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Phosphine-Initiated General Base Catalysis: Facile Access to Benzannulated 1,3-Diheteroatom Five-Membered Rings via Double-Michael Reactions of Allenes

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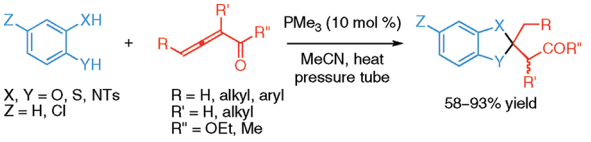
ABSTRACT



General base-catalyzed double-Michael reactions of allenes with various dinucleophiles are described. The reactions are facilitated most efficiently by a catalytic amount of trimethylphosphine, affording six types of C2-functionalized benzannulated five-membered heterocycles: benzimidazolines, benzoxazolines, benzothiazolines, 1,3-benzodioxoles, 1,3-benzoxathioles, and 1,3-benzodithioles. This atom-economical reaction is operationally simple and provides the product heterocycles in good to excellent yields. Careful mechanistic studies unveiled the phosphine-triggered general base catalysis pathway. Furthermore, the double-Michael reaction can serve as an alternative method for the selective monoketalization of β-diketones.

C2-Functionalized benzannulated 1,3-diheteroatom five-membered rings are useful compounds for medicinal purposes and in materials chemistry.[1] For instance, some 1,3-benzodioxoles display endothelin antagonist, anti-inflammatory, antimicrobial, and antitumor activities.[2] 1,3-Benzothiazolines are used as antioxidants to improve the oxidative stability of rubbers, polymers, and plastics.[3] These scaffolds are commonly synthesized through dehydrative condensation of 1,2-disubstituted benzenes with aldehydes or ketones in the presence of acid catalysts.[4] The reaction conditions are, however, often harsh, employing strong dehydrating agents (e.g., P_2O_5) or superstoichiometric amounts of acid, requiring tedious workup.[5] In addition, no single set of conditions reported previously can be applied to the preparation of all six benzannulated 1,3-diheteroatom five-membered rings.

The Michael reaction is one of the most versatile processes in organic synthesis.[6] While intramolecular Michael reactions of compounds featuring donor/acceptor groups are valuable for forming functionalized cyclic compounds from acyclic starting materials,[7] intermolecular double-Michael reactions are particularly powerful tools for assembling complex cyclic products from simple acyclic starting

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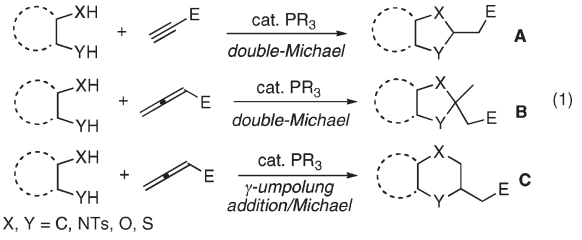
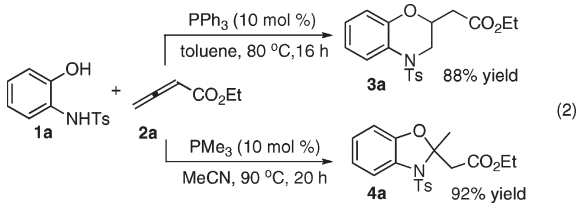
materials. Among the intermolecular double-Michael reactions, the union of two olefins, functioning as both acceptor and donor, is most common.[8] Recently, we disclosed the phosphine-catalyzed double-Michael reactions of dinucleophiles with acetylenes as a powerful method for synthesizing heterocycles **A** (eq 1).[9] Although, theoretically, disubstituted acetylenes could be used to introduce a quaternary center (as in **B**), we found that any additional substituent at the β-carbon atom of the activated acetylene prohibited its double-Michael reaction. Double-Michael reactions of dinucleophiles with allenes, which have the same degree of unsaturation as acetylenes yet enhanced reactivity, would conceivably also yield heterocycles **B**;[10] it has been reported, however, that allenes typically undergo tandem γ-umpolung addition/Michael cyclization, forming heterocycles **C**, in the presence of phosphines.[11] Herein, we report a new phosphine-triggered general base-catalyzed tandem double-Michael reaction of dinucleophiles with allenes, affording, under, simple and mild conditions, highly functionalized heterocycles **B** featuring fully substituted carbon centers.



