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SHORT COMMUNICATION

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Sequential Catalyst Phosphine/Secondary Amine Promoted [1+4]/Rearrangement Domino Reaction for the Construction of (2*H*)-Pyrans and 2-Oxabicyclo[2.2.2]oct-5-ene Skeletons

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Sequential catalysis of a [2+4] reaction between a Baylis–Hillman carbonate and a β,γ-unsaturated α-oxo ester for the synthesis of 2-methyl-2*H*-pyran was developed. The use of a Morita–Baylis–Hillman carbonate as a C_2 synthon is first disclosed in this reaction. This method offers a new approach to the construction of 2-methyl-2*H*-pyrans and 2-oxabicyclo[2.2.2]oct-5-ene skeletons.

Introduction

The 2*H*-pyran skeleton, which is widespread in natural products[1] (Figure 1), is a rich source of inspiration for the discovery of pharmaceutically relevant molecules and as probes for the investigation of chemical biology.[1a,2] For instance, the fungal metabolites SB238569 from *C. funicola* TCF6040 are inhibitors of several bacterial metallo-β-lactamases and potential guiding structures for antibiotic research.[2a] In addition, the importance of 2-methyl-2*H*-pyrans in synthetic chemistry is also well illustrated by the general occurrence of these motifs in the synthesis of the 2-oxabicyclo[2.2.2]oct-5-ene skeleton;[1,3] this is a core skeleton of many biologically active compounds, such as torreyanic acid, which was found to be cytotoxic against 25 different human cancer cell lines.[4] However, the 2*H*-pyran motif is an ongoing challenging target in organic synthesis,

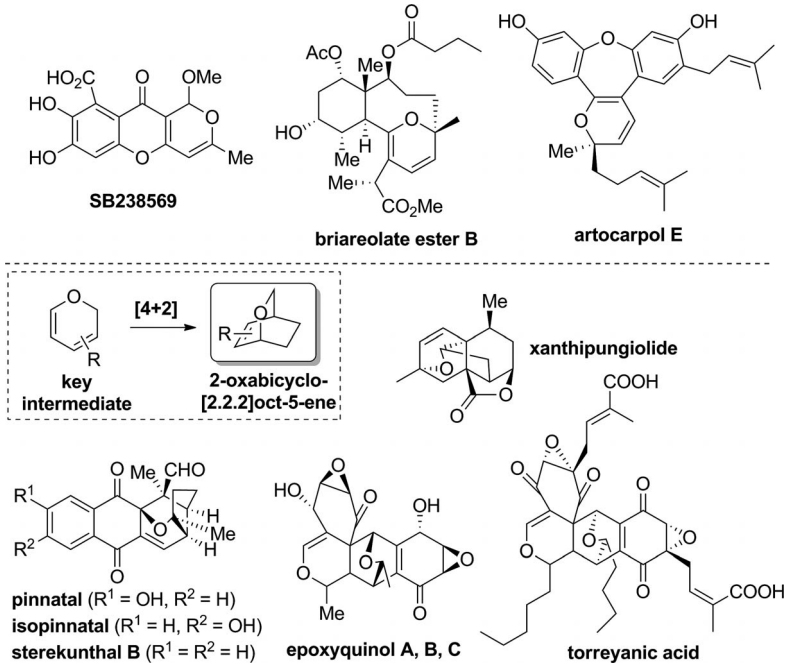

Figure 1. 2*H*-Pyrans in natural products; they also serve as key intermediates in organic synthesis.

