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Thermoinduced Free-Radical C−H Acyloxylation of Tertiary Enaminones: Catalyst-Free Synthesis of Acyloxyl Chromones and Enaminones

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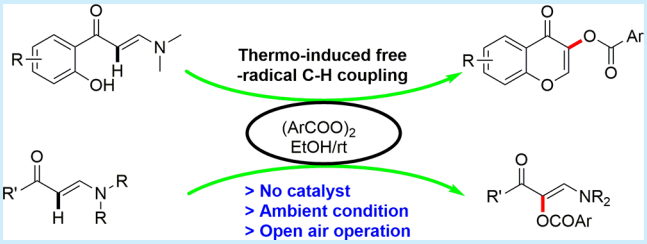
Supporting Information

ABSTRACT: In this paper, the direct acyloxylation of the α-C(sp^2)−H bond in tertiary β-enaminones is accomplished under catalyst-free conditions and ambient temperature by using aroyl peroxides as coupling partners. By means of a thermoinduced free-radical pathway, the present method enables facile and efficient synthesis of both acyloxylated chromones and enaminones.



Chromones are the central backbone of flavonoid natural products and many synthesized molecules with widespread applications in clinical medicines, biological screenings, and functional materials.[1] Correspondingly, the synthetic research toward densely functionalized chromones keeps receiving extensive interest from the chemical community.[2] In particular, C-3 oxygenated chromones such as 3-hydroxyl chromones and related esters represent an important class of chromone derivatives showing high merits in the discovery of bioactive molecules and the designation of functional materials. For example, the 3-hydroxy-2-(1-phenyl-3-aryl-4-pyrazolyl) chromones **A** are promising lead compounds with potent antifungal activity,[3] aryl-linked 3-hydroxyl chromones **B** are nucleobases possessing potential application in nucleic acid labeling,[4] and Karanjin (**C**) is a natural product with potent mosquito larvicidal activity.[5] In addition, Fisetin (**D**) and Quercetin (**E**) are both typical flavonoid natural products with enriched biological profiles (Figure 1).[6] Moreover, 3-hydroxyl chromone is also known as the central skeleton of many functional fluorescent molecules, as well as the main precursor in the synthesis of natural products.[7]

A survey of the literature indicates that functionalized chromones such as chromone carboxylates can presently be accessed via either the elaboration of prior prepared 3-hydroxyl chromones resulting from the oxidation of unsubstituted chromones via oxidative C−H/C−C bond cleavage[4,8] or the dehydrogenation/dehydrogenative hydroxylation of functionalized dihydrochromones.[9] Since these methods rely on chromone or related derivatives as reactants, their broad utilization is thus hampered by the tedious process required for preparing those chromone reactants. In this context, developing alternative methods allowing the synthesis of the 3-oxygen functionalized chromones with simple and easily available acyclic substrates is currently an urgent issue.

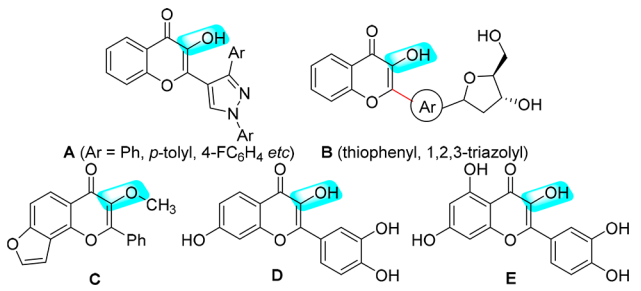


Figure 1. Representative functional 3-oxygenated chromones.

