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SHORT COMMUNICATION

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Synthesis of Substituted Furans through Domino Aldol/Homo-Michael Reactions of Formylcyclopropane 1,1-Diesters with 1,3-Dicarbonyls

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Keywords: Small ring systems / Domino reactions / Oxygen heterocycles / Michael addition / Aldol reactions

A Lewis acid catalyzed domino aldol/homo-Michael reaction of formylcyclopropane 1,1-diesters with dicarbonyls has been successfully developed. This method provides efficient and direct construction of highly functionalized furans from easily available starting materials.

Introduction

Furan is a common and important nucleus broadly existing in natural products (e.g., pseudopteranes, furanocembranes, and 4-oxybenzufurans; Figure 1),[1,2] pharmaceuticals, and agrochemicals. Additionally, furans can also be employed as useful intermediates in organic synthesis.[3] Although many synthetic methods have been developed for the synthesis of furans,[4,5] the development of a novel method for the synthesis of highly functionalized furans under mild conditions and from readily available starting materials remains an important goal.

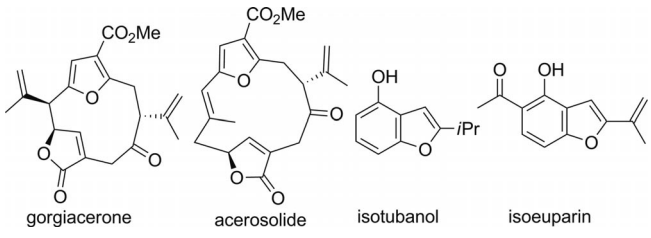
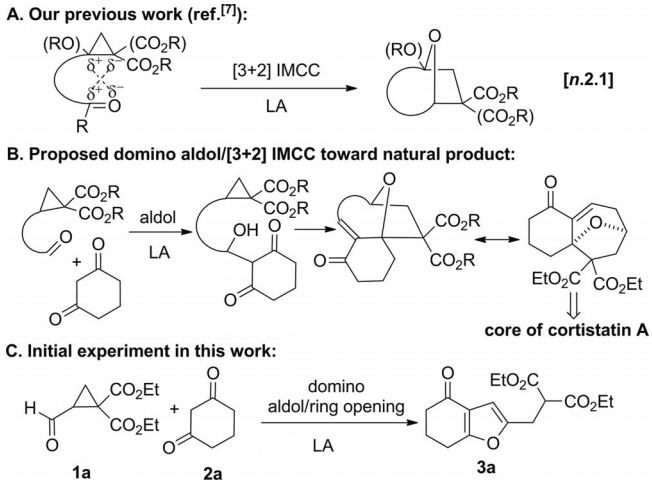


Figure 1. Representative furanoterpenoid and 4-oxybenzofuran natural products.

The domino reaction represents one of the most efficient transformations for cyclic skeletons.[6] We have recently developed a [3+2] IMCC (intramolecular [3+2] cross-cycloaddition) strategy on functionalized cyclopropanes for the construction of bridged [*n*.2.1] skeletons.[7] During the further development of the [3+2] IMCC-based domino process aimed at providing a more efficient method for the construction of polycyclic skeletons (e.g., cortistatin A[8]), we observed an unexpected domino process from readily available formylcyclopropane (FCP) 1,1-diester **1a**[9,10] and cyclohexane-1,3-dione (**2a**), by which substituted hydrobenzofuran **3a** was afforded efficiently (Scheme 1). Several suitably substituted examples (Figure 1) could be selected as potential targets for synthesis. Herein, we report our recent results.



Scheme 1.

Results and Discussion

The first experiment was carried out between FCP 1,1-diester **1a** and cyclohexane-1,3-dione (**2a**) in DCE (1,2-dichloroethane) at 40 °C under the catalysis of $Sc(OTf)_3$ (20 mol-%). After 40 h, instead of the bridged product, we obtained compound **3a**, which was supposed to be an interrupted [3+2] IMCC product (Table 1, Entry 10). Several other Lewis acids (LAs) were tested, among which $Sc(OTf)_3$ proved to be suitable. Solvent screening showed that DCE was the best choice. It was also discovered that increasing the amount of **1a** afforded a better result (Table 1, Entries 10, 14, and 20). Reaction at 25 °C (Table 1, Entry 22) gave a better yield than that at 40 °C (Table 1, Entry 21).

