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Tuning Vinylethylene Carbonates into [4 + 2] Cycloaddition via Silylation and Vinylogous Peterson Elimination

Wei Feng,† Li Xu,† Deng-Yuan Li,* and Pei-Nian Liu*

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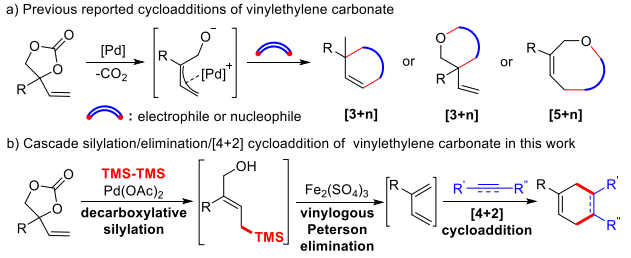
ABSTRACT: Vinylethylene carbonates have been extensively used to trigger [3 + *n*] or [5 + *n*] cycloaddition via the formation of η^3-allylic intermediates, while the important [4 + *n*] cycloaddition has not been explored yet. Here, we report a new strategy to convert vinylethylene carbonates into 4-(trimethylsilyl)but-2-en-1-ols, which can readily undergo [4 + 2] cycloaddition by in situ formation of 1,3-dienes. This novel reaction involves [Pd^{II}]-catalyzed decarboxylative silylation, [Fe^{III}]-catalyzed vinylogous Peterson elimination, and subsequent [4 + 2] cycloaddition to afford a multisubstituted cyclohexa-1,4-diene skeleton.

Vinylethylene carbonates have been widely used to generate η^3- allylic intermediates upon decarboxylation,[1] which react with various nucleophiles such as phenols, thiophenols, and anilines to construct various carbon−carbon and carbon−heteroatom bonds.[2,3] Recently, cycloadditions of vinylethylene carbonates such as [3 + *n*] or [5 + *n*] cycloaddition have attracted great interest, which allows construction of various carbocyclic and heterocyclic skeletons (Scheme 1a).[4−7] For instance, Zhang et al. achieved [3 + 2]

Scheme 1. Tunable Cycloadditions of Vinylethylene Carbonates



cycloadditions with various electrophilic partners,[5] and Zhao et al. and Glorius et al. independently reported [5 + 4] cycloadditions to synthesize highly functionalized rings of different sizes.[6a,b] Glorius et al. subsequently achieved the first enantioselective [5 + 2] annulation of vinylethylene carbonates with enals via cooperative *N*-heterocyclic carbene organocatalysis and palladium catalysis,[6c] while Liang et al. reported ligand-controlled [3 + 2] and [3 + 3] cycloadditions between vinylethylene carbonates and naphthols.[7] Despite these extensive studies, we are unaware of reports of [4 + *n*] cycloadditions of vinylethylene carbonates.

The [4 + *n*] cycloadditions, especially [4 + 2] cycloaddition, play key roles in synthetic organic chemistry because they can rapidly generate challenging but synthetically valuable cyclic frameworks, which are prevalent in drugs, agrochemicals, and bioactive molecules.[8] For example, Diels−Alder provides access to 6-membered cyclic motifs in an efficient and convergent manner.[9] Because the vinylethylene carbonate-derived η^3-allylic intermediates cannot be used directly in [4 + *n*] cycloaddition due to their reactivity properties, the development of [4 + *n*] cycloaddition of vinylethylene carbonates still remains a great challenge.