Over the past decade, the direct cross-coupling of the vinyl C−H bond in *NH* and NH_2-functionalized enaminones has exhibited widespread application in the synthesis of useful organic products.[10,11] Surprisingly, as a class of special enaminones, *N,N*-disubstituted enaminones have received much less attention as C−H bond donors, probably because of the weaker HOMO heightening effect of the fully substituted amino group to the vinyl C−H bond. Traditionally, transition metal catalysis has been found to be applicable in functionalizing the vinyl C−H bond of tertiary enaminones.[12] It is in rather recent years that the transition-metal-free operation has found application in the cross-coupling of such a C−H bond, particularly in the construction of C−S and C−Se bonds.[13] However, as an important chemical fragment, the C−O bond remains hard to access by a similar metal-free C−H bond transformation.[14] To address this challenge, the identification of proper oxo reaction partners is obviously the key point. In light of the free-radical pathway involved in the previous chromone synthesis based on the enaminone C−H coupling[13c] and the many known practical methods on radical-based C−H functionalization reactions,[15] we envisage that an

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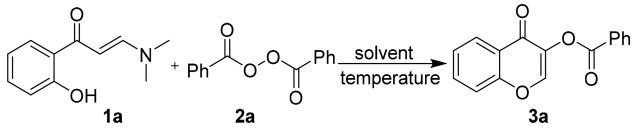
O-centered free-radical precursor would thus be applicable to design the expected C−O bond forming reaction. With this inspiration, the frequently utilized aroyl peroxides are thus elected as the radical precursors.[16] Herein, we report the first example on the synthesis of 3-acyloxylated chromones and tertiary enaminones via the free-radical-based C−H cross-coupling of tertiary enaminones by using aroyl peroxide.

Initially, the reaction of *o*-hydroxyphenyl enaminone **1a** and BPO was tentatively run in DMF, and we were delighted to find that 3-benzoyloxyl chromone **3a** was obtained in 44% yield by simply heating at 60 °C (entry 1, Table 1). Therefore,

Table 1. Optimization of the Reaction Conditions[a]



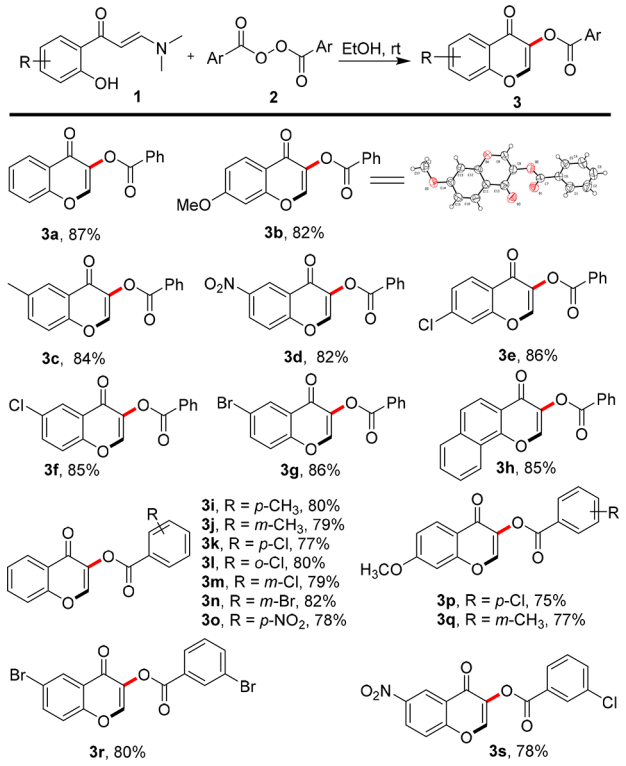
entry	solvent (mL)	*t* (°C)	yield (%)[b]
1	DMF	60	44
2	DMF	50	52
3	DMF	40	56
4	DMF	rt	60
5	DMSO	rt	68
6	toluene	rt	45
7	hexane	rt	10
8	EL	rt	62
9	EtOH	rt	70
10	1,4-dioxane	rt	65
11	H_2O	rt	10
12[c]	EtOH	rt	75
13[d]	EtOH	rt	83
14[e]	EtOH	rt	79
15[d,f]	EtOH	rt	84
16[d,g]	EtOH	rt	88
17[d,h]	EtOH	rt	82

[a]General conditions: **1a** (0.2 mmol), **2a** (0.2 mmol) in solvent (2.0 mL) based on **1a**, stirred for 12 h. [b]Yield of isolated product. [c]The amount of **2a** was 0.3 mmol. [d]The amount of **2a** was 0.4 mmol. [e]The amount of **2a** was 0.5 mmol. [f]The reaction time was 7 h. [g]The reaction time was 6 h, and benzoic acid was isolated in 81% yield from this entry. [h]The reaction time was 5 h.

