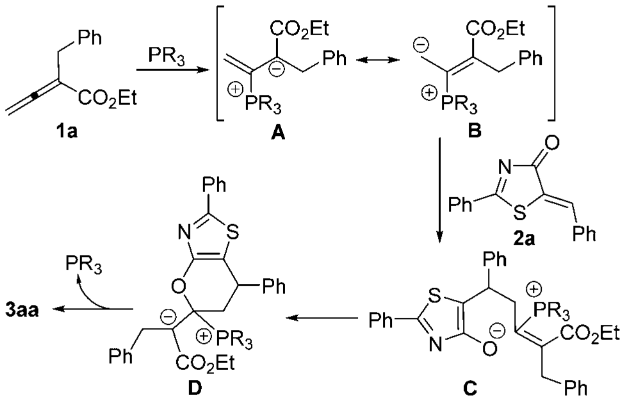


Figure 1. Excitation and emission spectra of **3aa** and **3ra**.

On the basis of our results and the previous studies, we proposed a reasonable mechanism for the formation of 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazoles (**3**) (Scheme 4). In the presence of tertiary phosphine, the β-phosphonium dienolate intermediate **B**, formed though conjugate addition of the phosphine to the allenoate **1a**, attacks α,β-unsaturated enone **2a** to give the enolate intermediate **C**. Subsequent intramolecular conjugate addition, followed by elimination of tertiary phosphine, leads to the formation of the product **3aa**. Generally, α-arylmethyl allenoates function as four-carbon synthons to react with electron-deficient alkenes, furnishing [4 + 2] annulation to give cyclohexene derivatives. In the current reaction, the thiazole ring formed through isomerization may stabilize the intermediate **C**, thus leading to a rare [2 + 4] pathway in which α-substituted allenoates serve as a C_2 synthon.[14]

Scheme 4. A Plausible Reaction Mechanism



In conclusion, we have developed a novel phosphine-catalyzed [2 + 4] annulation between α-arylmethyl allenoates and thiazolone-derived alkenes, leading to biologically significant functionalized 6,7-dihydro-5*H*-pyrano[2,3-*d*]thiazoles in good to excellent yields under mild reaction conditions.

Particularly, it is the first example of α-substituted allenoates serving as a C2 synthons in phosphine-catalyzed [2 + 4] annulation. Furthermore, an asymmetric variant of the reaction has also been realized with quite excellent enantioselectivities with the use of Kwon's phosphine as a chiral catalyst.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01571.

Experimental procedure, characterization data, HPLC analysis dada, NMR spectra, and X-ray crystallographic data (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: xiaoyumei@cau.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(14) In principle, phosphine-catalyzed annulation reactions are stepwise reactions. Under phosphine catalysis conditions, the current [2 + 4] annulation reaction follows the stepwise mechanism, which was accepted in the related literature, see: References 1, 8, and 9. The synergistic [2 + 4] cycloaddition of the intermediate **A** and oxodiene **2a** to form the intermediate **D** might not be a possible pathway.