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Phosphine-Catalyzed Domino Reaction: An Efficient Method for the Synthesis of Bicyclo[3.2.0]heptenes Skeleton

Jie Zheng, You Huang,* and Zhengming Li

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

hyou@nankai.edu.cn

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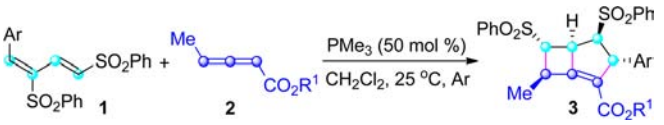
ABSTRACT



Dienic sulfones and γ-CH_3 allenoates can be converted into bicyclo[3.2.0]heptene derivatives in moderate to good yield using trimethylphosphine as the catalyst under mild conditions.

The organocatalyzed domino reactions have been one of the most efficient methods for the rapid construction of complex architectures from readily available substrates under mild conditions. These processes allow several bond-forming steps take place in a single operation.[1] In particular, phosphines have been employed to generate reactive intermediates for domino reactions, including various types of cycloaddition reactions.[2−9] Among the distinguished works, Lu et al. reported pioneering work in the phosphine-catalyzed [3 + 2] cycloaddition of allenoates and electron-deficient olefins in 1995 (Scheme 1).[5a] Kwon and co-workers realized [4 + 2] annulations by employing 2-substituted allenoates as substrates (Scheme 1).[4f] Recently, we discovered the first example of phosphine-catalyzed [4 + 2] cyclizations using γ-substituted allenoates.[10]

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However, there is no example of constructing a spiro, fused, or bridged ring system, while the reported results focus on the synthesis of single ring structures. Among the reactive intermediates, γ-CH_3 allenoate has been rarely reported.[3] In addition, we have a long-standing and continuing interest in the field of phosphine-catalyzed domino reactions especially with activated conjugated dienes[11−13] and γ-substituted allenoate.[10,14−16]

Very recently, we have reported the first phosphine-catalyzed domino benzannulation reaction which constructed biaryls from dienic sulfones (**1**, Scheme 1) and γ-CH_3 allenoates (**2**, Scheme 1).[16] During the optimization of the reaction conditions, we noticed a different reaction outcome when tributylphosphine was used as the catalyst. To our delight, instead of the biaryl products, bicyclo-[3.2.0]heptene derivative was formed in 8% yield (**3**, Scheme 1). The bicyclo[3.2.0]heptane skeleton is found in diverse natural products including kelsoene, sulcatine G, prespatane, repraesentin F, β-lumicolchicine, and tricycloclavulone (Figure 1).[17] Several synthetic strategies have been reported to obtain this useful structure,[18] such as (1) Michael addition of carbanion to triphenylphosphonium salt and subsequent intramolecular Wittig reaction,[19] (2) cycloaddition of bis-enones,[20] (3) intramolecular $[2\pi + 2\pi]$ cycloaddition of α,ω-dienes,[21] (4) 1,3-dipolar cycloaddition between Au carbenoid-containing carbonyl ylides and ethyl vinyl ether.[22] In addition, several drawbacks such as using noble metal, harsh reaction condition are still issues in this area. It aroused our enthusiasm to develop a much more convenient method for constructing this building block. Herein, we report the efficient synthesis of bicyclo-[3.2.0]heptene derivatives using trimethylphosphine as the only catalyst under mild conditions (Scheme 1).

At the outset of this investigation, we employed the dienic sulfones **1b** with allenoate **2a** in the presence of PBu_3 in CH_2Cl_2 to optimize the reaction conditions. To our delight, when the reaction was carried out at 40 °C, **3b** was isolated in 8% yield (Table 1, entry 1). When the reaction performed at 25, 0, and −20 °C the product was obtained in 39%, 51% and 45% yield, respectively (entries 2−4). Specifically, complete conversion occurred within 25 min at 25 °C (entry 2). However, 0 °C seemed better. Similar yield was obtained by changing the catalyst loading to 30 mol % (entry 5). Fortunately, when the catalyst loading was 30 mol %, the yield of **3b** was further increased to 56% at 25 °C in a short time (entry 6). However, the isolation was somewhat inconvenient. In addition, the reaction proceeded less efficiently in other solvents, such as $CHCl_3$, toluene, THF, CH_3CN, DMF, and DMSO (entries 7−12). When PhCOOH was added to the reaction mixture, no