the reaction was then executed under different temperatures, which indicated that room temperature was the most favorable (entries 2−4, Table 1). In addition, parallel reactions in different organic solvents such as toluene, hexane, ethyl lactate (EL), EtOH, dioxane, and water disclosed that EtOH was the best medium (entries 5−11, Table 1). Increasing the loading of **2a** led to evident improvement in the yield of **3a** (entries 12−14, Table 1). Further examination on the impact of reaction time, on the other hand, proved that 6 h was enough to enable the formation of **3a** with satisfactory yield (entries 15−17, Table 1). Notably, TLC analysis showed no occurrence of transesterification on product **3a**.

In the investigation of synthetic scope, a spectrum of functionalized *o*-hydroxylphenyl enaminones **1** and aroyl peroxides **2** were employed, respectively (product **3b**, CCDC 1842991). The results obtained from this section are shown in Scheme 1. First, when BPO **2a** was utilized to react with enaminones **1** containing different substituents in the phenyl ring, all related chromone products were provided in excellent yield (**3a**−**3h**, Scheme 1). On the other hand, when

Scheme 1. Enaminone C−H Acyloxylation for Acyloxyl Chromone Synthesis[a,b]



[a]General conditions: enaminone **1** (0.5 mmol), peroxide **2** (1 mmol) in EtOH (2 mL). Stirred at room temperature for 6 h. [b]Yield of isolated product based on **1**.

enaminone substrate **1a** was fixed to react with various aroyl peroxides **2**, corresponding products were given with similarly good to excellent yields (**3i**−**3o**, Scheme 1). As expected, the reactions employing both components containing additional substitutions also proceeded well to yield the acyloxylated products **3p**−**3s** (Scheme 1). No evident effect of the substituent on either substrate was observed with the present data, regardless of their distinctive electronic property or position. As an aliphatic acyl peroxide, the lauroyl peroxide was also subjected to react with **1a**, but only a trace amount of expected product was observed, probably because of the lower stability of the corresponding aliphatic carboxyl radical.

Following the excellent results acquired in the synthesis of **3**, we then turned to further investigate the application of the C−H functionalization to conventional tertiary enaminones **4**. Delightfully, with the identical operation, direct C−H acyloxylation proceeded smoothly to provide various aroyloxyl enaminones **5**, demonstrating the good tolerance of this synthetic protocol to functional substrates (Scheme 2). The successful synthesis of products of both types **3** and **5** confirmed the broad application of this thermoinduced free-radical coupling approach in affording divergent acyloxylated products. However, the experiment employing *E*-chalcone to react with BPO showed no transformation of the reactants, indicating the importance of an amino group in enaminone in activating the C−H bond for the target reaction.

Because of the simple operation and reaction conditions, we conducted a scaled-up experiment on the model reaction. As outlined in eq 1, the gram-scale experiment gave **3a** in 72%

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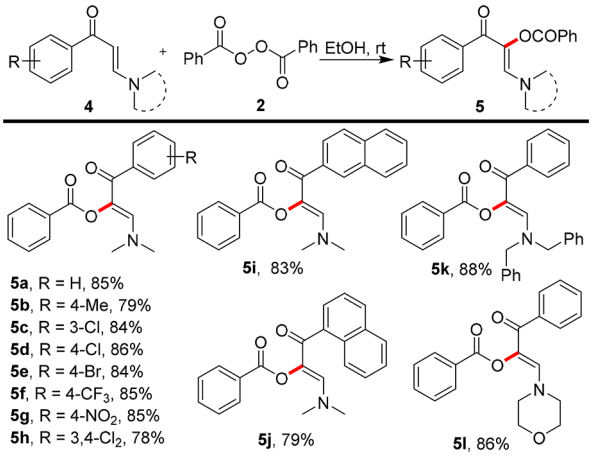
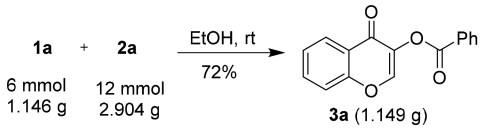
Scheme 2. Enaminone C−H Acyloxylation for the Synthesis of Acyloxylated Enaminones[a,b]



[a]General conditions: enaminone **4** (0.5 mmol), peroxide **2** (1.0 mmol) in EtOH (2 mL). Stirred at room temperature for 6 h. [b]Yield of isolated product based on **4**.