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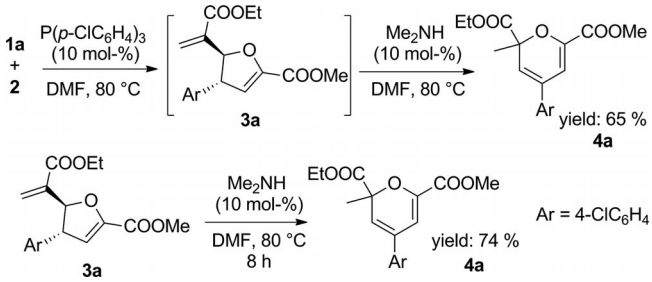
as it is quite reactive and has the tendency to undergo reversible electrocyclic ring opening or dimerization.[1,2b,5] The synthetic challenges posed by natural products and analogues intermediates thereof call for the development of new synthetic methods. To date, a few approaches including tandem Stille/oxo electrocyclization[6] and a myriad of formal [3+3] cycloadditions involving 1,3-dicarbonyl derivatives have been described.[1d,2b,7] Nonetheless, a large number of transformation steps and limited access to starting materials still restrict their widespread application.[2b] All of these techniques offer unique opportunities to discover novel strategies for the formation of 2*H*-pyrans.

Recently, sequential/relay catalysts,[8a–8e] which work in an almost biomimetic-like manner, have enabled novel transformations beyond those possible with single catalytic systems and have emerged as a viable and efficient approach to complex molecular architectures.[8f–8r] Moreover, phosphine-mediated domino reactions have shown remarkable performance in the construction of cyclic and heterocyclic compounds,[9] but few sequential catalytic systems concerning phosphine have been realized.[10] Herein, we report the first phosphine/secondary amine sequential catalyst promoted [1+4]/rearrangement process for the construction of highly functionalized 2*H*-pyrans and 2-oxabicyclo[2.2.2]-oct-5-enes. Moreover, density functional theory (DFT) studies give an understanding of the mechanism of the secondary amine catalyzed rearrangement process.

Results and Discussion

Morita–Baylis–Hillman carbonates **2** (Boc = *tert*-butoxycarbonyl), as a result of their convenient preparation and diverse reactivity, have emerged as appealing and powerful building blocks in phosphine-mediated reactions.[11] For example, Lu's pioneering work, in addition to other extensive work, disclosed that Morita–Baylis–Hillman carbonates could serve as 1,3-dilopar C_3 synthons in [3+*n*] (*n* = 2, 3, 4, 6) reactions.[11a–11j] Recently, the use of Morita–Baylis–Hillman carbonates as 1,1-dipolar C_1 synthons[11k–11n] was developed independently by Zhang[11k] and our group.[11l] Upon further investigation, we realized the tunable domino reaction for the selective construction of 2,3-dihydrofurans and multiaryl compounds.[12] During the course of our study, byproduct 2*H*-pyrans were detected along with the major [1+4] cycloaddition 2,3-dihydrofuran products (Scheme 1).[12b] This result suggested that Morita–Baylis–Hillman carbonates must have a distinct reactivity (C_2 synthon) towards 2*H*-pyrans.

Our initial investigation started with an attempt to improve the chemoselectivity and yield of 2*H*-pyran **4a**. Upon exposure to H_2O (2.0 equiv.), the desired product **4a** was isolated in 29% yield. To the best of our knowledge, *N*,*N*-dimethylformamide (DMF)[13] as a solvent is unstable in the presence of H_2O and releases Me_2NH and HCOOH. The effect of Me_2NH and HCOOH was then investigated. Me_2NH was found to be a competent coupling catalyst (Table 1, Entry 4), whereas HCOOH gave a totally contradictory result (Table 1, Entry 3). To confirm whether the 2*H*-pyran was generated from the 2,3-dihydrofuran in the presence of Me_2NH, the 2,3-dihydrofuran was isolated and then subjected to Me_2NH. As expected, **4a** was obtained in 74% yield under these conditions (Scheme 1). Other amines (Table 1, Entries 5–9) and a sterically hindered secondary amine (Table 1, Entry 9) were inefficient in this transformation; pyrrolidine gave the best result. Primary amines gave diminished yields. Upon adding the phosphine catalyst and pyrrolidine stepwise, the yield of **4a** improved to 78%. Decreasing or increasing the catalyst loading (Table 1, Entries 12–14) and the reaction temperature (Table 1, Entries 15 and 16) did not further improve the overall performance of this catalytic protocol. Tertiary amines provided lower yields or no product (Table 1, Entries 17–19). Inorganic bases were ineffective in this reaction (Table 1, Entries 20 and 21).

