Heterocycles

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Preparation of Furo[3,2-*c*]coumarins from 3-Cinnamoyl-4-hydroxy-2*H*-chromen-2-ones and Acyl Chlorides: A Bu_3P-Mediated C-Acylation/Cyclization Sequence**

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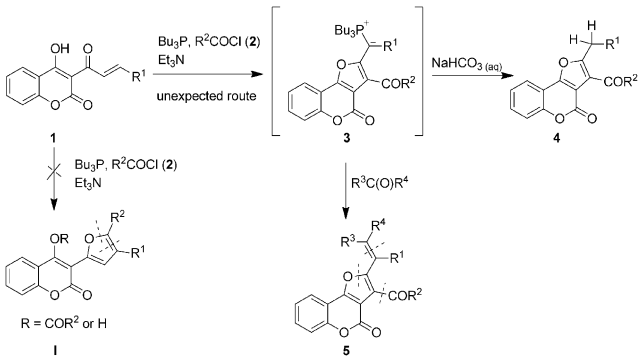
Abstract: *A Bu_3P-mediated cyclization reaction of 3-cinnamoyl-4-hydroxy-2H-chromen-2-ones though electrophilic addition of acyl chlorides towards the synthesis of highly functionalized furo[3,2-c]coumarins bearing a phosphorus ylide moiety is described. These unprecedented cyclization reaction proceeds under mild reaction conditions within short reaction times (1 min to 1 h), and can be further applied in the synthesis of alkenyl-substituted furo[3,2-c]coumarins by the treatment with carbonyl electrophiles under basic conditions.*

Given their frequent appearance in drugs and natural products, the efficient construction of highly functionalized furans and furo[3,2-*c*]coumarins is a major challenge in organic synthesis.[1] Tremendous work has been done within this field of chemistry, and thus various transition-metal-catalyzed cyclization reactions are well established.[2] As cheap and metal-free alternatives, phosphine-triggered reactions have recently attracted great interest.[3] Previously we demonstrated that multifunctionalized furan derivatives were afforded simply by treating Michael acceptors, such as α,β-unsaturated carbonyl compounds, with tributylphosphine in the presence of acyl chlorides using an intramolecular Wittig reaction as the key step.[3d–g] Based on this discovery, we were interested in the extension of this method to the application of coumarin derivatives, such as **1**, as Michael acceptors, which is proposed to give access to 3-furyl-4-hydroxycoumarin derivatives (**I**; Scheme 1).

Following our previously established protocol using 3-cinnamoyl-4-hydroxy-2*H*-chromen-2-ones **1** and acyl chlorides **2** as substrates in the presence of Et_3N as base, the expected adducts **I** could not be obtained (Scheme 1). Instead, the phosphorus ylides **3** were determined to be the major products. Remarkably, these ylide intermediates showed good reactivity for undergoing additional transformations in a one-pot approach: addition of a saturated $NaHCO_3$ solution directly led to the dephosophorated compounds **4**, whereas the treatment with carbonyl electrophiles afforded the corresponding Wittig products **5**.

A screening of the reaction conditions was pursued using the coumarin derivative **1a** and benzoyl chloride (**2a**) as model substrates (Table 1). Initially, THF was used as the solvent and Bu_3P as the nucleophile. After 3.5 hours, the reaction was quenched by saturated $NaHCO_{3(aq)}$, and the desired product **4aa** was obtained in 39% yield (NMR; entry 1). When other solvents such as CH_2Cl_2 and toluene were used, **4aa** was provided in 33–35% yields (entries 2 and 3). To our delight, the reaction proceeded more effectively in MeCN to afford **4aa** in 59% yield (entry 4). After further optimization of the reaction conditions (2.8 equiv of **2a** and 3.4 equiv of Et_3N), the adduct **4aa** could be furnished in 82% isolated yield within 1 hour (entries 4–6).[4] In addition, different phosphine sources, such as iBu_3P, Cy_3P, $MePh_2P$, $EtPh_2P$, and $(OEt)_3P$, as well as DABCO, were examined (entries 7–12). Presumably because of the lower nucleophilicity, only iBu_3P could successfully promote the reaction to provide **4aa**, albeit with low yield (entry 7).[5] Therefore, the use of MeCN as solvent, 1.1 equivalents of Bu_3P, 2.8 equivalents of acyl chloride, and 3.4 equivalents of Et_3N were selected as the optimal reaction conditions.[6]



