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Tandem Spirocyclopropanation/Rearrangement Reaction of Vinyl *p*-Quinone Methides with Sulfonium Salts: Synthesis of Spirocyclopentenyl *p*-Dienones

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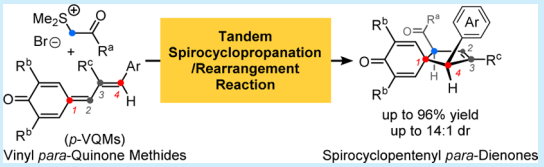
Supporting Information

ABSTRACT: A novel base-mediated tandem spirocyclopropanation/rearrangement reaction of vinyl *p*-quinone methides (*p*-VQMs) with sulfonium salts is described. The unprecedented reactivity of *p*-VQMs was explored for the first time in the spiroannulation cascade, providing a stereoselective approach to the construction of synthetically interesting, densely functionalized spirocyclopentenyl *p*-dienones.



The spirocyclopentyl *p*-dienone unit **A** (Figure 1) featuring the quaternary carbon center and cyclohexadiene moiety is

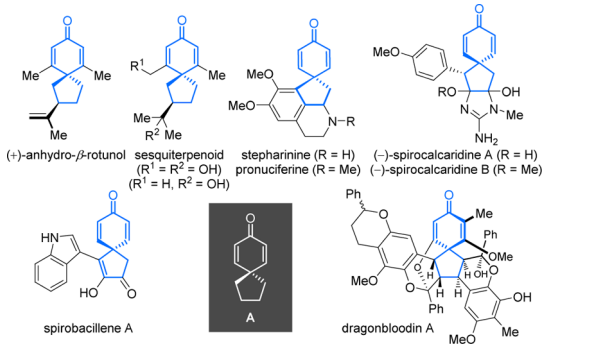
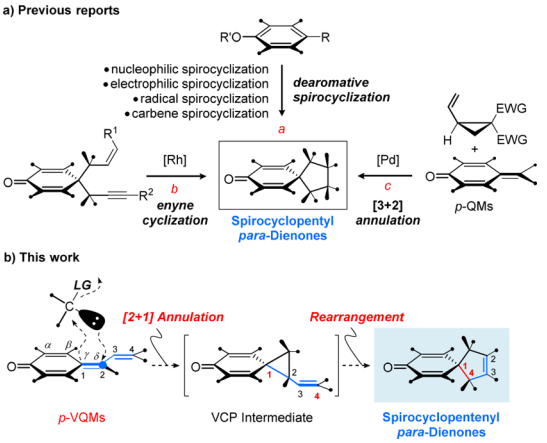


Figure 1. Representative natural products containing spirocyclopentyl *p*-dienones.

widely distributed in many biologically interesting natural products.[1] Chemically, its inherent characteristic with the enone group and the spirocyclic skeleton renders such functionalized carbocycles to be a class of synthetically useful building blocks in organic chemistry.[2] Because of its unique molecular architecture as well as synthetic potential, the development of methods to construct the spirocyclopentyl *p*-dienones has received considerable attention in the synthetic community. Among them, as shown in Scheme 1, dearomative spirocyclizations (route a) involving nucleophilic,[3] electrophilic,[4] radical,[5] or carbene[6] entities have been generally developed on the basis of various available phenol precursors. Meanwhile, 1,6-enyne cyclization (route b) has also been used in the construction of spirocyclopentyl *p*-dienones.[2] Focusing on this

Scheme 1. Approaches to Spirocyclopent(en)yl *p*-Dienones



topic, recently, two palladium-catalyzed [3 + 2] annulations of *p*-quinone methides with vinylcyclopropanes (route c) have been elegantly developed by Yao[7a] and Zhao,[7b] respectively. Despite this great progress, it still remains highly desirable to explore a novel methodology to access this class of synthetically interesting spirocycles characterized by the unique *p*-dienone unit.

p-Quinone methides (*p*-QMs)[8,9] have attracted increasing attention in the synthetic community due to their unique structural architecture featuring a bisvinylogous enone system. Several reaction modes of *p*-QMs have been discovered, mainly including 1,6-conjugate additions,[10,11] [2 + 1]-annulations,[12] [3

