Synlett Y.-K. Wu et al. Letter

Intercepting the Nazarov Oxyallyl Intermediate with α-Formylvinyl Anion Equivalents to Access Formal Morita–Baylis–Hillman Alkylation Products

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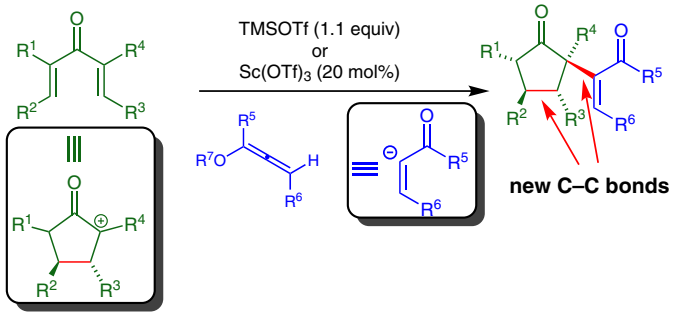


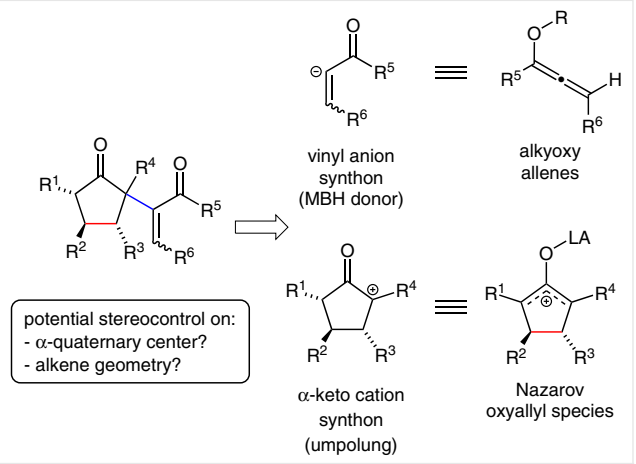
Received: 01.02.2017
Accepted after revision: 08.03.2017
Published online: 18.04.2017
DOI: 10.1055/s-0036-1588769; Art ID: st-2017-r0080-l

Abstract A Lewis acid catalyzed cationic domino reaction involving sequential electrocyclization and polar addition of allenol ethers onto the resulting oxyallyl species is described. The overall sequence allows a highly stereoselective synthesis of densely substituted cyclopentanoid compounds containing α-formylvinyl functionality which is formally equivalent to products of a Morita–Baylis–Hillman alkylation process.

Key words interrupted Nazarov cyclization, oxyallyl cation, allenol ethers, carbonyl umpolung, Morita–Baylis–Hillman alkylation

Domino and tandem reactions feature one-pot construction of complex molecular architecture from simple precursors in which multiple rings, bonds, and stereogenic centers can be installed in a well-defined manner.[2] One paradigm for inventing novel domino processes is to divert the mechanistic course of a reactive intermediate deliberately into more sophisticated bond-forming pathways under carefully controlled conditions.[3] Along these lines, there has been considerable interest in exploiting the Nazarov cyclization[4] as a platform for initiating cationic domino reaction sequences.[5] Over the past decade, we have described a series of 'interrupted Nazarov' reactions[6] wherein the cyclic oxyallyl species resulting from the initial electrocyclization were incorporated into a range of complexity-enhancing events in the presence of appropriate trapping agents. A prominent aspect of these studies has been the recruitment of the Nazarov oxyallyl cation as a formal α-carbonyl umpolung subject to nucleophilic capture for divergent synthesis of functionalized cyclopentanoid compounds.[7,8] In an effort to probe the scope of the interrupted Nazarov process, we aim to identify new trapping modalities for use in branching cascades[9] initiated by the 4π-electrocyclization.