Scheme 1. Unexpected formation of the products **4** and **5** by treating **1** with Bu_3P, acyl chlorides **2**, and Et_3N.

With the optimized reaction conditions in hand, the substrate scope of this novel cyclization was investigated (Table 2). A wide range of aryl-substituted acyl chlorides was screened, and good to excellent results could be achieved within short reaction times (entries 1–8). Heteroaryl-substituted (entries 9 and 10) as well as aliphatic acyl chlorides (entries 11 and 12) were also employed successfully for this

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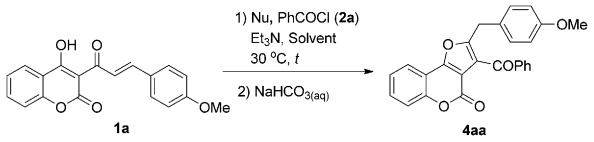
Table 1: Optimization of reaction conditions.[a]



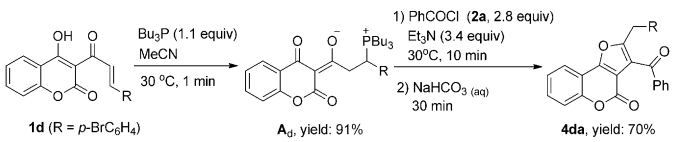
Entry	Solvent	Nu	**2a** (equiv)	Et_3N (equiv)	*t* [h]	Yield [%][b]
1	THF	Bu_3P	2.2	2.3	3.5	39
2	toluene	Bu_3P	2.2	2.3	3.5	35
3	CH_2Cl_2	Bu_3P	2.2	2.3	3.5	33
4	MeCN	Bu_3P	2.2	2.3	3.5	59
5	MeCN	Bu_3P	2.8	3.4	1	82[c]
6	MeCN	Bu_3P	1.3	1.5	1	26
7	MeCN	iBu_3P	2.8	3.4	1 (12)	25 (31)
8	MeCN	Cy_3P	2.8	3.4	1 (12)	0 (0)
9	MeCN	$MePh_2P$	2.8	3.4	1 (12)	2 (3)
10	MeCN	$EtPh_2P$	2.8	3.4	1 (12)	1 (2)
11	MeCN	$(OEt)_3P$	2.8	3.4	1 (12)	0 (0)
12	MeCN	DABCO	2.8	3.4	1 (12)	0 (0)

[a] Reaction conditions: Step 1: 0.2 mmol of **1a** and 1.1 equiv of the nucleophile (Nu) were utilized in dry solvent (1 mL) under N_2 atmosphere. Step 2: Saturated $NaHCO_{3(aq)}$ (3 mL) was added and stirred for additional 30 min. [b] Yield determined by NMR analysis of the crude reaction mixture using $CHPh_3$ as an internal standard. Values within parentheses represent the yield of the product after a reaction time of 12 hours. [c] Yield of isolated product. DABCO = 1,4-iazabicyclo-[2.2.2]octane, THF = tetrahydrofuran.

protocol, albeit in slightly reduced yields. Furthermore, different coumarin derivatives (**1a**, **1c**, and **1d**) have been examined with various acyl chlorides **2**. Delightfully, under the given reaction conditions, the corresponding products **4** were provided in moderate to excellent yields (entries 13–24).