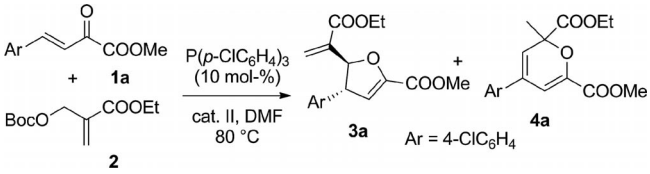


Scheme 1. The transformation from 2,3-dihydrofurans into 2*H*-pyrans.

To ascertain the generality of the domino reaction, we examined reactions between various types of substituted β,γ-unsaturated α-oxo esters **1** and Morita–Baylis–Hillman carbonates **2**. In most cases, the reactions proceeded smoothly to afford the desired products in modest to high yields (Table 2). The electronic properties (see **4a**–**f**) and the position of the substituents (see **4a**,**g**–**k**) on **1** had a limited effect on the process. Substrates with strong electron-withdrawing or electron-donating substituents (see **4e**,**f**,**o**) also delivered the desired products, albeit in lower yields. However, sterics on **2** were found to influence the yield and reaction time negatively (see **4n**). In addition, the yields were more sensitive to the size of the ester substituent of **2** than that of **1** (see **4l**–**n**). Moreover, (1*E*,5*E*)-1,6-bis(4-bromophenyl)hexa-1,5-diene-3,4-dione also gave the desired product in good yield (see **4p**). The incorporation of a phosphonate was also well tolerated (see **4q**). Heteroaryl- (i.e., furanyl- and thiophenyl-) -substituted β,γ-unsaturated α-oxo esters were also employed in this domino reaction (see **4r**,**s**). However, if **1** was substituted with an alkyl (R^1 = Me) group [i.e., (*E*)-diethyl but-2-enoylphosphonate], only formal Rauhut–Currier product **4t** was obtained, rather than the ideal 2-methyl-2*H*-pyran (see the Supporting Information).

The utility of the generated 2-methyl-2*H*-pyrans was demonstrated by application to the synthesis of 2-oxabicyclo[2.2.2]oct-5-ene skeletons, which were successfully obtained in high yield from 2-methyl-2*H*-pyrans **4** through a

Table 1. Determination of the optimal catalyst and conditions.[a]



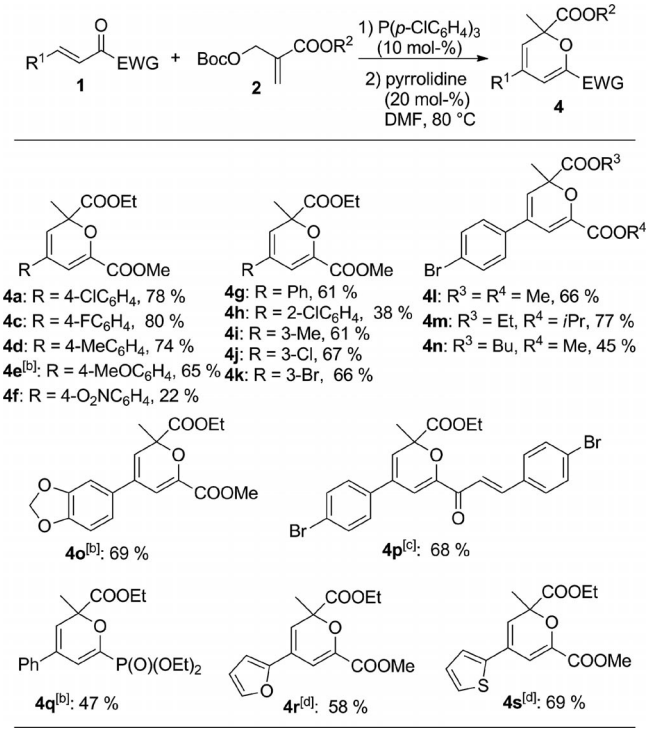
Entry	Cat. II (mol-%)	t (t_2) [h]	Yield **3a**/**4a** [%][b]
1	–	4	86:4
2	H_2O (200)	4	33:29
3	HCOOH (20)	4	43:trace
4	Me_2NH (20)	4	trace:65
5	L-proline (20)	10	68:trace
6	Et_2NH (20)	8	trace:61
7	pyrrolidine (20)	7	trace:67
8	piperidine (20)	12	trace:67
9	iPr_2NH (20)	8	83:trace
10	$EtNH_2$(20)	15	17:21
11[c]	pyrrolidine (20)	1.5 (1.0)	trace:78
12[c]	pyrrolidine (50)	1.5 (10 min)	trace:68
13[c]	pyrrolidine (10)	1.5 (3.5)	trace:77
14[c,d]	pyrrolidine (20)	1.5 (30 min)	trace:80
15[c,e]	pyrrolidine (20)	1.5 (2.0)	trace:70
16[c,f]	pyrrolidine (20)	1.5 (1.0)	trace:71
17[c]	DABCO (20)	1.5 (2.0)	trace:65
18[c]	NEt_3 (20)	1.5 (5.0)	85:/trace
19[c]	DBU (20)	1.5 (5.0)	83:trace
20[c]	Cs_2CO_3 (20)	1.5 (2.0)	trace:trace
21[c]	K_2CO_3 (20)	1.5 (2.0)	trace:trace