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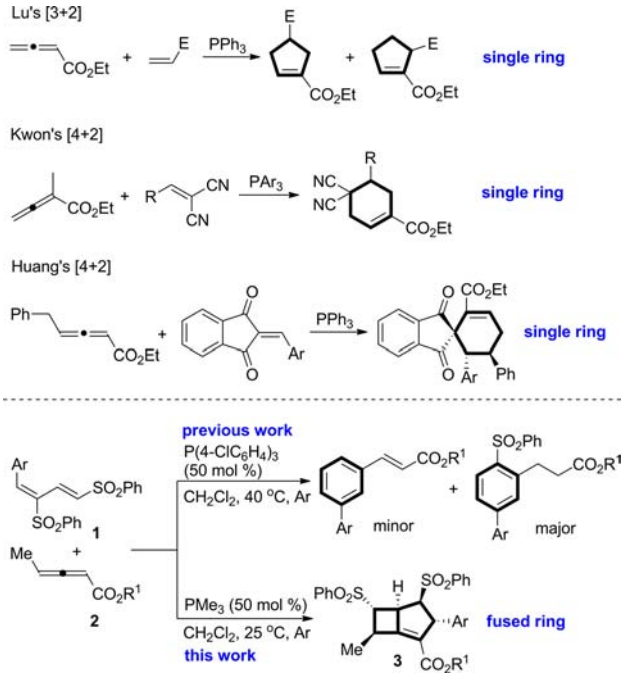
Scheme 1. Previous Works and This Work



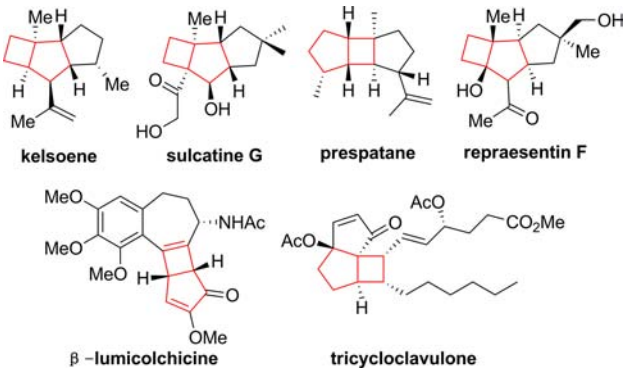
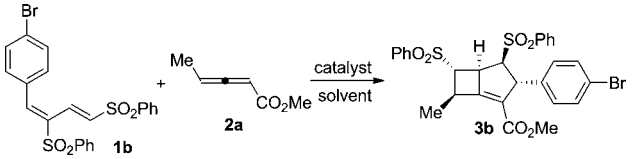


Figure 1. Representative natural products containing the bicyclo-[3.2.0]heptane scaffold.

reaction occurred (entry 13). Other additives, such as K_2CO_3, Cs_2CO_3, and H_2O, did not improve the efficiency (entries 14–16). Concentrating or diluting the reaction turned out to be ineffective (entries 17 and 18). We then turned our attention to the catalyst. Among the alkylphosphines evaluated, 50 mol % of trimethylphosphine can promote the process with good efficiency and easy isolation of the desired product (entries 19–22). Lowering the temperature led to a slightly lower conversion (entry 23).

Having established the best protocol for the reaction, we next surveyed the scope of this transformation with respect to dienic sulfones and γ-CH_3 allenoates. The reaction behaved well when phenyl-substituted dienic sulfone were employed (Scheme 2, **3a**). With regard to *para*-substituents, electron-withdrawing groups afforded products in a

Table 1. Optimization of the Reaction Conditions[a]