4-(Trimethylsilyl)but-2-en-1-ols are important compounds and have been widely applied to construct various cyclic skeletons because they can undergo [4 + *n*] cycloaddition via 1,3-diene generated by vinylogous Peterson elimination.[10−12] However, only a few 4-(trimethylsilyl)but-2-en-1-ols are reported from propargyl alcohols by a multistep operation.[10,11] In addition, the vinylogous Peterson elimination of 4-(trimethylsilyl)but-2-en-1-ols is relatively underexploited.[11]

Silylation, by introducing silicon functional groups,[13] can make reactions much more selective and flexible. For example, a cross-aldol reaction between two α-H-carbonyl compounds proceeds with poor selectivity because the two reactants can serve as both electrophiles and nucleophiles. In contrast, after the conversion of one carbonyl compound into an enol silane via silylation, the so-called Mukaiyama aldol reaction between the enol silanes (nucleophile only) and the other carbonyl compounds is much more selective.[14] Taking advantage of silylation, we here report a new strategy to tune the reactivity of vinylethylene carbonates to generate 4-(trimethylsilyl)but-2-en-1-ols, which can readily undergo [4 + 2] cycloaddition by in

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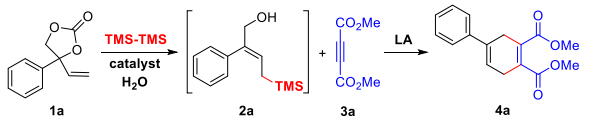
situ formation of 1,3-dienes (Scheme 1b). The cascade silylation/elimination/[4 + 2] cycloaddition reaction affords multisubstituted cyclohexa-1,4-dienes in good yields. The reaction involves [Pd^{II}]-catalyzed decarboxylative silylation and [Fe^{III}]-catalyzed vinylogous Peterson elimination. To the best of our knowledge, this is the first example of tuning vinylethylene carbonates into [4 + *n*] cycloaddition.

Initially, we carried out the reaction between vinylethylene carbonate **1a** and 1,1,1,2,2,2-hexamethyldisilane (HMDS) in the presence of $Pd(OAc)_2$ (10 mol %) at 60 °C in THF (Table 1). The silylated product (*E*)-2-phenyl-4-(trimethylsilyl)but-2-en-1-ol (**2a**) was isolated in 6% yield, and no *Z*-**2a** was observed (entry 1, Table 1). Addition of H_2O slightly increased the yield of **2a** (entry 2, Table 1), and the best yield was obtained with 20 equiv of H_2O (entries 3 and 4, Table 1). Increasing or decreasing the reaction temperature reduced the yield of **2a** (entries 5 and 6, Table 1). Screening many common solvents, including THF, MeCN, DMF, toluene, DMSO, MeOH, DCM, and dioxane identified THF as the best (see Supporting Information, Table S1). Of various palladium catalysts, $Pd(OAc)_2$ was found to be the most suitable (entries 7–11, Table 1). Notably, neither $Pd(PPh_3)_4$ nor $PdCl_2$ led to formation of **2a**.

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	LA	H_2O (equiv)	yield[b] (**2a**, %)	yield[c] (**4a**, %)
1	$Pd(OAc)_2$			6	
2	$Pd(OAc)_2$		4	23	
3	$Pd(OAc)_2$		12	48	
4	$Pd(OAc)_2$		20	55	
5[d]	$Pd(OAc)_2$		20	39	
6[e]	$Pd(OAc)_2$		20	17	
7	$Pd(OPiv)_2$		20	53	
8	$Pd_2(dba)_3$		20	38	
9	$Pd(TFA)_2$		20	22	
10	$PdCl_2$		20	ND	
11	$Pd(PPh_3)_4$		20	ND	
12[f]	$Pd(OAc)_2$		20	77	
13[g]	$Pd(OAc)_2$		20	77	
14[h]	**$Pd(OAc)_2$**		**20**	77 (75)[i]	
15[h]	$Pd(OAc)_2$	$FePO_4$	20		ND
16[h]	$Pd(OAc)_2$	$Fe(OTf)_3$	20		47
17[h]	$Pd(OAc)_2$	$FeCl_3$	20		62
18[h]	$Pd(OAc)_2$	$Fe_2(SO_4)_3$	20		68
19[h,j]	**$Pd(OAc)_2$**	**$Fe_2(SO_4)_3$**	20		**68 (66)**[i]
20[h,k]	$Pd(OAc)_2$	$Fe_2(SO_4)_3$	20		63