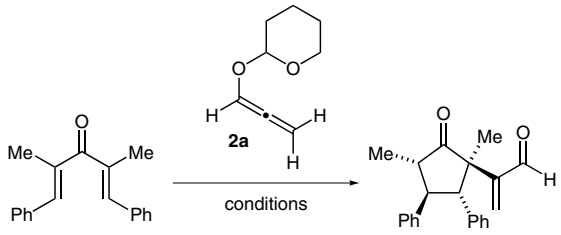
The Morita–Baylis–Hillman (MBH) reaction is an exceptionally versatile method for coupling the α-position of a polarized alkene with a carbon electrophile.[10] The zwitterionic enolate intermediate, originating from the first elementary step of the MBH reaction, is effectively a vinyl anion synthon.[11] Inspired by several fascinating applications of MBH donor in alkylation reactions,[12] we sought to secure a nucleophilic trap that is competent for intercepting the Nazarov oxyallyl intermediate (Scheme 1). Allenol derivatives have been elegantly utilized as a surrogate for the MBH donor in different contexts,[13] and we envisioned such reactants as potential π-nucleophiles in an interrupted Nazarov process. Here we describe the successful trapping of the Nazarov oxyallyl intermediate with allenol ethers to afford 2-enoylated cyclopentanone products with high stereoselectivity.



Scheme 1 Proposed route to MBH-type products through intercepting the Nazarov intermediate with allenes

Initial experiments showed that silyl allenol ethers were very prone to hydrolysis; however, the THP-protected counterpart **2a**, prepared via base-catalyzed isomerization of the corresponding propargyl ether,[14] is more durable so it was carried forward in subsequent investigations. Treatment of **1a** and **2a** with the optimized conditions for previously described homologous Mukaiyama reactions[7c] yielded the desired α-(propenal-2-yl) cyclopentanone **3a** in low yield along with a fair amount of intractable material (Table 1, entry 1). The structural assignment of **3a** was ascertained by X-ray diffraction analysis (Figure 1). A high level of diastereoselectivity arising from attack of the trapping reagent from the face opposite to the adjacent phenyl substituent was observed. Conditions were then varied to improve conversion into **3a** (Table 1). When TMSOTf was employed as the Lewis acid, domino electrocyclization/formal MBH alkylation reaction proceeded smoothly giving **3a** in good yield (entry 2). We also examined the effect of catalytic amount of metal triflate Lewis acids, including $Cu(OTf)_2$, $Zn(OTf)_2$, and $Sc(OTf)_3$, and found that higher temperature and longer reaction time were crucial for the success of those reactions (entries 3–5). With $Cu(OTf)_2$, a complex mixture was produced in which **3a** could only be isolated in low yield. While $Zn(OTf)_2$ is a relatively unexplored initiator in Nazarov chemistry, the reaction of **1a** and **2a** catalyzed by zinc(II) triflate gave the desired product in 47% yield. Use of $Sc(OTf)_3$ as catalyst led to the formation of **3a** in a yield comparable to the example using stoichiometric amounts of TMSOTf.

Table 1 Optimization of the Interrupted Nazarov Reaction with Tetrahydropyranyl (THP) Allenol Ether **2a**[a]



1a **3a**

Entry	Reaction conditions	Yield of **3a** (%)[b]
1	$BF_3{\cdot}OEt_2$ (1.1 equiv), CH_2Cl_2, –78 °C, 15 min	24
2	TMSOTf (1.1 equiv), CH_2Cl_2, –78 °C, 15 min	63
3	$Cu(OTf)_2$ (20 mol%), $(CH_2Cl)_2$, r.t., 30 min	15
4	$Zn(OTf)_2$ (20 mol%), $(CH_2Cl)_2$, r.t., 30 min	47
5	$Sc(OTf)_3$ (20 mol%), $(CH_2Cl)_2$, r.t., 30 min	58

[a] Dienone **1a** (0.4 mmol) and the allenol ether **2a** (2 equiv) were stirred with Lewis acid at the indicated temperature.
[b] Isolated yields.

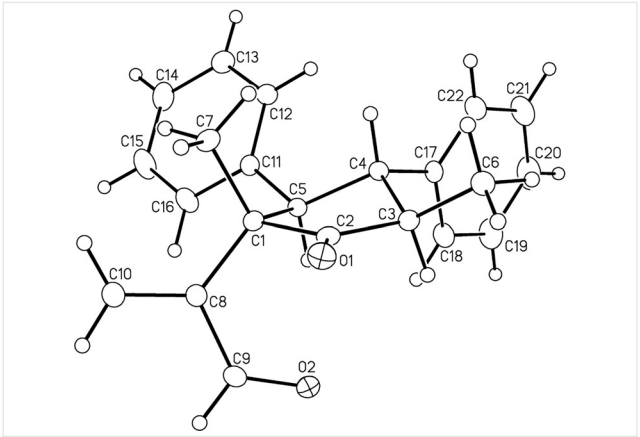
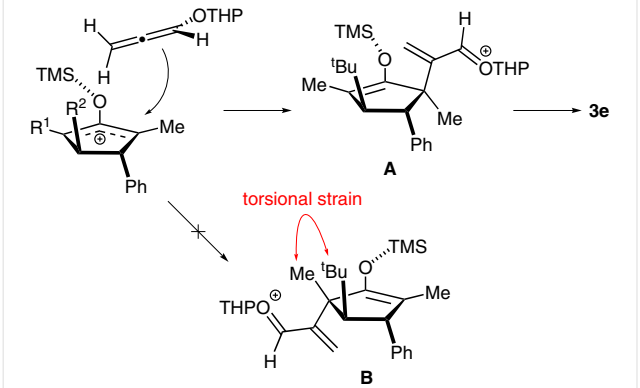