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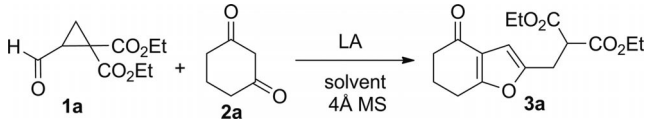
Table 1. Optimization of the reaction conditions.



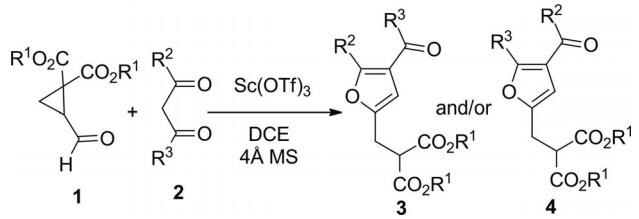
Entry	T [°C]	Catalyst	Solvent	t [h]	Yield[d] [%]
1[a]	15	—	DCE	24	0
2[a]	40	CuOTf	DCE	40	38
3[a]	40	$Cu(OTf)_2$	DCE	40	35
4[a]	40	$Sn(OTf)_2$	DCE	40	20
5[a]	40	AgOTf	DCE	40	11
6[a]	40	$Bi(OTf)_3$	DCE	40	24
7[a]	40	$Yb(OTf)_3$	DCE	40	29
8[a]	40	$ZnCl_2$	DCE	40	–
9[a]	40	$Zn(OTf)_2$	DCE	40	–
10[a]	40	$Sc(OTf)_3$	DCE	40	43
11[a]	80	$Sc(OTf)_3$	DCE	20	18
12[b]	40	$Sc(OTf)_3$	PhMe	40	28
13[b]	40	$Sc(OTf)_3$	THF	40	28
14[b]	40	$Sc(OTf)_3$	DCM	40	27
15[b]	40	$Sc(OTf)_3$	$CHCl_3$	40	28
16[b]	40	$Sc(OTf)_3$	CCl_4	40	21
17[b]	40	$Sc(OTf)_3$	EtOH	40	9
18[b]	40	$Sc(OTf)_3$	DCE	40	50
19[b,f]	40	$Sc(OTf)_3$	DCE	24	20
20[c]	40	$Sc(OTf)_3$	DCE	40	69[e]
21[c]	40	$Sc(OTf)_3$	DCE	72	64[e]
22[c]	25	$Sc(OTf)_3$	DCE	40	84[e]
23[c]	–78 to 25	$TiCl_4$	DCE	40	67[e]

[a] Reaction conditions: **1a** (1.0 equiv.), **2a** (1.5 equiv.), catalyst (20 mol-%), 4 Å MS (50 mg), and the solvent (5 mL, 0.1 M) under a N_2 atmosphere. The crude product was purified by column chromatography. [b] **1a** (1.0 equiv.), **2a** (2.0 equiv.). [c] **1a** (2.0 equiv.), **2a** (1.0 equiv.). [d] Isolated yield based on **1a**. [e] Isolated yield based on **2a**. [f] Anhydrous $MgSO_4$ (250 mg) was added instead of 4 Å MS.

With the optimal reaction condition in hand, the scope of both FCP 1,1-diesters **1** and 1,3-dicarbonyls **2** was investigated. The results of these experiments are summarized in Table 2. Reactions between FCP 1,1-diester **1** with symmetrical 1,3-diketones **2** afforded **3**. Both aryl and alkyl diketones worked well. Whereas pentane-2,4-dione (**2b**) gave product **3d** in excellent yield (Table 2, Entry 4), 1,3-diphenylpropane-1,3-dione (**2c**) gave product **3e** in moderate yield (Table 2, Entry 5). For unsymmetrical 1,3-diketones, two regioselective isomers were obtained (Table 2, Entries 6–10). We also delightfully found that β-keto esters also worked well (Table 2, Entries 11–17). In some examples (Table 2, Entries 9, 10, and 17), together with the main products, decarbonylative products were obtained as by-products.[11] Both phenyl- and alkyl-substituted β-keto esters gave domino products **3** in moderate to excellent yields.