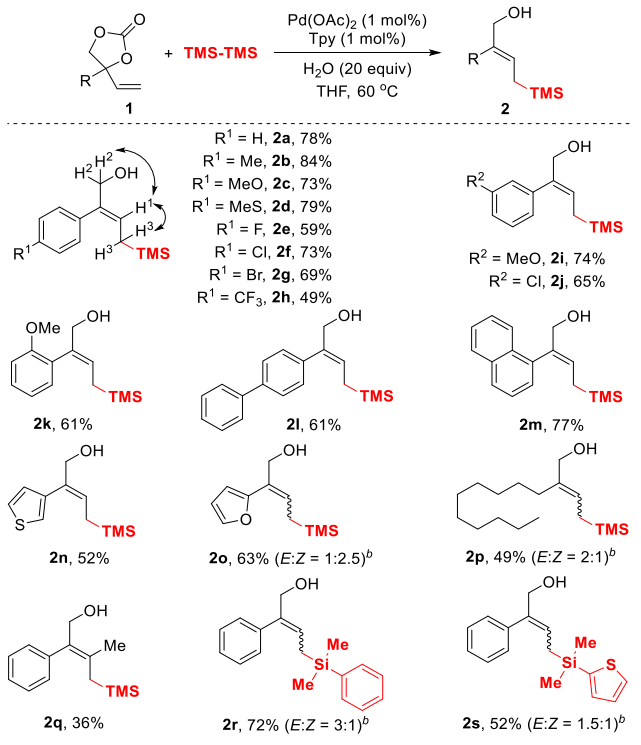
[a]Reaction conditions: **1a** (0.5 mmol), HMDS (0.75 mmol), $Pd(OAc)_2$ (0.05 mmol), THF (1.5 mL), 60 °C, under Ar for 12 h, then **3a** (1 mmol), LA (0.125 mmol), THF (1.5 mL), 80 °C, under Ar for 12 h. [b]The yield was determined by ^1H NMR using trimethyl(phenyl)silane as the internal standard. [c]Isolated yields are indicated. [d]30 °C. [e]90 °C. [f]Tpy (0.05 mmol) was added. [g]$Pd(OAc)_2$ (0.025 mmol) and Tpy (0.025 mmol) were used. [h]$Pd(OAc)_2$ (0.005 mmol) and Tpy (0.005 mmol) were used, 24 h. [i]Isolated yield at 1.0 mmol scale. [j]$Fe_2(SO_4)_3$ (0.075 mmol) was used. [k]$Fe_2(SO_4)_3$ (0.05 mmol) was used.

We screened ligands in order to improve the yield of **2a**. Of various common ligands, the tridentate ligand terpyridine (Tpy) is the best, increasing the yield of **2a** to 77% (entry 12, Table 1; see Supporting Information, Table S2). The Tpy ligand may work well because the Tpy-chelated [Pd^{II}] catalysts is quite stable and possesses greater electrophilicity to activate alkene of **1a**.[15] We also tried to optimize catalyst and ligand loading. Decreasing the amounts of catalyst and ligand simultaneously to 5 mol % or even 1 mol % afforded the best result to generate **2a** in 77% yield (entries 13 and 14, Table 1).

Using the optimal conditions to form **2a**, we proceeded to investigate cascade silylation/elimination/[4 + 2] cycloaddition of vinylethylene carbonates with alkynes. Of various common Fe catalysts, $Fe_2(SO_4)_3$ gave the best results, furnishing cyclohexa-1,4-diene **4a** in 68% isolated yield (entries 15–18, Table 1). Other common Lewis acids such as Ag_2SO_4, $CeSO_4$, $CoSO_4{\cdot}H_2O$, $Bi_2(SO_4)_3$, and $In_2(SO_4)_3$ did not improve the results (see Supporting Information, Table S3). We were able to reduce catalytic loading to 15 mol % while maintaining 68% isolated yield (entries 19 and 20, Table 1). It is noteworthy that the structure of **4a** was confirmed using single-crystal X-ray diffraction analysis, NMR, and high-resolution mass spectrometry (see the Supporting Information).