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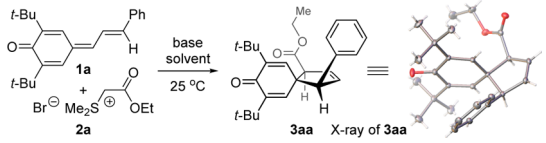
+ 2]-annulations,[13,7] and [4 + 2]-annulations.[14] Compared with many reports on the application of *p*-QMs in organic synthesis, surprisingly, there is little known on the methodology design based on the chemistry of vinyl *p*-quinone methides (*p*-VQMs), despite the fact that *p*-VQMs have been described in organic chemistry for decades.[15] With our continuing interest in the chemistry of *p*-QMs,[11a,j,k] together with our previous exploration in the spirocyclopropanation of *p*-QMs with sulfonium salts,[12c] recently we have developed a novel tandem spiroannulation reaction of *p*-VQMs with sulfonium salts (Scheme 1) wherein an unprecedented cascade process including a spirocyclopropanation and subsequent spontaneous vinylcyclopropane (VCP) rearrangement is involved. This tandem reaction provides an effective method for the synthesis of various functionalized spirocyclopentenyl *p*-dienones. Herein, we report our preliminary results on this aspect.

We commenced our investigation by using *p*-VQM **1a** and dimethylsulfonium acetate bromide **2a** as the model substrates. As tabulated in Table 1, several inorganic bases (e.g., hydroxides,

Table 1. Optimization of Reaction Conditions[a]



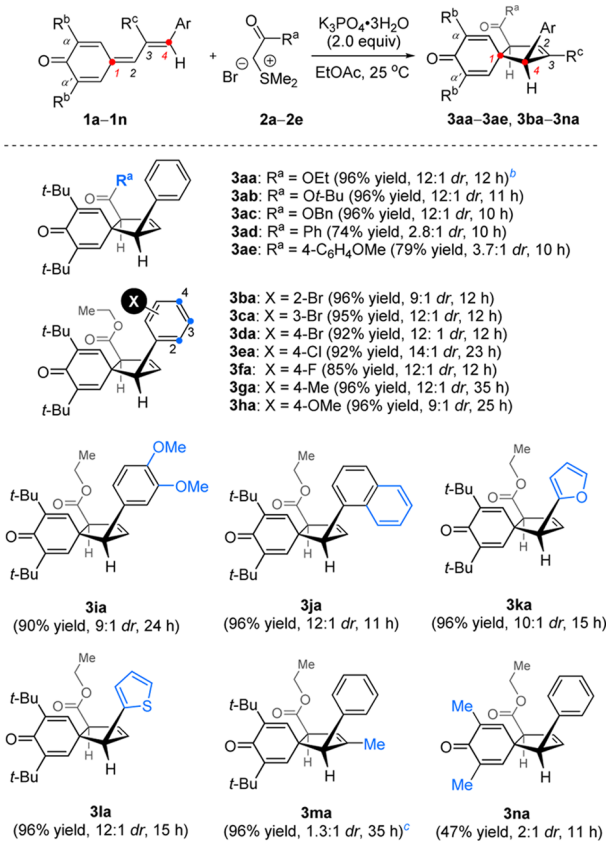
entry	base	solvent	time (h)	yield[b] (%)	dr[c]
1	Na_2CO_3	CH_2Cl_2	48	0	ND
2	NaOH	CH_2Cl_2	48	76	11:1
3	K_2CO_3	CH_2Cl_2	48	39	12:1
4	KOH	CH_2Cl_2	12	81	11:1
5	Cs_2CO_3	CH_2Cl_2	24	86	12:1
6	**$K_3PO_4·3H_2O$**	**CH_2Cl_2**	**20**	**90**	**11:1**
7	*t*-BuOK	CH_2Cl_2	15	72	4:1
8	DBU	CH_2Cl_2	17	76	3:1
9	DABCO	CH_2Cl_2	48	<5	ND
10	TMG	CH_2Cl_2	24	84	7:1
11	$K_3PO_4·3H_2O$	$PhCH_3$	48	60	12:1
12	$K_3PO_4·3H_2O$	$CHCl_3$	36	89	10:1
13	$K_3PO_4·3H_2O$	CH_3CN	11	49	6:1
14	**$K_3PO_4·3H_2O$**	**EtOAc**	**12**	**96**	**12:1**
15	$K_3PO_4·3H_2O$	THF	11	83	11:1
16	$K_3PO_4·3H_2O$	DMSO	1	0	ND

[a]Performed with *p*-VQM **1a** (0.1 mmol) and sulfonium salt **2a** (0.15 mmol) in the presence of base (0.2 mmol) in solvent (2 mL) at 25 °C. [b]Yield of isolated product. [c]Determined by the crude NMR. ND = not determined, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane, TMG = 1,1,3,3-tetramethylguanidine.