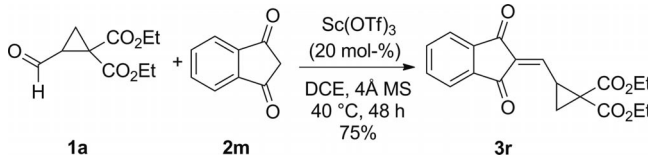
The reaction of FCP 1,1-diester **1a** with 1*H*-indene-1,3(2*H*)-dione (from Aldrich) only gave aldol/dehydration product **3r** (Scheme 2). Because of the noted and unusual interruption of furan generation, and to further explore the possible mechanism, several other experiments were carried out (Scheme 3). First, we examined the process in Table 1 to find out whether similar aldol/dehydration products existed but were not captured at a low temperature (Table 1, Entry 23). Then, a mono-ketone was introduced to take the place of the 1,3-diketones under standard aldol conditions,

Table 2. Investigation of the reaction scope.[a]

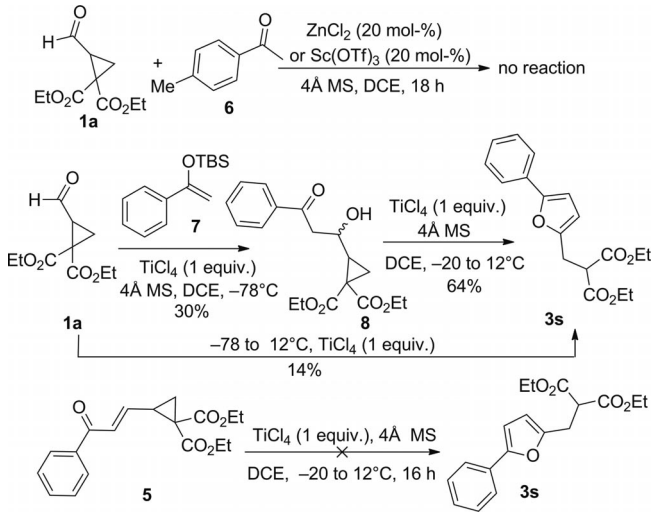


Entry	R^1	2	R^2	R^3	t [h]	Product	Yield[b] [%]
1	Et	**2a**	$–(CH_2)_3–$		40	**3a**	84
2	Me	**2a**	$–(CH_2)_3–$		40	**3b**	67
3	*i*Pr	**2a**	$–(CH_2)_3–$		40	**3c**	61
4	Et	**2b**	Me	Me	18	**3d**	90
5	Et	**2c**	C_6H_5	C_6H_5	40	**3e**	56
6	Et	**2d**	C_6H_5	Me	40	**3f/4f**	32/41
7	Et	**2e**	C_6H_5	*i*Bu	40	**3g/4g**	26/49
8	Et	**2f**	C_6H_5	Et	40	**3h/4h**	38/42
9	Et	**2g**	*p*-MeC_6H_4	Me	40	**3i/4i**	42/28
10	Et	**2h**	*p*-ClC_6H_4	Me	40	**3j/4j**	25/34
11	Et	**2i**	Me	OEt	40	**3k**	100
12	Et	**2j**	C_6H_5	OEt	12	**3l**	99
13	Me	**2j**	C_6H_5	OEt	2.5	**3m**	98
14	Me	**2k**	Me	OMe	18	**3n**	86
15	Et	**2k**	Me	OMe	14	**3o**	62
16	Me	**2i**	Me	OEt	14	**3p**	50
17	Et	**2l**	CH_2CO_2Et	OEt	14	**3q**	28

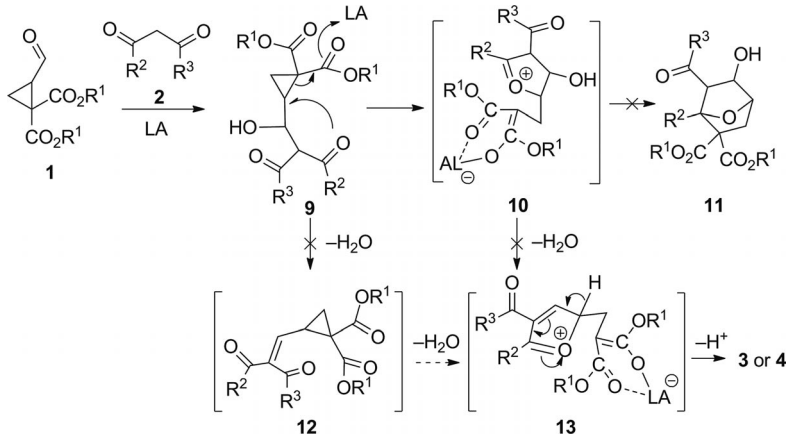
[a] Reaction conditions: **1** (2.0 equiv.), **2** (1.0 equiv.), $Sc(OTf)_3$ (20 mol-%), 4 Å MS (50 mg), and DCE (5 mL, 0.1 M) under a N_2 atmosphere at room temperature. [b] Isolated yield based on **2**.



