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Lewis Acid-Mediated Reactions of 1-Cyclopropyl-2-arylethanone Derivatives with Allenic Ester, Ethyl Acetoacetate, and Methyl Acrylate

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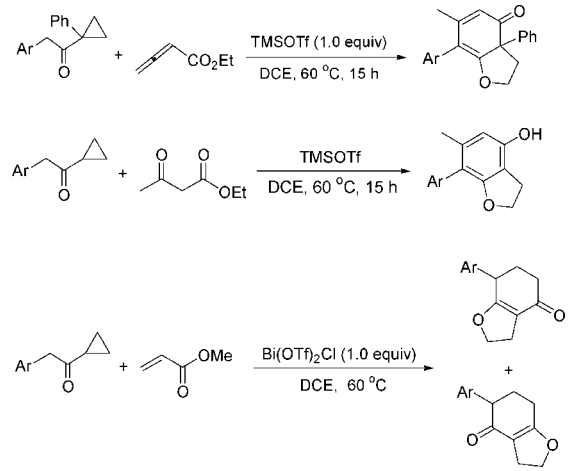
Received March 18, 2008



TMSOTf-mediated reactions of 2-aryl-1-(1-phenylcyclopropyl)ethanones **1** with allenic esters afford a novel method for the synthesis of 6-methyl-3a,7-diaryl-3,3a-dihydro-2*H*-benzofuran-4-one derivatives **2** in moderate yields. In addition, we also found that TMSOTf-mediated reactions of 1-cyclopropyl-2-arylethanones with ethyl acetoacetate can provide the corresponding 2,3-dihydrobenzofuran-4-ol and dihydrofuro[2,3-*h*]chromen-2-one in moderate yields via a sequential reaction involving a nucleophilic ring-opening reaction of the cyclopropane by H_2O, one intermolecular aldol type reaction and two intramolecular aldol type reactions, a cyclic transesterification, dehydration, and aromatization. Moreover, by using methyl acrylate to replace allenic ester, the corresponding 7-aryl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one and 5-aryl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one can be formed in moderate to high yields in the presence of $Bi(OTf)_2Cl$. Plausible reaction mechanisms have also been provided on the basis of control experiments.

Introduction

Cyclopropane-containing compounds, as versatile building blocks in organic synthesis, have been well understood.[1] The ring-opening reactions of cyclopropyl ketones are synthetically useful reactions that have been studied extensively.[2] Previously, we reported $SnCl_4$ and trimethylsilyl trifluoromethanesulfonate (TMSOTf)-mediated reactions of cyclopropyl alkyl ketones with α-ketoesters and allenic esters to afford novel methods for the synthesis of 1,6-dioxaspiro[4.4]non-3-en-2-ones with high stereoselectivities as well as dihydrofuro[2,3-*h*]chromen-2-one and 2,3-dihydrobenzofuran-4-ol derivatives in moderate to good yields under mild conditions

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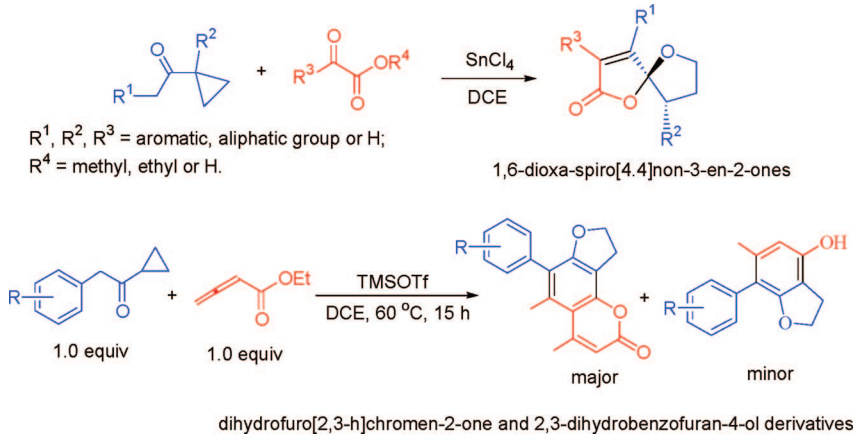
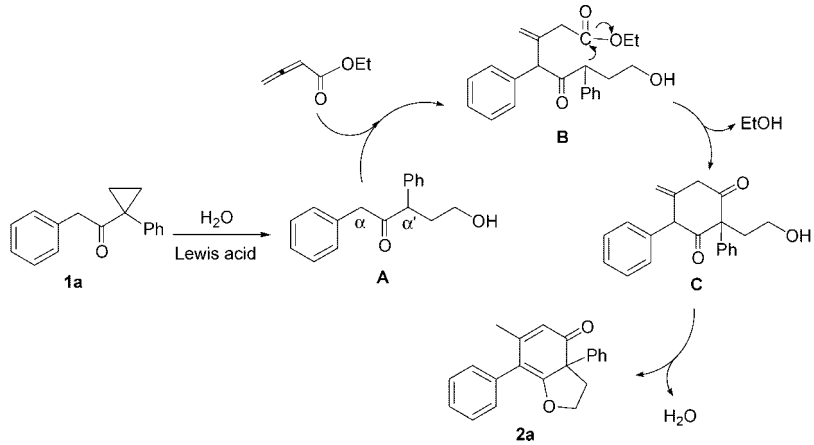
10.1021/jo800608h CCC: $40.75 © 2008 American Chemical Society
Published on Web 06/21/2008