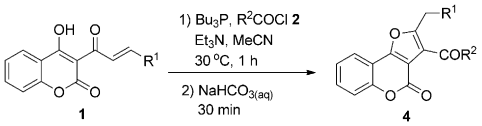
Further transformation of the phosphorus ylide **3** was realized through intermolecular Wittig reactions.[8] In the presence of additional carbonyl electrophiles (**6**), the corresponding adducts **5** and **5′** could be furnished in one-pot reactions (Table 3). Moderate to excellent yields of **5** and **5′** were obtained using ethyl glyoxylate (**6a**) and ninhydrin (**6b**), respectively, as trapping reagents.

A control experiment was carried out to demonstrate the existence of the phosphorus zwitterion **A-d** as the key intermediate for the generation of **4da** (Scheme 2). The zwitterionic adduct **A-d** resulting from **1d** and Bu_3P was afforded in 91% isolated yield, and characterized by X-ray analysis.[7] It is worth mentioning that, compared to the work of Kwon and co-workers, we also did not observe any intramolecular electrostatic interaction in the zwitterion **A-d**.[7,9] After treatment of **A-d** with benzoyl chloride (**2a**) in the presence of Et_3N, and subsequent quenching with saturated $NaHCO_{3(aq)}$, the product **4da** was furnished in 70% yield.



Scheme 2. Confirmation of the phosphorus zwitterion **A-d** as the reaction intermediate in the control experiment.

Table 2: Synthesis of furo[3,2-*c*]coumarin derivatives **4** from **1**, Bu_3P, acyl chlorides **2** and Et_3N.[a]



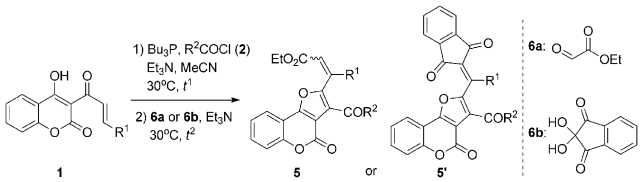
Entry	R^1	R^2	Yield [%][b]
1	Ph (**1b**)	Ph (**2a**)	86 (**4ba**)[c]
2	Ph	*p*-$MeOC_6H_4$ (**2b**)	83 (**4bb**)
3	Ph	*p*-$NO_2C_6H_4$ (**2c**)	77 (**4bc**)
4	Ph	*p*-ClC_6H_4 (**2d**)	79 (**4bd**)
5	Ph	*m*-ClC_6H_4 (**2e**)	94 (**4be**)
6	Ph	*o*-ClC_6H_4 (**2f**)	85 (**4bf**)
7	Ph	*p*-BrC_6H_4 (**2g**)	80 (**4bg**)
8	Ph	*o*-BrC_6H_4 (**2h**)	82 (**4bh**)
9	Ph	2-thienyl (**2i**)	40 (**4bi**)
10	Ph	2-furyl (**2j**)	33 (**4bj**)
11	Ph	Cy (**2k**)	74 (**4bk**)
12	Ph	*i*Pr (**2l**)	49[d] (**4bl**)
13	*p*-$MeOC_6H_4$ (**1a**)	Ph (**2a**)	82 (**4aa**)
14	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$ (**2b**)	81 (**4ab**)
15	*p*-$MeOC_6H_4$	*p*-$NO_2C_6H_4$ (**2c**)	92 (**4ac**)
16	*p*-$MeOC_6H_4$	*p*-ClC_6H_4 (**2d**)	86 (**4ad**)
17	*p*-$MeOC_6H_4$	*m*-ClC_6H_4 (**2e**)	90 (**4ae**)
18	*p*-$MeOC_6H_4$	*o*-ClC_6H_4 (**2f**)	60 (**4af**)
19	*p*-$MeOC_6H_4$	*p*-BrC_6H_4 (**2g**)	83 (**4ag**)
20	*p*-MeC_6H_4 (**1c**)	*p*-$MeOC_6H_4$ (**2b**)	52 (**4cb**)
21	*p*-MeC_6H_4	*p*-ClC_6H_4 (**2d**)	82 (**4cd**)
22	*p*-MeC_6H_4	*p*-BrC_6H_4 (**2g**)	79 (**4cg**)
23	*p*-MeC_6H_4	Cy (**2k**)	54 (**4ck**)
24	*p*-BrC_6H_4 (**1d**)	Ph (**2a**)	74[e] (**4da**)