Scheme 2. Unusual interruption of furan generation.



Scheme 3. Protocol used to explore the possible mechanism.



Scheme 4. Possible mechanism.

but unfortunately, the reaction of FCP 1,1-diester **1a** with 1-(*p*-tolyl)ethanone (**6**) failed. However, Mukaiyama aldol product **8** was successfully obtained from **1a** and *tert*-butyldimethyl [(1-phenylvinyl)oxy]silane (**7**) under $TiCl_4$ catalysis (100 mmol-%), which was subsequently converted into furan product **3s** when the temperature was elevated from –78 °C to higher than 12 °C (Scheme 3). Also, a one-pot experiment gave the same result. At last, compound **5** was synthesized independently (see the Supporting Information), but no reaction occurred when compound **5** was treated under the $TiCl_4$ catalytic conditions. These results indicated that the final furan product came from intermediate **8** instead of dehydration intermediate **5**. Only if dehydration gave a more stable product would furan generation be terminated (i.e., **3r**).

On the basis of these results, a possible mechanism was proposed (Scheme 4), which is similar to that of the Feist–Benary reaction[12] of formyl epoxide with 2-haloketone: reaction between **1** and **2** gives aldol product **9**, which can subsequently undergo an intramolecular S_N2-like homo-Michael reaction[7c,13] to afford ring-opened intermediate **10**. Instead of [3+2] IMCC product **11**, intermediate **10** undergoes a dehydration/deprotonation process to afford furan product **3** or **4** through intermediate **13**. Depending on the experimental results, the pathway to **12** by dehydration of **9** has been proved to be impossible.

These furan products also have potential utilization. 4-Oxybenzofuran is a common substructure existing in natural and synthetic compounds (Figure 1) and synthetic biologically active compounds. Oxidation of **3a** easily afforded compound **14** in excellent yield (Scheme 5).[14] This supplied an efficient method to prepare suitably substituted benzofuran products and their analogues.

Scheme 5. Oxidation of **3a**.

Conclusions

We have developed a new LA-catalyzed domino aldol/homo-Michael reaction of FCP 1,1-diesters with dicarbonyls. Features of this reaction include mild reaction conditions, readily available and structurally diverse starting materials, and good yields. This supplies a convenient method for the synthesis of substituted furans.

Experimental Section

General Procedure for Lewis Acid Catalyzed Domino Reactions of FCP 1,1-Diesters 1 and 1,3-Dicarbonyls 2: To an oven-dried, 50-mL, three-necked flask was charged with 4 Å molecular sieves (50 mg) and $Sc(OTf)_3$ (50 mg, 0.1 mmol). 1,3-Dicarbonyl **2** (0.5 mmol), FCP 1,1-diester **1** (1.0 mmol), and dry DCE (5 mL) were then added sequentially under a positive pressure of nitrogen. The reaction mixture was stirred at room temperature for the given period of time. After completion of the reaction (as monitored by TLC), the solvent was evaporated in vacuo, and the residue was purified by flash chromatography to afford products **3**.

Supporting Information (see footnote on the first page of this article): General methods, complete experimental details, and characterization data for all compounds.

Acknowledgments

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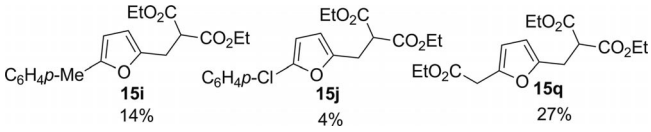
[11] In some examples (Table 2, Entries 9, 10, and 17), together with the main products, certain amounts of decarbonylative products were also obtained.



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