(1)

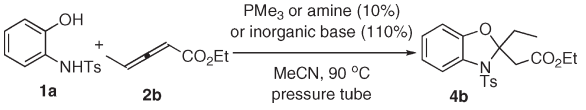
The tandem umpolung addition/Michael cyclization of dinucleophiles and allenoates is typically facilitated by PPh_3.[11] Indeed, treatment of *N*-tosyl-2-aminophenol (**1a**)[12] and the allene **2a** with PPh_3 (10 mol %) provided the benzomorpholine **3a** in 88% yield (eq 2). Switching the catalyst to PMe_3, however, led to production of the double-Michael product **4a** in 92% yield.[13] The addition of PMe_3 to allenoate **2a** is speculated to form a phosphonium enolate that acts as a general base and promote the formation of the double-Michael product **4a** (see mechanistic studies below). To test this hypothesis, we also examined the double-Michael reactions mediated by amines and inorganic bases.



(2)

N-Tosyl-2-aminophenol (**1a**) was reacted with allene **2b** in the presence of an amine (0.1 equiv) or an inorganic base (1.1 equiv) in MeCN at 90 °C (Table 1). While PMe_3 provided the double-Michael adduct **4b** in 86% yield (entry 1), amine bases displayed varying degrees of success. Among the common nucleophilic amine bases, DMAP performed better than quinuclidine, 3-hydroxyquinuclidine (3-HQD), and DABCO, exhibiting efficiency comparable with that of PMe_3 (entries 2−5). Neither the basicity[14] nor the nucleophilicity[15] of the amine base followed the same trend as the reaction efficiency, hinting at a complex multistep reaction mechanism (*vide infra*). The inorganic bases also facilitated the reaction, albeit with much diminished efficiency (entries 6−8). Focusing on the double-Michael reaction with PMe_3 and DMAP, we investigated a variety of nucleophiles and allenes for the construction of benzannulated 1,3-diheteroatom five-membered cycles.

Table 1. Double-Michael Reactions of the Amidophenol **1a** and the Allene **2b** Mediated by Different Bases[a]



entry	base[b]	pK_a(H_2O)[c]	nucleophilicity[d]	yield (%)[e]
1	PMe_3	8.7	15.49[f]	86
2	quinuclidine	11.3	20.54[g]	26
3	3-HQD	9.9		54
4	DABCO	8.7	18.80[g]	77
5	DMAP	9.2	15.80[h] (14.95)[g]	82
6	Na_2CO_3	10.3		35
7	$NaHCO_3$	6.3		16
8	NaOAc	4.8		53

[a] Reactions were performed using 0.4 mmol of **1a** and 1.1 equiv of **2b**. [b] For the complete list of bases tested, see the Supporting Information. [c] Reference 14. [d] Reference 15. [e] Isolated yield. [f] The value is the nucleophilicity of PBu_3 (in CH_2Cl_2). [g] Nucleophilicity in MeCN. [h] Nucleophilicity in CH_2Cl_2.

The PMe_3-mediated double-Michael reaction was generally applicable to a variety of ortho-substituted phenol, aniline, and thiophenol dinucleophiles (Table 2). Under the simple conditions of heating the dinucleophile at 90 °C in MeCN in the presence of the allenoate **2a** and PMe_3 (10 mol %), 2-mercaptophenol provided the 1,3-benzoxathiole **4c** in 93% yield (entry 1).[16] The 1,3-benzodioxole **4d** and the 1,3-benzodithiole **4e** were also formed readily in good yields (entries 2 and 3). In contrast, *N*-tosyl-2-

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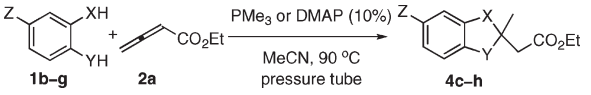
aminothiophenol[17] and *N*,*N*′-ditosyl-1,2-diaminobenzene[18] produced only their mono-Michael adducts at 90 °C; a temperature of 120 °C was required to facilitate full conversions to their double-Michael products, the benzothiazoline **4f** and the benzimidazoline **4g**, respectively (entries 4 and 5). The presence of a chlorine substituent did not affect the double-Michael reaction of **1g**, giving the benzoxazoline **4h** in 84% yield (entry 6). When DMAP (10 mol %) was used, only moderate amounts of the benzothiazoline **4f** and the benzimidazoline **4g** were obtained (entries 4 and 5).

Table 2. Double-Michael Annulations of Various Dinucleophiles[a]

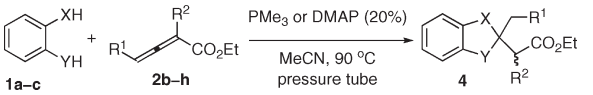


				yield (%)[b]	
entry	X, Y	Z	product	PMe_3	DMAP
1	O, S (**1b**)	H	**4c**	93	
2	O, O (**1c**)	H	**4d**	80	
3	S, S (**1d**)	H	**4e**	74	
4[c]	S, NTs (**1e**)	H	**4f**	68	53
5[c]	NTs, NTs (**1f**)	H	**4g**	79	38
6	O, NTs (**1g**)	Cl	**4h**	84	

[a] Reactions were performed using 0.4 mmol of **1** and 1.1 equiv of **2a**. [b] Isolated yield after chromatography. [c] Reaction performed initially at 90 °C to obtain the mono-Michael adduct; the temperature was then raised to 120 °C for full conversation to the double-Michael product.