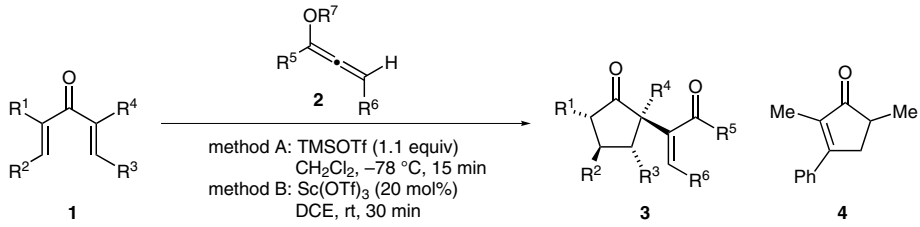
Figure 1 ORTEP diagram of **3a**

The scope of this process with other 1,4-dien-3-ones and allenol ethers **2** was then evaluated (Table 2).[15] In the presence of TMSOTf, symmetrical dienones **1b**,**c** reacted with **2a** to give single α-addition products **3b** and **3c**, respectively (entries 2 and 3). In the examples of unsymmetrically substituted dienones **1d** and **1e**, excellent regioselectivity in the trapping event was observed, giving in each case **3d** and **3e** (entries 4 and 5). The regioselectivity of polar addition furnishing **3d** can be attributed to the steric difference between allyl termini of the cyclized cationic intermediate. On the other hand, it is surprising to note that the regiocontrol seen in **3e** appears to be dictated by the β-substituent residing on the opposite face to the incoming nucleophile. Such high levels of selectivity may originate from avoidance of torsional strain arising between R^1 and R^2 as the reaction progresses toward intermediate **B** (Scheme 2). The employment of less substituted dienone **1f** afforded only cyclopentenone **4**, and furnished none of the possible interrupted Nazarov products, highlighting the critical role of β-substituents in this domino process (entry 6). We hypothesize that replacement of a β-phenyl group with hydrogen decreases the lifetime of the oxyallyl cation



Scheme 2 Regioselectivity governed by torsional steering

Table 2 Scope of Formal Morita–Baylis–Hillman Alkylations[a]



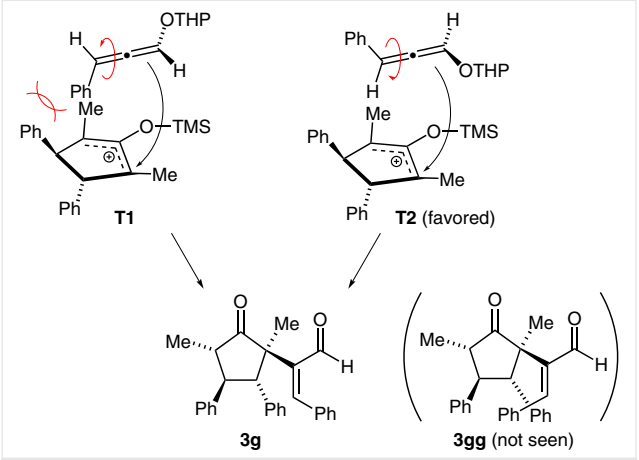
Entry	1	R^1	R^2	R^3	R^4	2	R^5	R^6	R^7	Method	Product	Yield (%)[b]
1	**1a**	Me	Ph	Ph	Me	**2a**	H	H	THP	A/B	**3a**	63 (58)
2	**1b**	Me	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Me	**2a**	H	H	THP	A/B	**3b**	37 (55)
3	**1c**	Me	4-ClC_6H_4	4-ClC_6H_4	Me	**2a**	H	H	THP	A/B	**3c**	58 (47)
4	**1d**	*n*-Pr	Ph	Ph	Me	**2a**	H	H	THP	A/B	**3d**	63 (51)
5	**1e**	Me	*t*-Bu	Ph	Me	**2a**	H	H	THP	A/B	**3e**	42 (33)
6	**1f**	Me	Ph	H	Me	**2a**	H	H	THP	B	**4**	67
7	**1a**	Me	Ph	Ph	Me	**2b**	Ph	H	TBS	A	**3f**	23
8	**1a**	Me	Ph	Ph	Me	**2c**	H	Ph	THP	A	**3g**	46
9	**1d**	*n*-Pr	Ph	Ph	Me	**2c**	H	Ph	THP	A	**3h**	51