Next we explored the scope of the silylation of vinylethylene carbonates (Scheme 2). First, vinylethylene carbonates **1** containing electron-donating groups such as Me, MeO, or MeS at the *para* position of the benzene ring reacted with HMDS, providing the products **2b–2d** in yields of 73–84%. The

Scheme 2. Substrate Scope of Silylation[a]



[a]Reaction conditions: **1** (0.5 mmol), HMDS (0.75 mmol), $Pd(OAc)_2$ (0.005 mmol), Tpy (0.005 mmol), H_2O (20 equiv), THF (1.5 mL), under Ar for 24 h. Isolated yields are indicated. [b]The *E*/*Z* ratio was determined by ^1H NMR.

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substitution of electron-withdrawing F, Cl, Br, or CF_3 groups at the same position also gave products **2e**−**2h** in moderate yields. NOESY experiments with **2b** showed that H^1 was close to H^2 and H^3, confirming the *E*-configuration of the silylated products (see the Supporting Information). It is noteworthy that the similar reactions catalyzed by [Pd^0] catalysts via formation of η^3-allylic intermediates produce the *Z*-stereoisomer.[3a,b] The result of obtaining *E*-stereoisomer of **2b**, as well as the ineffectiveness of $Pd(PPh_3)_4$ catalyst (entry 11, Table 1), suggest that the catalyst in this reaction may be [Pd^{II}] instead of [Pd^0].

Vinylethylene carbonates substituted with electron-donating MeO or electron-withdrawing Cl at the *meta*-position reacted well with HMDS, selectively producing **2i** and **2j** in respective yields of 74% and 65%. Vinylethylene carbonates substituted with *o*-MeO also gave the desired product **2k** in 61% yield. Biphenyl and naphthyl vinylethylene carbonates reacted to give the corresponding products **2l** and **2m** in good yield. The substrate 3-thienyl vinylethylene carbonate gave **2n** as a single stereoisomer in 52% yield. The substrate 2-furanyl vinylethylene carbonate gave **2o** in 63% yield as a mixture of two stereoisomers, reflecting the oxygen atom in the furan ring might affect the catalytic process. Alkyl vinylethylene carbonate also gave the desired product **2p** in 49% yield as a mixture of two stereoisomers. Interestingly, 4-phenyl-4-(prop-1-en-2-yl)-1,3-dioxolan-2-one generated **2q** as a single stereoisomer with only 36% yield, suggesting that substitution on the C = C bond impeded silylation.

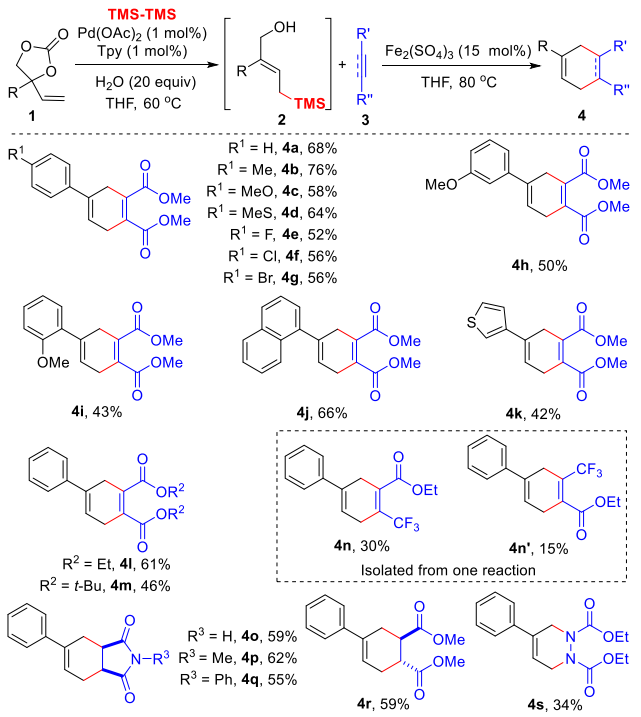
Next, we investigated the scope of organosilicon sources. $(Me_2PhSi)_2$ and $(Me_2ThSi)_2$ underwent silylation with **1a** to produce the two stereoisomers **2r** and **2s** in respective yields of 72% and 52%. $(Ph_3Si)_2$, in contrast, gave no desired product, presumably because of steric effect.