[a] Reaction conditions: Step 1: **1** (0.2 mmol), Bu_3P (1.1 equiv), **2** (2.8 equiv), and Et_3N (3.4 equiv) in dry MeCN (1 mL) were stirred for 1 h under N_2 atmosphere. Step 2: Saturated $NaHCO_{3(aq)}$ (3 mL) was added and stirred for additional 30 min. [b] Yield of isolated product. [c] The structure of **4ba** was determined by X-ray analysis.[7] [d] Reaction time: 3 h. [e] Reaction time: 10 min.

As presented in Tables 1–3, 2.8 equivalents of acyl chloride **2** was necessary to obtain reasonable yields of **4**, although only one acyl group is incorporated into the product.[4] To understand the exact function of **2**, additional investigations were carried out (Scheme 3). The substrate **1b** was treated with 1.1 equivalents of Bu_3P and 0.9 equivalents of benzoyl chloride (**2a**) [Eq. (1)]. After 10 minutes, 1.8 equivalents of 4-nitrobenzoyl chloride (**2c**) and Et_3N (3.4 equiv) were added, and the reaction mixture was stirred for another hour. By quenching with $NaHCO_{3(aq)}$, ^1H NMR analysis of the crude reaction mixture revealed that only trace amounts of the benzoyl-substituted product **4ba** was formed. Instead, **4bc** could be identified as the major product. The other control experiment with reversed addition sequence of **2a** and **2c**showed comparable results with contrary product ratio [Eq. (2)].

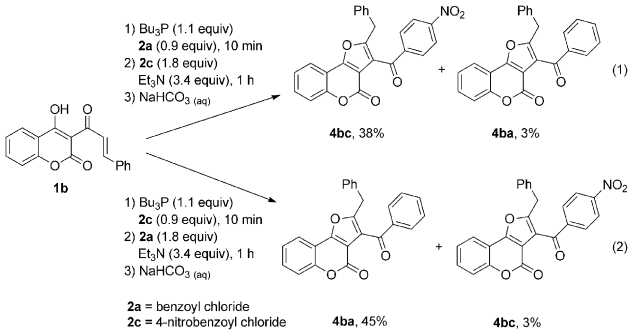
Based on these results, we propose a plausible reaction mechanism (Scheme 4). First, the phosphorus zwitterion **A** is formed by Michael addition of Bu_3P to **1**. The zwitterionic intermediate **A** then undergoes acylation with **2** (RCOCl) to provide the intermediate **B**. Under basic conditions, the elimination reaction of **B** takes place, thus leading to the formation of the corresponding allene intermediate **C**.[10]

Table 3: Synthesis of either **5** or **5′** by using **1**, Bu_3P, **2**, Et_3N, and **6**.[a]