carbonates, the phosphate) were first tested for this reaction in CH_2Cl_2 at room temperature (entries 1−6). Among them, $K_3PO_4·3H_2O$ delivered the desired product **3aa** with 11:1 dr in a higher yield of 90% yield (entry 6), wherein the relative *cis*-configuration of spirocyclopentenyl *p*-dienone **3aa** was assigned by X-ray crystallographic analysis.[16] It is noteworthy that some organic bases (e.g., *t*-BuOK, DBU, DABCO, and TMG) were also examined in the current model reaction (entries 7−10), but there was no positive improvement observed in the reaction reactivity (up to 84% yield) and diastereoselectivity (3:1 to 7:1). Encouraged by the above promising results, the influence of solvents in this model reaction was then examined (entries 11−16). In terms of yield and stereoselectivity, EtOAc as the reaction solvent gave the best result (96% yield, 12:1 dr, entry 14).

With the optimized conditions in hand, we then preliminarily explored the scope of sulfonium salts (**2b−e**). As shown in Scheme 2, sulfonium salts containing ester groups (R^a = *t*-BuO,

Scheme 2. Scope of Substrates[a,b]



[a]Performed with *p*-VQMs **1a−n** (0.2 mmol) and sulfonium salts **2a−e** (0.3 mmol) in the presence of $K_3PO_4·3H_2O$ (0.4 mmol) in EtOAc (4 mL) at 25 °C. The yields refer to the isolated products, the dr's were determined by the crude NMR, and major isomers were indicated graphically for all cases. [b]The relative configuration of **3aa** was established by X-ray crystallographic analysis, and accordingly, the reaction stereoselectivity in other cases was assigned by analogy. [c]Performed at 40 °C.

BnO) could smoothly afford the corresponding annulation products **3ab** and **3ac** with high yields (96% yield) and good diastereoselectivities (12:1 dr). However, compared with the ester sulfonium salts having a less acidic α-hydrogen, the ketone ones **2d** (R^a = Ph) and **2e** (R^a = 4-methoxyphenyl) led to a decrease both in reaction efficiency and stereoselectivities, giving **3ad** (74% yield, 2.8:1 dr) and **3ae** (79% yield, 3.7:1 dr), respectively. After the above investigations on the one-carbon component in this tandem annulation reaction, a series of structurally diverse vinyl *p*-quinone methides (*p*-VQMs) as a four-carbon component were further probed. For *p*-VQMs (**1b−j**) bearing electronically different aryl substituents, generally the expected spirocyclic products **3ba−ja** could be afforded in good to excellent yields (85−96% yield) with satisfactory stereoselectivities (9:1−14:1 dr), but prolonging the reaction time was necessary for the reaction of *p*-VQMs (**1g−i**) with an electron-donating C4-aryl group. In addition, two *p*-VQMs (**1k** and **1l**) having the heteroaryl groups (Ar = 2-furanyl, 2-thienyl) were also

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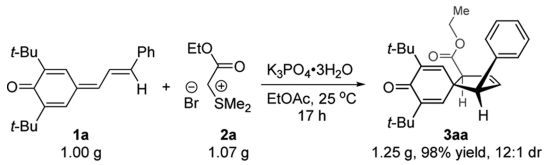
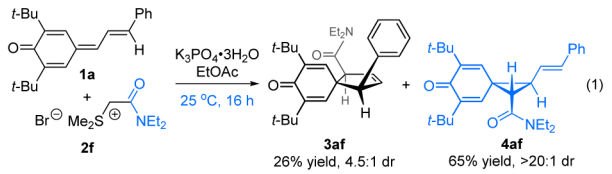
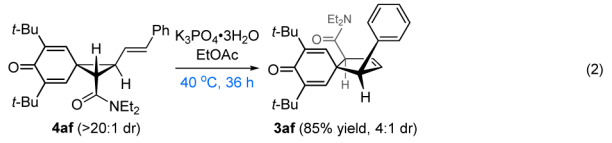
examined, giving the corresponding products **3ka** (96% yield, 10:1 dr) and **3la** (96% yield, 12:1 dr). Moreover, one example using *p*-VQM **1m** (R^b = *t*-Bu, R^c = Me, Ar = Ph, *E*/*Z* 1.5:1) with a mixture of geometrical isomers was also conducted, and the product **3ma** was obtained with poor diastereoselectivity (1.3:1 dr) despite a high yield (96% yield). Meanwhile, *p*-VQM **1n** (R^b = Me, R^c = H, Ar = Ph) containing two methyl groups at the α,α'-position gave the desired product **3na** only in 47% yield and 2:1 dr, showing a negative influence of less bulky α,α'-substituents in *p*-VQM on the reactivity and selectivity. To explore the synthetic utility of this protocol, a gram-scale reaction of **1a** and **2a** was additionally conducted (Scheme 3), delivering the model product **3aa** with analogous reactivity (98% yield) and selectivity (12:1 dr).