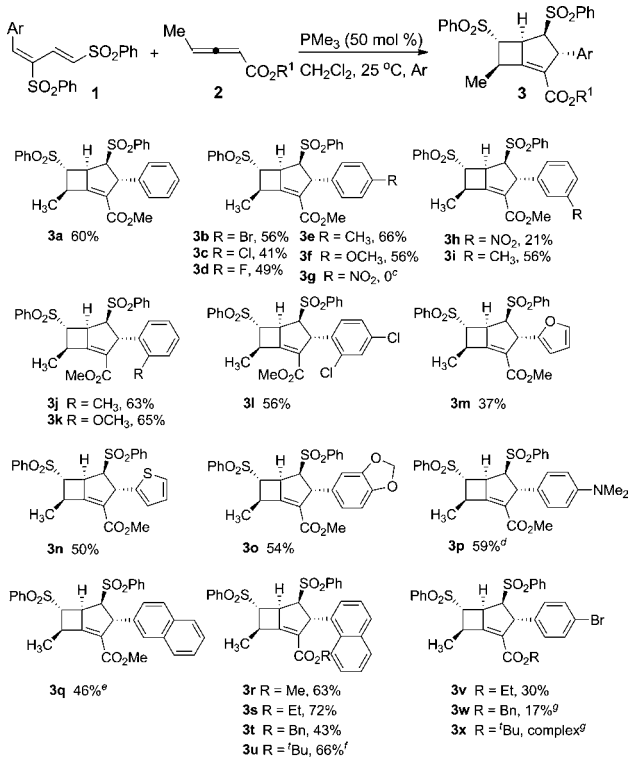
entry	catalyst	mol %	solvent	t(°C)	time	yield (%)[b]
1	PBu_3	50	CH_2Cl_2	40	35 h	8
2	PBu_3	50	CH_2Cl_2	25	25 min	39
3	PBu_3	50	CH_2Cl_2	0	3 h	51
4	PBu_3	50	CH_2Cl_2	−20	8 h	45
5	PBu_3	30	CH_2Cl_2	0	9 h	52
6	PBu_3	30	CH_2Cl_2	25	25 min	56
7	PBu_3	30	$CHCl_3$	25	25 min	25
8	PBu_3	30	toluene	25	7 h	NP
9	PBu_3	30	THF	25	1 h	23
10	PBu_3	30	CH_3CN	25	12 h	complex
11	PBu_3	30	DMF	25	25 min	trace
12	PBu_3	30	DMSO	25	25 min	0
13[c]	PBu_3	30	CH_2Cl_2	25	5 h	NR
14[d]	PBu_3	30	CH_2Cl_2	25	25 min	38
15[e]	PBu_3	30	CH_2Cl_2	25	25 min	32
16[f]	PBu_3	30	CH_2Cl_2	25	2 h	36
17[g]	PBu_3	30	CH_2Cl_2	25	25 min	28
18[h]	PBu_3	30	CH_2Cl_2	25	25 min	44
19	$P(NEt_2)_3$	30	CH_2Cl_2	25	4 h	NR
20	PMe_3	30	CH_2Cl_2	25	24 h	trace
21	**PMe_3**	**50**	**CH_2Cl_2**	**25**	**25 min**	**56**
22	PMe_3	70	CH_2Cl_2	25	25 min	32
23	PMe_3	50	CH_2Cl_2	0	7 h	41
24[i]	PMe_3	50	CH_2Cl_2	25	4 h	14
25[j]	PMe_3	50	CH_2Cl_2	25	45 min	37

[a] Reaction conditions: 1.0 equiv (0.3 mmol) of **1b**, 3.0 equiv (0.9 mmol) of **2a**, 5 mL of solvent. [b] Isolated yields. [c] 30 mol % of PhCOOH. [d] 30 mol % of K_2CO_3. [e] 30 mol % of Cs_2CO_3. [f] 1 mL of H_2O. [g] 1 mL of CH_2Cl_2. [h] 10 mL of CH_2Cl_2. [i] The ratio of **1b**:**2a** was 1:1. [j] The ratio of **1b**:**2a** was 1:2.