[a] Unless otherwise noted, the reaction was performed on a 0.5 mmol scale in solvent (3.0 mL) at 80 °C. The ratio of **1**/**2** was 1.0:2.0. Me_2NH (33% aqueous solution). DABCO = 1,4-diazabicyclo[2.2.2]octane; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; Cat. II = 2nd catalyst in the sequential catalysis. [b] Yield of isolated product. [c] After completing the formation of the 2,3-dihydrofuran, Cat. II was then added. [d] 5.0 mL of solvent was used. [e] The temperature was raised to 120 °C after Cat. II was added. [f] The temperature changed to 50 °C after Cat. II was added.

simple Diels–Alder reaction (Table 3; products **5a**,[14] **5b**, and **5c**). In addition, a three-component reaction of β,γ-unsaturated α-oxo ester **1**, Morita–Baylis–Hillman carbonate **2**, and 1-phenyl-1*H*-pyrrole-2,5-dione was preliminary investigated. As shown in Table 2, the sequential-catalytic/single-flask process performed well for the synthesis of 2-oxabicyclo[2.2.2]oct-5-enes **5a**,**d**,**e**.

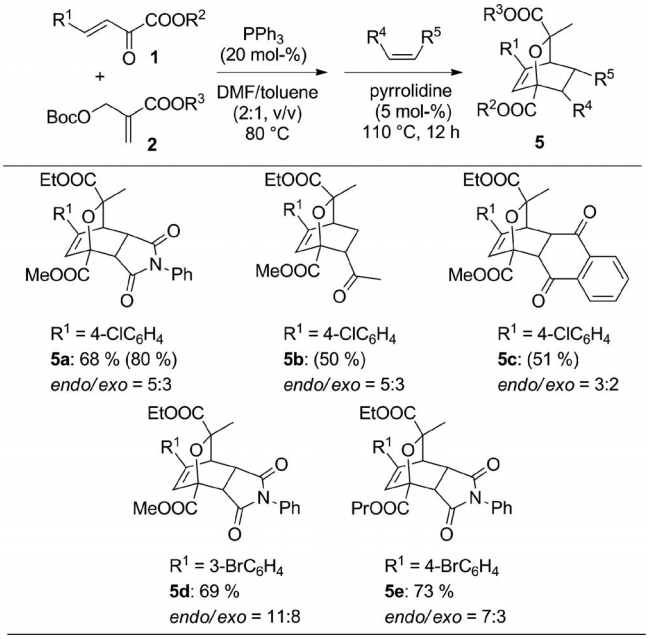
According to our experimental results (Scheme 1) and some related studies,[11k–11n,12] we propose the following mechanism. Phosphine initiates this transformation through [1+4] annulation to afford the 2,3-dihydrofurans.[12b] This is followed by an isomerization process in the presence of a secondary amine. To gain insight into the mechanism, pyrrolidine-catalyzed isomerization from the 2,3-dihydrofurans to the 2*H*-pyrans was studied by DFT calculations[15] (Figure 2, see the Supporting Information for details). All of the DFT calculations were performed with the Gaussian 03 program package.[16a] Geometry optimization of all the minima and transition states involved were performed at the B3LYP level of theory with the 6-31+G(d) basis set.[16b,16c] The vibrational frequencies were