To form fully substituted C2 centers decorated with groups other than Me and CH_2CO_2Et units, we surveyed the reactions of various α- and γ-substituted allenoates (Table 3). Allenoates with γ-substituents[19] of varying steric and electronic demand were well suited to double-Michael reactions with *N*-tosyl-2-aminophenol, 2-mercaptophenol, and catechol (entries 1−11). Furthermore, the reactions of α-substituted allenoates[20] with catechol provided the 1,3-benzodioxoles **4t**−**v** in excellent yields (entries 12−14). With *N*-tosyl-2-aminophenol as the dinucleophile, α-substituted allenoates generated mixtures of diastereoisomers with poor selectivity, albeit in excellent yields (entries 15−17). In general, DMAP was a less-efficient catalyst than PMe_3, with some exceptions (entries 2, 4, and 6). We observed a particularly noteworthy improvement in the product yield when DMAP was used for the reaction of the γ-benzyl allenoate **2d** (entries 2 and 6). The lower yield with PMe_3 was likely due to isomerization of the γ-benzyl allenoate **2d** to the corresponding diene.[21] The generally superior performance of PMe_3 over DMAP might be due to the phosphonium cation being better than the pyridinium ion at forming a spectator countercation for the general bases.

Table 3. Double-Michael Annulations of Substituted Allenoates[a]



				yield (%)[b]	
entry	X, Y	R^1, R^2	product	PMe_3	DMAP
1	O, NTs	Ph, H (**2c**)	**4i**	83	
2	O, NTs	Bn, H (**2d**)	**4j**	61	77
3	O, NTs	*t*-Bu, H (**2e**)	**4k**	69	51
4	O, S	Me, H	**4l**	74	76
5	O, S	Ph, H	**4m**	86	
6	O, S	Bn, H	**4n**	65	89
7	O, S	*t*-Bu, H	**4o**	58	48
8	O, O	Me, H	**4p**	70	68
9	O, O	Ph, H	**4q**	77	
10	O, O	Bn, H	**4r**	89	74
11	O, O	*t*-Bu, H	**4s**	82	68
12	O, O	H, Me (**2f**)	**4t**	89	
13	O, O	H, Bn (**2g**)	**4u**	86	
14	O, O	H, CH_2CO_2Et (**2h**)	**4v**	80	
15[c]	O, NTs	H, Me	**4w**	81[d]	
16[c]	O, NTs	H, Bn	**4x**	73[d]	
17[c]	O, NTs	H, CH_2CO_2Et	**4y**	84[d]	

[a] Reactions were performed using 0.4 mmol of **1** and 1.35 equiv of **2**. [b] Isolated yield. [c] NaOAc (50 mol %) was added. [d] Diastereoisomeric ratio determined using ^1H NMR spectroscopy. Diastereomeric ratios 1:1, 2:1, and 1.2:1 for **4w**, **4x**, and **4y**, respectively.

We gleaned clues regarding the mechanism of this new phosphine-mediated double-Michael reaction from the isolation of the mono-Michael product **5a**[13] of *N*-tosyl-2-aminophenol (**1a**) and the allenoate **2b** (eq 3). Intriguingly, when we heated **5a** in MeCN in the presence of catalytic PMe_3, we obtained almost no cyclized product **4b**. On the other hand, exposure of **5a** to catalytic PMe_3 and the allenoate **2b** in MeCN at 90 °C provided the double-Michael product **4b** in 80% yield. Most interestingly, treatment of **5a** with catalytic PMe_3 and 1.1 equiv of the allenoate **2a** also rendered formation of the benzoxazoline **4b**. Notably, we detected no product **4a**, arising from the elimination of **1a** from **5a** and subsequent double-Michael

