**Selective synthesis of 3-formylbenzofuran and 3-acylbenzofuran using a chalcone rearrangement strategy†**

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We developed a method for highly selective synthesis of two benzofuran isomers, by rearranging and subsequently transforming 2-hydroxychalcones. Depending on the reaction conditions, synthesis of 3-formylbenzofurans, unconventional products, and 3-acylbenzofurans was achieved through cyclized 2,3-dihydrobenzofurans obtained from the rearranged products. The facile synthesis of 3-formylbenzofurans facilitated synthesis of the natural product, puerariafuran, from the corresponding chalcone.

**Introduction**

Benzofuran and its derivatives are present as scaffolds in many natural products and biologically active compounds. These compounds have attracted much attention in the pharmaceutical and pesticide industries because of their promising antibacterial, antimicrobial, antitumor, and antidiabetic activities. Hence, the synthesis of benzofurans has aroused considerable interest and various methodologies have been reported and applied for the synthesis of natural products.  

Our current research focuses on the development of methods for synthesizing various heterocycles used for the rearrangement of chalcones. Combination of chalcones and rearrangement reactions has been reported, but has limited utility for the construction of isoflavones. We also reported the synthesis of pterocarpin via isoflavones, through hypervalent iodine-mediated oxidative rearrangement of 2,2′-hydroxychalcone derivatives. In this study, we found that 3-acylbenzofuran was formed from 2-hydroxychalcone derivatives. The synthesis of 3-acylbenzofurans is an unexplored topic; little is known about routes to effective synthesis. For example, Friedel–Crafts acylation of benzofurans results in low C2/C3 regioselectivity, and most existing methods can synthesize 3-acylbenzofurans with substituents at the C2 position.

We recently developed a method for concise one-pot synthesis of 3-acylindoles. This method first rearranges the N-COCF₃-protected 2-aminochalcone with phenyliodine diacetate (PhI(OAc)₂); 3-acylindoles are then produced under basic conditions via deprotection and a cyclization reaction (Scheme 1A). To apply the chalcone-rearrangement strategy for the synthesis of 3-acylbenzofurans, we investigated the reaction of the protected 2-hydroxychalcone. Unexpectedly, our approach produced not only 3-acylbenzofuran, but also 3-formylbenzofuran (with high selectivity) from 2,3-dihydrobenzofuran (Scheme 1B).

**Results and discussion**

We started by testing the rearrangement conditions using 2-hydroxychalcone 1 with a hypervalent iodine reagent (Scheme 2). No rearrangement product 2 was obtained without the protecting group (R = H). Attempts were made to synthesize chalcones protected with the trifluoroacetyl group used in our previous indole synthesis, but the chalcones were unstable and

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**Scheme 1** Chalcone rearrangement strategies for synthesis of heterocycles.
could not be isolated. Then, the reaction was evaluated with chalcones bearing various protecting groups, such as t-butyloxy carbonyl (Boc), acetyl (Ac) and benzoyl (Bz), but no rearranged products were obtained. The desired product was obtained with methoxymethyl (MOM) protection. The reaction of MOM-protected hydroxychalcone with two equivalents of hydroxy(tosyloxy)iodobenzene (PhI(OH)OTs) gave the corresponding rearranged product 2a in 64% yield.

We next examined deprotection followed by simultaneous cyclization to the corresponding 3-acylbenzofuran under acidic conditions (Table 1). With excess AcOH, no reaction was observed, even with reflux (entry 1). The desired benzo furan 4a was not obtained using trifluoroacetic acid (TFA), whereas 2,3-dihydrobenzofuran 3a, the precursor of 4a, was isolated in 56% yield (entry 2). The use of p-toluensulfonic acid (p-TsOH) increased the yield of 3a slightly to 62% (entry 3), but 3a was not obtained, and nor was 4a with heating (entry 4). The use of the solvents CH2Cl2, THF, and MeOH did not yield the desired 4a. We finally optimized the conditions to obtain 3a in 80% yield using 0.1 equivalent of p-TsOH (entry 5).

Subsequently, the transformation of 2,3-dihydrobenzofuran 3a into 4a was studied under basic and acidic conditions (Table 2). When the reaction was performed using K2CO3, aromatization proceeded at room temperature affording 3-acylbenzofuran 4a in 97% yield (entry 1). Pyridine was ineffective and only trace amounts of 4a were obtained upon reflux (entry 2). However, 4a was obtained in 98% yield in AcOH (entry 3). Other acids (pyridinium p-toluensulfonate (PPTS) and TFA) in toluene also gave 4a in high yields under reflux conditions (entries 4 and 5). Surprisingly, unexpected formation of 3-formylbenzofuran 5a was observed with p-TsOH when 1,1,1,3,3,3-hexafluoro-2-propanol was used as a solvent. 3-Formylbenzofurans are found in the skeletons of natural products, and few synthetic methods are known.