Table 2. Scope of the one-pot reaction.[a]



[a] Reaction conditions: unless otherwise specified, see the Experimental Section. EWG = electron-withdrawing group. [b] PPh_3 (20 mol-%) was used. [c] $P(p\text{-}ClC_6H_4)_3$ (20 mol-%) was used. [d] PPh_3 (10 mol-%) was used.

Table 3. Sequential-catalytic/single-flask process for the synthesis of 2-oxabicyclo[2.2.2]oct-5-ene skeletons.[a]



[a] Reaction conditions: see the Experimental Section. Yields in parentheses are the results of the direct Diels–Alder reactions from the 2-methyl-2*H*-pyrans.

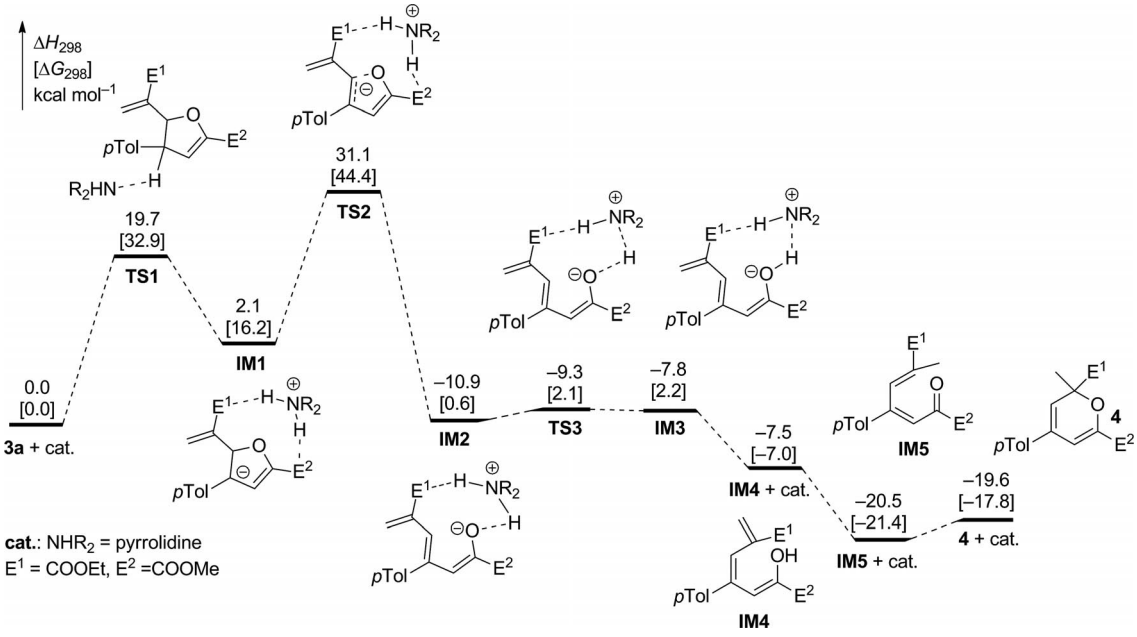


Figure 2. Proposed mechanism for the rearrangement process and the DFT-computed energy surfaces.

computed at the same level of theory to check whether each optimized structure was an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE).