[a] See ref. 15 for representative procedures following methods A and B.
[b] Isolated yields for method A. Yields in parentheses were obtained when method B was applied.

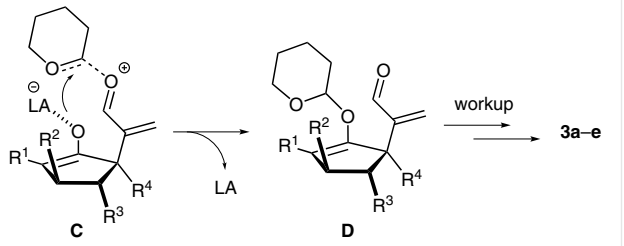
intermediate, allowing rapid elimination by deprotonation in place of nucleophilic capture by the allene nucleophile, perhaps due to greater kinetic acidity at the remaining benzylic position as a result of decreased steric congestion.

TMSOTf-mediated interrupted Nazarov reaction of **1a** and 1-phenyl siloxy allene **2b** was not efficient (entry 7), possibly owing to the relative instability of **2b** in acidic media. Utilizing 3-phenyl allenyl ether **2c** furnished a single adduct **3g** in moderate yield (entry 8) and stereochemical assignment of **3g** was supported by diagnostic 2D TROESY correlations. Notably, the transformation demonstrated complete control over the alkene geometry, thus introducing a 2-(*cis*-cinnamoyl) segment at the α-carbon of the cyclopentanone. In addition, unsymmetrical dienone **1d** reacted with **2c** cleanly to give **3h** with excellent regio- and diastereoselectivity (entry 9). Approach of axially chiral allene **2c** to the Nazarov intermediate should in theory favor a trajectory that alleviates nonbonded interactions (**T1** vs. **T2**, Scheme 3), However, in either of the proposed transition states (**T1** or **T2**), the phenyl group is expected to rotate away from the sterically demanding cyclopentyl moiety as the bond begins to form between the oxyallyl terminus and sp carbon of allenol ether, accounting for the high level of *Z*-selectivity observed in these examples.

The catalytic interrupted Nazarov reactions of dienones **1a–e** and allene **2a** were examined with $Sc(OTf)_3$, where excellent stereoselectivity and moderate yields were observed in comparison to the results with TMSOTf. As noted by Frontier and co-workers,[4g,16] catalytic Nazarov processes are typically limited to strongly polarized substrates.[17] The success of the present work, utilizing relatively unpolarized divinyl ketones with catalysis, is founded on the diversion of the reaction from eliminative termination via nucleophilic trapping.[18] We hypothesize that intramolecular transfer of tetrahydropyranyl group of intermediate **C** to generate a labile THP-enol ether may take place to permit catalyst release from the product (Scheme 4). We were not able to observe the putative intermediate **D**, though it is expected to undergo rapid hydrolysis upon workup.



Scheme 3 Diastereoselective capture of the Nazarov intermediate by allene **2c**



Scheme 4 Proposed mechanism for the catalyst turnover (LA = Lewis acid)

In summary, we have established a new entry to MBH-type products via interception of the Nazarov oxyallyl intermediate with tetrahydropyranyl allenol ethers. Densely substituted cyclopentanoid products bearing enal or enone functionality at the α-carbon could be rapidly constructed with good stereocontrol over multiple newly formed stereogenic centers and the conjugated alkene moiety. Moreover, the cationic domino interrupted Nazarov sequences could be implemented with catalytic amounts of Lewis acid. The results of this work further generalize the umpolung reactivity of the Nazarov oxyallyl intermediate toward electron-rich carbon nucleophiles.