On optimizing the conditions for the selective synthesis of benzofuran isomers, the transformation was extended to various 2,3-dihydrobenzofurans 3 with aryl or alkyl groups on the ketone moiety (Table 3). A series of electron-donating groups (e.g., p-methyl and o-methoxy) and electron-withdrawing substituents (e.g., p-chloro) on the phenyl ring reacted smoothly to give the respective 3-acylbenzofurans 4b–4d and 3-formylbenzofuran (5b–5d) in excellent yields. The reaction with 2,3-dihydrobenzofuran with a thiophenyl group afforded 4e and 5e in yields of 96% and 90%, respectively. During the transformation of 3f and 3g with alkyl groups, 3-acylbenzofurans (4f and 4g) and 3-formylbenzofuran 5f were obtained in high yields, whereas the yield of 3-formylbenzofuran 5g was decreased slightly.

Next, we applied this novel 3-formylbenzofuran synthesis method to natural products (Scheme 3). Puerafuran was chosen as the synthetic target, as it exhibits biological activities such as the inhibition of advanced glycation end products (AGEs). Recently, Lin et al. synthesized puerafuran, the number of steps and total yield could be improved. First, chalcone 8 was prepared by condensing MOM-protected aldehyde 6 and acetophenone 7 in 93% yield. Oxidative rearrangement with hypervalent iodine reagent was achieved by [bis(trifluoroacetoxycetoxy)iodo]benzene (Phi[OCOF3]2), affording 9 in 69% yield. To synthesize 2,3-dihydrobenzofuran 10, we attempted to perform simultaneous deprotection and cyclization reactions under acidic conditions. Partial decomposition

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\begin{align*}
\text{Scheme 2 Rearrangement of protected chalcone 1.}
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\begin{align*}
\text{Table 1 The transformation of 2a under acidic conditions.}
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\begin{align*}
\text{Table 2 The transformation of 3a to benzofurans.}
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\]
was observed as the reaction progressed, but adding an excess of EtOH suppressed the decomposition and dihydrobenzofuran 10 was obtained in 56% yield.\(^1^1\) Final conversion to the 3-formylbenzofuran skeleton was achieved on treatment with p-TsOH in (CF\(_3\))\(_2\)CHOH, giving puerariafuran in 80% yield. Our protocol for puerariafuran synthesis has seven steps and an overall yield of 18% from commercial aldehyde and acetophenone; it is more efficient than the previous synthesis method (11 steps and 5.3% total yield).

The reaction mechanism for obtaining two types of benzofuran from 2,3-dihydrobenzofurans 3 under acidic conditions was thought to be as follows (Scheme 4). Using relatively weak acids, 3-acylbenzofurans 4 were obtained via aromatization in association with methanol elimination (path i). The mechanism of 3-formylbenzofuran 5 formation is via a diprotonated intermediate A (path ii),\(^1^2\) which is stabilized with (CF\(_3\))\(_2\)CHOH.\(^1^3,^1^4\) Subsequent THF ring opening of intermediate A gives B, and the ring-closure at the ketone moiety then lead to 5 after aromatization and hydrolysis. According to Zanatta,\(^1^5\) another possible pathway for the formation of 5 is isomerization from 4. However, the reaction of 4 with p-TsOH and some MeOH in (CF\(_3\))\(_2\)CHOH resulted in no reaction.\(^1^6\)
Conclusions

In summary, we developed a new method for highly selective synthesis of two benzofuran isomers based on rearrangement of the MOM-protected 2-hydroxychalcone. The key intermediates, 2,3-dihydrobenzofurans, could be selectively transformed into different benzofuran isomers using different reaction conditions. 3-Acylbenzofurans were obtained under basic or weakly acidic conditions in THF. Using (CF₃)₂CHOH as a solvent with p-TsOH generated 3-formylbenzofurans selectively. A variety of 2,3-dihydrobenzofurans were selectively converted into benzofuran isomers in high yields, and the efficient total synthesis of puerarifuran proves the practicality of this method. Currently, we are developing this methodology for application to other heterocycles.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by JSPS KAKENHI Grant No. 19K16329 and 18K05132, and also supported by 2021 Kindai University Research Enhancement Grant (KD2106). We also thank the Kindai University Joint Research Center for use of their facilities.

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