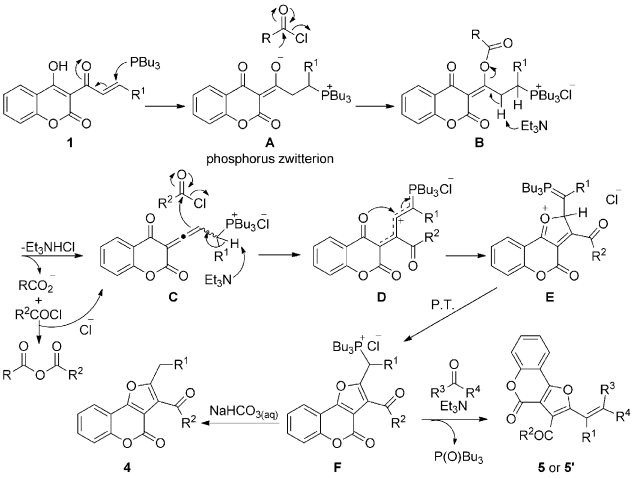


Entry	R^1	R^2	t^1 [min]	t^2 [h]	Yield [%][b]
1	*p*-$MeOC_6H_4$	Ph	60	1	88 (3.7:1)[c] (**5 aa**)
2	Ph	*p*-ClC_6H_4	60	1	91 (3.5:1)[c] (**5 bd**)
3	*p*-$NO_2C_6H_4$	Ph	10	0.5	75 (3.2:1)[c] (**5 ea**)
4	*p*-MeC_6H_4	Ph	60	1	77 (3.6:1)[c] (**5 ca**)
5	*p*-BrC_6H_4	Ph	10	0.5	75 (3.0:1)[c] (**5 da**)[d]
6	*p*-$MeOC_6H_4$	Ph	30	1	86 (**5′aa**)[d]
7	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	30	1.5	41 (**5′ab**)
8	*p*-$MeOC_6H_4$	*p*-BrC_6H_4	30	3	78 (**5′ag**)
9	Ph	*p*-$MeOC_6H_4$	30	5	61 (**5′bb**)
10	Ph	Ph	30	1	84 (**5′ba**)
11	Ph	*p*-$NO_2C_6H_4$	30	5	75 (**5′bc**)
12	Ph	*p*-ClC_6H_4	30	1	90 (**5′bd**)
13	Ph	*i*Pr	30	1	45 (**5′bl**)
14	*p*-MeC_6H_4	Ph	30	3	88 (**5′ca**)
15	*p*-BrC_6H_4	Ph	10	0.5	71 (**5′da**)
16	*p*-$NO_2C_6H_4$	Ph	5	0.5	66 (**5′ea**)
17	*p*-$NO_2C_6H_4$	*p*-$MeOC_6H_4$	5	1	48 (**5′eb**)
18	*p*-$NO_2C_6H_4$	*p*-ClC_6H_4	1	1	74 (**5′ed**)
19	*p*-$NO_2C_6H_4$	*i*Pr	5	1	34 (**5′el**)

[a] Reaction conditions: Step 1: **1** (0.2 mmol), Bu_3P (1.1 equiv), **2** (2.8 equiv), and Et_3N (3.0 equiv) were stirred in dry MeCN (1 mL) under N_2 atmosphere. Step 2: Et_3N (1.0 equiv) and **6** (1.3 equiv) were added to the reaction mixture. [b] Yield of the isolated product. [c] The isomeric ratio of **5** (*Z*/*E*). [d] The structures of **5 da** and **5′aa** were determined by X-ray analysis.[7]



Scheme 3. Control experiments: elucidating the roles of acyl chlorides **2** in the reaction mechanism. Reaction conditions: Step 1: The reaction of **1 b** (0.2 mmol) and all the indicated reagents were carried out in dry MeCN (1 mL) at 30 °C under N_2 atmosphere. Step 2: Saturated $NaHCO_{3(aq)}$ (3 mL) was added and stirred for additional 30 min.

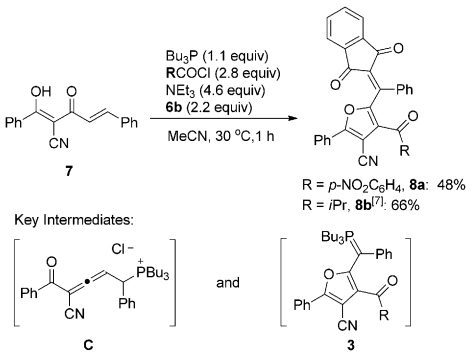


Scheme 4. Proposed mechanism for the Bu_3P-mediated cyclization reaction.