slightly lower yield than electron-donating groups (Scheme 2, **3b**–**f**,**p**). Reaction was forbidden with the aryl having a strongly electron-withdrawing nitro (Scheme 2, **3g**). It was found that yields for **3** were obviously dependent on electronic influence from aryl. Also, with *meta*- and *ortho*-substituents on the aryl, the products were formed in good yields except for electron-withdrawing group (Scheme 2, **3h**–**k**). We were pleased to find that all the reactions with a methyl group at the *ortho*, *meta*, or *para* position of the phenyl ring showed good reactivity (Scheme 2, **3e**, **3i**, and **3j**). Similarly, aryl can be 2-furyl, thienyl, piperonyl, or β-naphthyl with favorable reactivity (Scheme 2, **3m**–**q**). With regard to the substitutions on the allenoates, it is noteworthy that the increased steric hindrance did not result in a significant decrease in efficiency when aryl was α-naphthyl (Scheme 2, **3r**–**u**). However, changing the substituent on the dienic sulfone from α-naphthyl to p-bromophenyl had adverse effect on the results (Scheme 2, **3v**–**x**).

With regard to the reaction mechanism, we have proposed a possible pathway (Scheme 3). The reaction was

Scheme 2. Scope of the Reaction[a,b]

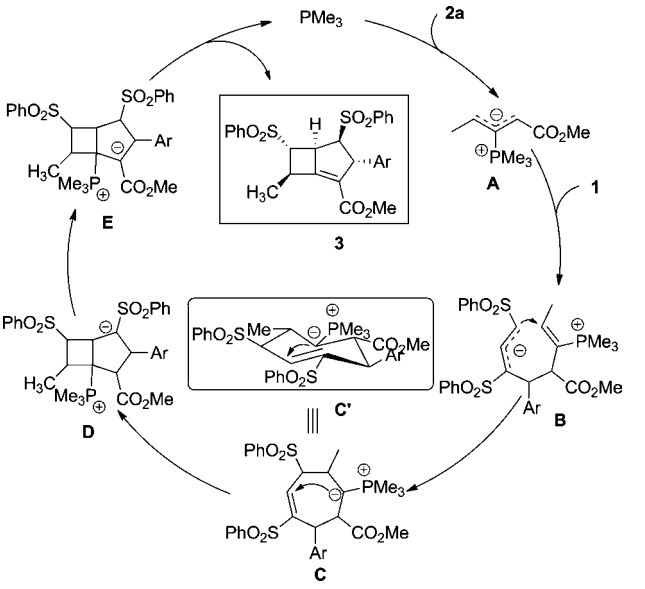


[a] Reaction conditions: 1.0 equiv (0.3 mmol) of **1**, 3.0 equiv (0.9 mmol) of **2**, 50 mol % of PMe_3 in 5 mL of CH_2Cl_2 at 25 °C for 25 min under Ar. [b] Isolated yields. [c] 4 h. [d] 40 °C. [e] 40 °C, 50 min. [f] 40 °C, 45 min. [g] 3.5 h.

triggered by nucleophilic addition of trimethylphosphine to allenoate **2a**. Then the zwitterionic intermediate **A** added to the dienic sulfone **1** to give intermediate **B**, which underwent an intramolecular nucleophilic attack to give another zwitterionic intermediate **C** (the stable configuration resulted in the high diastereoselectivity). Intramolecular Michael addition followed by proton transfer and elimination of the catalyst from the resulting zwitterionic intermediate **E** afforded the corresponding adduct **3**. To gain mechanistic insight, we attempted to trap intermediate **C** using benzaldehyde. Unfortunately, only bicyclo product was detected with fully conversion of dienic sulfone in 5 min.

In conclusion, we have presented an efficient methodology for the preparation of a multifunctionalized bicyclo-[3.2.0]heptene ring system by direct reaction of dienic

Scheme 3. Proposed Mechanism



sulfones and γ-CH_3 allenoates using trimethylphosphine as the only catalyst under mild conditions. With regard to aryl-substituents, electron-donating groups afforded products in a slightly higher yield than that of electron-withdrawing groups. From the synthetic point of view, this protocol represents an extremely simple and atom-economic way to construct complex cyclic building blocks. The simplicity of the reaction is noteworthy as it requires neither the participation of a metal catalyst nor the use of dry solvent. We believe that the approach delineated in this paper will find application in the design of DOS libraries.

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Supporting Information Available. Detailed experimental procedures and spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.