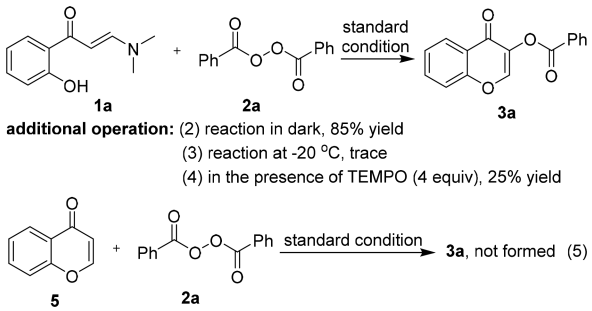
yield, indicating the practicality of the present method in the large-scale preparation of the chromone scaffold.



(1)

In order to probe the possible reaction pathway, several control experiments were conducted. First, when the model reaction was performed under dark conditions, **3a** was provided with an equally excellent yield (eq 2, Scheme 3). In

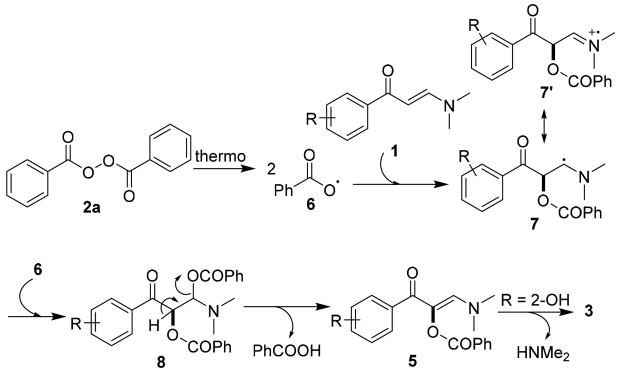
Scheme 3. Control Experiments



addition, another entry run at low temperature (−20 °C) gave the target product with only a trace amount (eq 3, Scheme 3). The above experiments supported that the reaction was a thermoinduced transformation. In combination with the result of the significantly lower product yield from the reaction employing additional TEMPO (eq 4, Scheme 3), it can be initially concluded that the reaction proceeds via a thermoinduced free-radical pathway. Furthermore, the reaction of chromone with BPO **2a** was also conducted under the standard conditions, wherein **3a** was not observed (eq 5, Scheme 3), suggesting that **5** is unlikely the reactive intermediate during the product generation.

According to the information provided by the control experiments, the possible mechanism of these reactions is proposed. As is shown in Scheme 4, the reaction starts from the thermoinduced O−O bond cleavage providing *O*-centered

Scheme 4. Proposed Reaction Mechanism



radical species **6**. The addition of **6** to enaminone **1** generates another radical intermediate **7**/**7′**, which undergoes the chain propagation in the presence of **6** to give intermediate **8**. The elimination of carboxylic acid on **8** yields acyloxylated enaminones **5**. For 2-hydroxylphenyl functionalized enaminones, a classical chromone annulation further takes place to yield products **3**.

In conclusion, we have disclosed the first free-radical-based C−H bond acyloxylation of tertiary enamionone, which enables the synthesis of 3-acyloxyl chromones and α-acyloxyl enaminones with high efficiency. By employing aroyl peroxides as the coupling reagents, the reactions proceed well at room temperature without using any catalyst, providing a reliable route in the synthesis of these useful heterocyclic chromones and densely functionalized alkenes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b01536.

General experimental information, procedures for the synthesis of **3** and **5**, full characterization data, ^{1}H and ^{13}C NMR spectra of all products, and the crystal structure of **3b** (PDF)

Accession Codes

CCDC 1842991 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.

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Notes

The authors declare no competing financial interest.

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