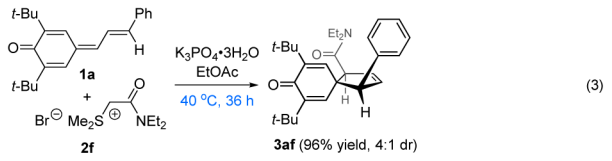
Scheme 3. Gram-Scale Reaction



Notably, when the sulfonium salt **2f** bearing an amide group was subjected to the optimized conditions, as shown in eq 1, the



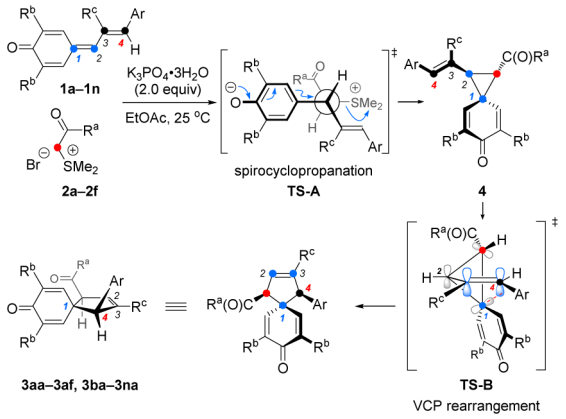




desired spirocyclopentenyl *p*-dienone **3af** was procured only as the minor product (26% yield, 4.5:1 dr), wherein the unexpected spirocyclopropane **4af** (>20:1 dr) was isolated as the major product in 65% yield.[17] Interestingly, the spirocyclopropane **4af** (>20:1 dr) could be smoothly transformed into the spirocyclopentene **3af** (4:1 dr) in 85% yield in the presence of $K_3PO_4 \cdot 3H_2O$ at 40 °C (eq 2). Compared with the standard conditions described in eq 1, a controlled experiment using **1a** and **2f** at 40 °C was then performed, furnishing the desired spirocyclopentene **3af** in 96% yield with 4:1 dr (eq 3). Importantly, the present results obtained from the above experiments mechanistically imply the possibility that the spirocyclopropane intermediate resulting from the spirocyclopropanation process could be involved in this tandem annulation reaction.

According to the above-mentioned results, as shown in Scheme 4, a plausible reaction mechanism was then proposed. First, a nucleophilic 1,6-addition of sulfonium salts **2a–f** to *p*-VQMs **1a–n** takes place in the presence of $K_3PO_4 \cdot 3H_2O$ as base, and subsequently, a diastereoselective spirocyclopropanation

Scheme 4. Plausible Mechanism



process undergoes an intramolecular S_N2-type nucleophilic substitution in a favorable steric zwitterionic **TS-A**, generating the spirocyclopropanyl *p*-dienone intermediate **4** with a *trans*-configuration.[12c] Due to the driving force of ring strain of the vinylcyclopropane framework in **4**, a vinylcyclopropane(VCP)–cyclopentene rearrangement[18,19] involving a C1–C2 cleavage and a concomitant C1–C4 connection through an orbital symmetry allowed **TS-B** might account for the stereoselective formation of major products **3aa–af** and **3ba–na** with *cis*-configuration.

In conclusion, an unprecedented and highly efficient approach for the synthesis of spirocyclopentenyl *p*-dienones was developed via a base-mediated tandem spirocyclopropanation/rearrangement reaction of *p*-VQMs with sulfonium salts. A series of highly functionalized spirocycles were achieved in good yields (up to 96% yield) and diastereoselectivities (up to 14:1 dr) under mild conditions. This reaction not only provides a new pathway to the spirocyclopentenyl *p*-dienone building blocks but also manifests the new reactivity of *p*-VQMs in methodology design. Further exploration of the chemistry of *p*-VQMs in organic synthesis is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00516.

X-ray data for compound **3aa** (CIF)

Experimental procedure, characterization data, and ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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