Funding Information

Natural Sciences and Engineering Research Council of Canada (249822)

Acknowledgment

This work was generously supported by NSERC. We thank Dr. Michael J. Ferguson (University of Alberta, X-ray Crystallography Lab) for obtaining X-ray crystal structures of **3a**. Y.K.W. gratefully thanks the Alberta Innovates-Technology Futures for a PhD graduate scholarship. R.L. is thankful to the University of Alberta for the generous award of a Queen Elizabeth II Scholarship.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0036-1588769.

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(15) **Representative Procedures**

Preparation of 3h via Method A

Dienone **1d** (41.5 mg, 0.14 mmol) and allenol ether **2c** (61.9 mg, 0.29 mmol, 2.0 equiv) were dissolved in CH_2Cl_2 (2 mL, 0.1 M in dienone) under argon and cooled to –78 °C (acetone/dry ice bath). TMSOTf (27.8 µL, 0.15 mmol, 1.1 equiv) was added dropwise. The reaction mixture was stirred at the same temperature for 15 min, then was quenched with sat. aq $NaHCO_3$ (5 mL) and warmed to r.t. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), the combined organic layers were washed with brine solution (1 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation providing a crude residue that was purified by flash column chromatography (silica gel, 8:1 hexane–EtOAc) to give 29.9 mg (51%) of **3h** as a colorless oil.

IR (film): 3060, 3028, 2958, 1737, 1670, 1601, 1498, 1452 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.86 (s, 1 H), 7.43–7.40 (m, 3 H), 7.40–7.36 (m, 2 H), 7.33–7.28 (m, 2 H), 7.25–7.21 (m, 3 H), 7.21–7.16 (m, 2 H), 7.15–7.10 (m, 2 H), 7.06–7.02 (m, 2 H), 3.97 (d, *J* = 11.9 Hz, 1 H) 3.59 (app. t, *J* = 11.8 Hz, 1 H), 3.23 (app. p, *J* = 5.8 Hz, 1 H), 1.77–1.68 (m, 1 H), 1.68–1.58 (m, 1 H), 1.47–1.35 (m, 1 H), 1.29–1.17 (m, 1 H), 0.93 (s, 3 H), 0.83 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 218.6, 192.5, 149.5, 143.3, 141.9, 136.5, 133.9, 130.0, 129.3, 128.5, 128.5, 128.0, 127.8, 126.8, 126.7, 56.0, 56.0, 55.9, 48.8, 31.5, 20.1, 16.0, 14.3 [one sp^2 carbon signal is missing due to peak overlap]. HRMS (EI, M^+): *m/z* calcd for $C_{30}H_{30}O_2$: 422.2246; found: 422.2253.

Preparation of 3b via Method B

Dienone **1b** (47.8 mg, 0.148 mmol) and allenol ether **2a** (41.6 mg, 0.296 mmol, 2.0 equiv) were dissolved in DCE (2 mL, 0.1 M in dienone) under argon at r.t. $Sc(OTf)_3$ (14.5 mg, 0.029 mmol, 0.2 equiv) was added. The reaction mixture was stirred at the same temperature for 30 min then was quenched with sat. aq $NaHCO_3$ (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), the combined organic layers were washed with brine (1 × 15 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation providing a crude residue that was purified by flash column chromatography (silica gel, 8:1 hexane–EtOAc) to give 30.6 mg (55%) of **3b** as a colorless oil.

IR (film): 3034, 2958, 1739, 1689, 1612, 1583, 1514, 1463 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 9.60 (s, 1 H), 7.25–7.21 (m, 2 H), 6.91–6.87 (m, 2 H), 6.80–6.75 (m, 2 H), 6.74–6.70 (m, 2 H), 6.28 (s, 1 H), 6.10 (s, 1 H), 3.84 (d, *J* = 12.1 Hz, 1 H), 3.73 (s, 3 H), 3.72 (s, 3 H), 3.27 (app. t, *J* = 11.9 Hz, 1 H), 3.03 (dq, *J* = 11.7, 7.1 Hz, 1 H), 1.17 (d, *J* = 7.1 Hz, 3 H), 0.86 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 218.8, 194.0, 158.4, 158.4, 152.1, 138.3, 133.0, 130.1, 128.7, 128.4, 114.0, 113.3, 55.1, 55.1, 54.8, 53.8, 51.9, 50.7, 16.2, 13.6. HRMS (EI, M^+): *m/z* calcd for $C_{24}H_{26}O_4$: 378.1831; found: 378.1831.

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