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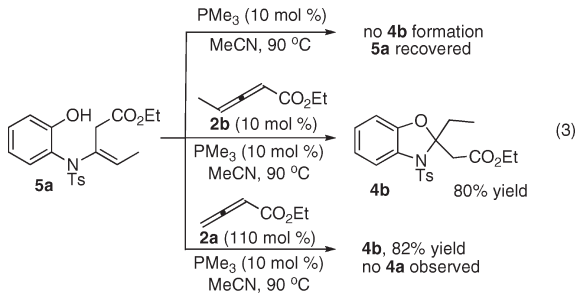
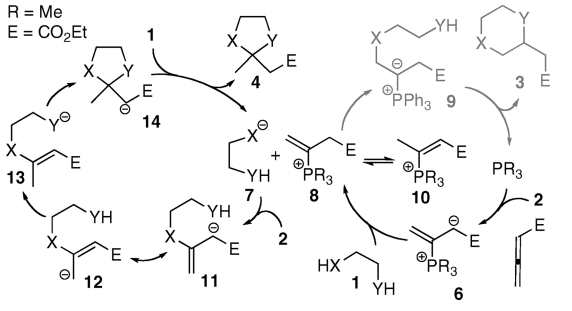
reaction of the allenoate **2a**.



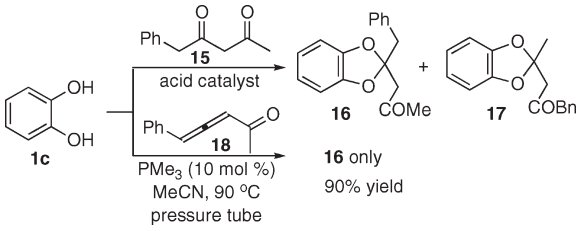
Based on these insights, we propose the following mechanism for the double-Michael reaction (Scheme 1). Nucleophilic addition of the phosphine to the allenoate **2** results in the phosphonium enolate **6**. Protonation of **6** by the pronucleophile **1** leads to the formation of a nucleophile/phosphonium salt pair **7**·**8**, which undergoes γ-umpolung addition to yield the ylide **9** when PPh_3 is employed as the catalyst.[11] In contrast, the more-electron-rich phosphine PMe_3 does not facilitate umpolung addition.[22] As we had observed for the double-Michael reactions of acetylenes, the β,β-disubstituted enoate **10** did not undergo the Michael reaction.[9] Instead, the nucleophile **7** adds to the allenoate **2**. The resulting dienolate **11** undergoes γ-protonation to form the α,β-unsaturated enoate **13**, which is primed for a second Michael addition. The cyclic enolate **14** can further facilitate the double-Michael reaction cycle by deprotonating the pronucleophile **1** (or mono-Michael product; e.g., **5a** in Scheme 1) to produce the product **4**, supporting the notion of general base catalysis.[23] The observation of no cyclized product derived from the allenoate **2a** in eq 3 also suggests that the second Michael addition is facile and that the intermediate **11** does not revert back to the allenoate **2** and the nucleophile **7**.

Scheme 1. Mechanism of the Double-Michael Reactions of Allenes



Scheme 2 demonstrates an additional application of this double-Michael reaction: what amounts to the selective ketalization of asymmetric β-diketones. The ketalization of the β-diketone **15** with catechol would produce a mixture of the acetals **16** and **17**. Conversely, the double-Michael reaction of catechol with the allenone **18**[24] produced only the acetal **16** in 90% yield.

Scheme 2. Selective Synthesis of a β-Diketone Mono-acetal



In summary, we have developed a phosphine-triggered general base-catalyzed double-Michael reaction that enables the syntheses of six different C2-functionalized benzannulated 1,3-diheteroatom five-membered rings from dinucleophiles and allenes. The reported processes are operationally simple and atom-economical, minimize the generation of chemical waste, and employ mild reaction conditions. Based on the results of experiments performed using an isolated mono-Michael adduct, we have established a general base catalysis mechanism for what appears to be a phosphine catalysis reaction. Such mechanistic insight introduces a new twist to the growing number of phosphine-catalyzed annulation reactions[25] and suggests what might be a general role of phosphines in other annulation processes. This highly efficient methodology also circumvents the synthetic problem of nonselective ketalization of β-diketones. Our focus is now on expanding the scope of the pronucleophile, examining the diastereoselectivity of the double-Michael reaction when using α-substituted allenes, and exploring the umpolung addition/Michael reaction using 1,2-disubstituted benzenes.

Acknowledgment. This research was supported by the NIH (R01GM071779, P41GM081282). O.K. thanks Profs. Daniel A. Singleton (Texas A&M University) and Louis S. Hegedus (Colorado State University) for helpful discussions.

Supporting Information Available. Representative experimental procedures, characterization data, and copies of ^1H and ^{13}C NMR spectra for all new compounds (PDF). Crystallographic data for **3b**, **4b**, and **5c** (CIF). This information is available free of charge via the Internet at http://pubs.acs.org.

(22) Tricyclohexylphosphine, which is comparable in size to triphenylphosphine, produced only the double-Michael product **4a** (in yields of 93%) when mixed with the allene **1a** and the nucleophile **2a**.

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