Using the optimized conditions to form **4a**, we analyzed the scope of vinylethylene carbonates **1** (Scheme 3). Regardless of whether R^1 on its phenyl group was electron-donating or -withdrawing, the vinylethylene carbonates readily underwent the cascade reaction with alkyne **3a** to give products **4a**−**4i** in yields of 43−76%. Changing the benzene ring of the vinylethylene carbonates to a naphthalene or thiophene ring and then reacting it with alkyne **3a** afforded products **4j** and **4k** in respective yields of 66% and 42%.

When we analyzed the scope of alkynes **3**, we found that vinylethylene carbonate **1a** reacted with diethyl but-2-ynedioate to give **4l** in 61% yield. Di-*tert*-butyl but-2-ynedioate also reacted with **1a** to afford **4m**, albeit in slightly lower yield. Interestingly, the reaction of ethyl 4,4,4-trifluorobut-2-ynoate with **1a** gave the mixture of cyclohexa-1,4-dienes **4n** and **4n′** in respective yields of 30% and 15%, revealing the indistinctive regioselectivity of the cycloaddition. However, diaryl- or alkylacetylene did not afford the desired cyclohexa-1,4-dienes under optimized reaction conditions.

To further explore the flexibility of this cascade reaction, we tried to react vinylethylene carbonate **1a** with other dienophiles. Various *N*-substituted maleimides reacted with **1a** to afford the desired *cis*-products **4o**−**4q** in yields of 55−62%, and dimethyl fumarate reacted with **1a** to form the corresponding *trans*-product **4r** in 59% yield. Interestingly, diethyl diazene-1,2-dicarboxylate also reacted with **1a**, forming **4s** in slightly lower yield. Notably, the moderate yields for the cascade reaction might be caused by self-cycloaddition of in situ generated dienes to form dimers, which were detected by GC−MS.

Scheme 3. Substrate Scope of Cascade Silylation/Elimination/[4 + 2] Cycloaddition[a]



[a]Reaction conditions: **1** (0.5 mmol), HMDS (0.75 mmol), $Pd(OAc)_2$ (0.005 mmol), Tpy (0.005 mmol), H_2O (20 equiv), THF (1.5 mL), 60 °C, under Ar for 24 h, then **3** (1 mmol), $Fe_2(SO_4)_3$ (0.075 mmol), THF (2 mL), 80 °C, under Ar for 12 h. Isolated yields are indicated.

To demonstrate the usefulness of the cascade silylation/elimination/[4 + 2] cycloaddition, further transformation of products **4** was investigated. DDQ efficiently oxidized **4a**−**4d** to dimethyl [1,1′-biphenyl]-3,4-dicarboxylate **5a**−**5d** in 86−89% yields. Treating **4a** with $LiAlH_4$ in Et_2O generated 2,5-dihydro-[1,1′-biphenyl]-3,4-diyl)dimethanol **6** in 64% yield (see the Supporting Information).

To clarify the promoting effect of H_2O, the silylation of **1a** was carried out under the standard conditions without H_2O. GC−MS analysis of the reaction mixture indicated that most of **1a** was converted to (*E*)-trimethyl(3-phenyl-4-((trimethylsilyl)oxy)but-2-en-1-yl)silane (**D**), which was then converted to **2a** after quenching with H_2O. The results indicate that H_2O promotes the hydrolysis of **D** to form **2a**. Furthermore, when $Pd(OAc)_2$, Tpy ligand and HMDS were combined in THF, TMS-OAc could be detected by GC−MS, suggesting that Tpy-chelated [Pd^{II}]-TMS complex might be generated as the active catalyst.