Calculations indicated that ring opening of **3** in the presence of a secondary amine was stepwise. The secondary amine first attacks **3** by passing a barrier (see **TS1**) of 32.9 kcal mol^{-1}. Resulting intermediate **IM1** is 16.2 kcal mol^{-1} less stable than **3** + cat. The following ring-opening process (i.e., **IM1**–**TS2**–**IM2**) crossing a barrier (see **TS2**) of 28.2 kcal mol^{-1} is assisted by hydrogen-bonding interaction. Subsequently, proton transfer from the nitrogen atom to the oxygen atom occurs easily to give intermediate **IM3**. Finally, facile rearrangement and oxa-6π electrocyclization delivers the final 2*H*-pyran product. The rearrangement process, which is catalyzed by the secondary amine and which converts dihydrofurans into pyrans, is exothermic by 19.6 kcal mol^{-1} and exergonic by 17.8 kcal mol^{-1}.

Conclusions

We developed a novel method for the construction of functionalized 2*H*-pyrans. In this method, phosphine and secondary amine catalysts worked in a sequential manner, that is, the phosphine initiated a domino reaction of allylic carbonates and β,γ-unsaturated α-oxo esters through [1+4] annulation to give 2,3-dihydrofurans, which was followed by a secondary amine catalyzed rearrangement process to produce 2*H*-pyrans in one pot. The mechanism of the rearrangement process from 2,3-dihydrofurans to 2*H*-pyrans was investigated by DFT calculations. Moreover, a Morita–Baylis–Hillman carbonate was for the first time used as a C_2 synthon in this reaction. We also demonstrated that the 2*H*-pyrans could be easily converted into important biologically active 2-oxabicyclo[2.2.2]oct-5-ene molecular skeletons.

Experimental Section

General Procedure for the Synthesis of 2*H*-Pyrans 4: Tris(4-chlorophenyl)phosphine (0.05 mmol, 0.1 equiv.) was added to a mixture of β,γ-unsaturated α-oxo ester **1** (0.5 mmol, 1.00 equiv.) and allylic carbonate **2** (2.00 equiv.) in DMF (3.0 mL). The resulting suspension was maintained at 80 °C until the formation of 2,3-dihydrofuran **3** was complete (as monitored by TLC). Pyrrolidine (0.1 mmol, 0.2 equiv.) was then added, and the reaction mixture was maintained at 80 °C until the transformation was complete [transformation of the 2,3-dihydrofuran into the (2*H*)-pyran was monitored by TLC]. Dichloromethane (30 mL) was added to the resulting mixture, which was then washed with water (3 × 10 mL). The organic layer was separated and dried with sodium sulfate. After filtration and concentration, the residue was purified by column chromatography on silica gel (gradient eluant: petroleum ether/ethyl acetate, 15:1–10:1) to afford 2*H*-pyran **4**.

General Procedure for the Synthesis of 2-Oxabicyclo[2.2.2]oct-5-ene in One Pot: PPh_3 (0.10 mmol, 0.2 equiv.) was added to a mixture of β,γ-unsaturated α-oxo ester **1** (0.5 mmol, 1.00 equiv.) and allylic carbonate **2** (2.00 equiv.) in DMF (3.0 mL). The resulting suspension was maintained at 80 °C until the formation of 2,3-dihydrofuran **3** was complete (as monitored by TLC). Pyrrolidine (0.025 mmol, 0.05 equiv.) and 1-phenyl-1*H*-pyrrole-2,5-dione (0.75 mmol, 1.5 equiv.) were then added, and the reaction mixture was maintained at 110 °C until the transformation was complete (as monitored by TLC). Dichloromethane (30 mL) was then added to the resulting mixture, which was washed with water (3 × 10 mL). The organic layer was separated and dried with sodium sulfate. After filtration and concentration, the residue was purified by column chromatography.

Supporting Information (see footnote on the first page of this article): Details of the DFT calculations and spectroscopic data for all new compounds as well as the crystal structure of **5a**.

Acknowledgments

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