Because of their instability and high reactivity we were not able to isolate **B** and **C**. However, their appearance could be verified by in situ ESI-HRMS analysis of the reaction mixture.[11] The intermediate **C** then undergoes C-acylation with **2** (R^2COCl), thus furnishing the corresponding phosphonium chloride **D**. Thereafter, the intramolecular cyclization of **D** proceeds to afford **E**, which further isomerizes to generate the ylide precursor **F**.[12] The phosphonium chloride **F** can be activated in the presence of Et_3N to react with a carbonyl electrophile (**6**), thus giving either the corresponding adduct **5** or **5′**.

With regard to the proposed reaction mechanism, we anticipated that this protocol is not only limited to coumarin derivatives but also could be extended to a more versatile substrate scope. Hence, in our preliminary study, the acyclic compound **7** was examined under the given reaction conditions (Scheme 5). Without further optimization, moderate yields of **8 a** and **8 b** could be achieved after 1 hour, thus demonstrating the generality of this novel phosphine-triggered reaction.

In summary, we have developed a novel phosphine-promoted C-acylation/cyclization reaction of **1**, **2**, and Bu_3P in the presence of Et_3N to access to the phosphorus ylides **3** under very mild reaction conditions. The in situ generated ylide intermediates **3** can efficiently react with carbonyl electrophiles **6** or be quenched with saturated $NaHCO_{3(aq)}$,



Scheme 5. Preliminary results for the synthesis of **8 a**,**b** by using our one-pot approach.

thus furnishing either the corresponding furo[3,2-*c*]coumarin derivatives **5, 5′**, or **4**, respectively, in moderate to excellent yields. Furthermore, the substrate scope can be further extended to the acyclic precursor **7** according to our developed concept. A plausible reaction mechanism is also proposed and supported by control experiments. Further

investigations on this chemistry are currently ongoing in our laboratory.

Experimental Section

Typical procedure for the preparation of **4**: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1** (0.2 mmol), dry MeCN (1 mL), Bu_3P (1.1 equiv), acyl chloride **2** (2.8 equiv), and Et_3N (3.4 equiv). The reaction mixture was stirred for 1 h at 30 °C. Then the reaction was quenched by sat. $NaHCO_3$ solution (3 mL), stirred for an additional 30 min, and extracted with EtOAc (3 × 20 mL). Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide **4**.

Typical procedure for the preparation of **5** or **5′**: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **1** (0.2 mmol), dry MeCN (1 mL), Bu_3P (1.1 equiv), acyl chloride **2** (2.8 equiv), and Et_3N (3.4 equiv). The reaction mixture was stirred at 30 °C until **1** was fully consumed. Then Et_3N (1.2 equiv) and either ethyl glyoxalate (**6a**) or ninhydrin (**6b**; 1.3 equiv) were added, and the resulting reaction mixture was stirred until the reaction was completed. Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide either **5** or **5′**.

Typical procedure for the preparation of 8: A dry and nitrogen-flushed 10 mL Schlenk flask, equipped with a magnetic stirring bar and a septum, was charged with **7** (0.2 mmol), dry MeCN (1 mL), Bu_3P (1.1 equiv), the acyl chloride **2** (2.8 equiv), Et_3N (4.6 equiv), and ninhydrin (**6b**; 2.2 equiv, dissolved in 2 mL MeCN). The reaction mixture was stirred for 1 h at 30 °C. Thereafter, the solvent was removed by evaporation in vacuo. The crude reaction mixture was purified by flash column chromatography to provide **8**.

Keywords: acylation · cyclizations · heterocycles · ylides · zwitterion

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[6] For a detailled overview of all screening experiments, please see the Supporting Information.

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[11] For the details of ESI-HRMS results, please see the Supporting Information.

[12] The original phosphonium salt **F** with chloride as the counterion is too unstable to be identified. We therefore quenched the reaction by HBF_4 to afford the more stable intermediate **F** (R^1 = *p*-$MeOC_6H_4$, R^2 = Ph) with BF_4^- as the counterion, which was confirmed by NMR and HRMS analysis. For the experimental details, please see the Supporting Information.

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