On the basis of the above studies as well as literature reports,[2d] a tentative mechanism involving [Pd^{II}]-catalyzed decarboxylative silylation, [Fe^{III}]-catalyzed vinylogous Peterson elimination, and [4 + 2] cycloaddition has been proposed (Scheme 4). First, $Pd(OAc)_2$ reacts with Tpy and HMDS to generate the active Tpy-[Pd^{II}]-TMS catalyst, which coordinates with the alkene **1** to generate **A**. Regioselective addition produces alkyl-[Pd^{II}] intermediate **B**. After C−O bond cleavage and elimination of CO_2, intermediate **C** forms and then reacts with HMDS to afford intermediate **D**, and the regenerated Tpy-[Pd^{II}]-TMS catalyst. **D** undergoes hydrolysis to give product **2**. Finally, [Fe^{III}]-catalyzed vinylogous Peterson elimination of **2** forms 1,3-diene **E**,[10,11] which undergoes [4 +

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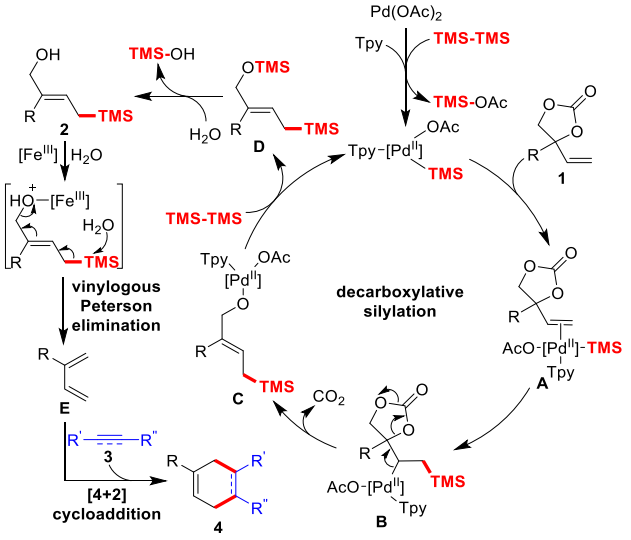
Scheme 4. Proposed Mechanism



2] cycloaddition with dienophiles **3** to give the cascade product **4**.

In summary, we have developed a cascade silylation/elimination/[4 + 2] cycloaddition reaction of vinylethylene carbonates, which efficiently constructs multisubstituted cyclohexa-1,4-diene skeleton in good yields. The reaction proceeds via the [Pd^{II}]-catalyzed decarboxylative silylation of vinylethylene carbonates to form 4-(trimethylsilyl)but-2-en-1-ols, which undergo the sequential [Fe^{III}]-catalyzed vinylogous Peterson elimination and [4 + 2] cycloaddition with dienophiles. This new protocol tuning vinylethylene carbonates into [4 + 2] cycloaddition may be applied to the generation of 6-membered cyclic frameworks, which are prevalent in drugs, agrochemicals, and bioactive molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01690.

Further transformations of products **4a**–**4d**, detailed experimental procedures, characterization data of products (NMR, HRMS, etc.), spectra of the products (PDF)

Accession Codes

CCDC 1972854 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

Deng-Yuan Li − *Shanghai Key Laboratory of Functional Materials Chemistry, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Key Laboratory for Advanced Materials and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*; Email: dengyuanli@ecust.edu.cn

Pei-Nian Liu − *Shanghai Key Laboratory of Functional Materials Chemistry, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Key Laboratory for Advanced Materials and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*; orcid.org/0000-0003-2014-2244; Email: liupn@ecust.edu.cn

Authors

Wei Feng − *Shanghai Key Laboratory of Functional Materials Chemistry, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Key Laboratory for Advanced Materials and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*

Li Xu − *Shanghai Key Laboratory of Functional Materials Chemistry, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Key Laboratory for Advanced Materials and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01690

Author Contributions

†W.F. and L.X. contributed equally.

Notes

The authors declare no competing financial interest.

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