SCHEME 1. $SnCl_4$ and TMSOTf-Mediated Reactions of 1-Cyclopropyl-2-arylethanones with α-Ketoesters and Allenic Esters



SCHEME 2. Mechanism for the Formation of 6-Methyl-3a,7-diphenyl-3,3a-dihydro-2*H*-benzofuran-4-one Derivative 2



(Scheme 1).[3] In this paper, we wish to report the full details on the Lewis acid-mediated reactions of 1-cyclopropyl-2-arylethanone derivatives with allenic ester, ethyl acetoacetate, and methyl acrylate for the construction of dihydrofuro[2,3-*h*]chromen-2-one, 2,3-dihydrobenzofuran-4-ol, 6-methyl-3a,7-diphenyl-3,3a-dihydro-2*H*-benzofuran-4-one, and 7-aryl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one skeletons along with the detailed mechanistic investigations.

Results and Discussion

As shown in our previous communication, a plausible mechanism for the formation of dihydrofuro[2,3-*h*]chromen-2-one and 2,3-dihydrobenzofuran-4-ol derivatives has been proposed on the basis of a ring-opening reaction of 1-cyclopropyl-2-arylethanone, intermolecular and intramolecular aldol reactions as well as aromatization (also see Scheme 3).[3b] To get more mechanistic insight into this reaction, we decided to use 2-phenyl-1-(1-phenylcyclopropyl)ethanone **1a** instead of 1-cyclopropyl-2-arylethanone to react with allenic ester under the standard conditions because we assumed that the substituent at the cyclopropane could block out one side of the aldol-type reaction, subsequently affording one product regioselectively.

Initial examination revealed that the reaction of 2-phenyl-1-(1-phenylcyclopropyl)ethanone **1a** with allenic ester proceeded smoothly in 1,2-dichloroethane (DCE) at 60 °C to give the corresponding 6-methyl-3a,7-diphenyl-3,3a-dihydro-2*H*-benzofuran-4-one derivative **2a** in 41% yield in the presence of TMSOTf (1.0 equiv) within 15 h (Table 1, entry 1). We further attempted to optimize the reaction conditions by use of other Lewis acids and find out the best solvent in this reaction. The results of these experiments are summarized in Tables 1 and 2, respectively. As can be seen from Tables 1 and 2, changing Lewis acid and solvent did not significantly improve the yield of **2a**. Using Brønsted acid trifluoromethanesulfonic acid CF_3SO_3H (HOTf) as a promoter afforded **2a** in 36% yield in DCE (Table 1, entry 4). The best conditions are to carry out the reaction in DCE at 60 °C with TMSOTf as a Lewis acid (Table 1, entry 1). With these optimal conditions being identified, we next attempted to examine the scope and limitations of this reaction using a

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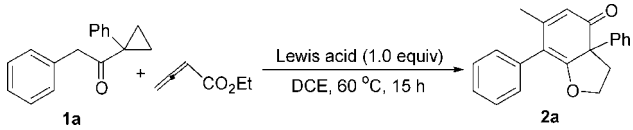
TABLE 1. Lewis Acid-Mediated Reactions of 2-Phenyl-1-(1-phenylcyclopropyl)ethanone 1a with Allenic Ester

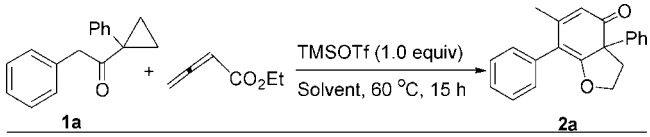


1a 2a

entry	Lewis acid	yield [%][a] of **2a**
1	TMSOTf	41
2	$Zr(OTf)_4$	12
3	$Sc(OTf)_3$	trace
4	HOTf	36
5	$Bi(OTf)_2Cl$	23

[a] Isolated yields.

TABLE 2. Solvent Effects on the TMSOTf-Mediated Reactions of 2-Phenyl-1-(1-phenylcyclopropyl)ethanone 1a with Allenic Ester



1a 2a

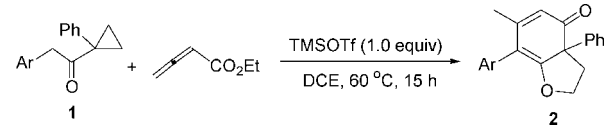
entry	solvent	yield [%][a] of **2a**
1	toluene	30[b]
2	CH_3CN	complex
3	THF	N.R.
4	DCM	33

[a] Isolated yields. [b] The reaction temperature was 100 °C.

variety of 2-aryl-1-(1-phenylcyclopropyl)ethanones **1** as the substrates. The results are summarized in Table 3. The corresponding products **2** were obtained in 22−54% yields (Table 3, entries 1−7). The low to moderate yields of this TMSOTf-mediated transformation are presumably due to some unidentified byproduct being formed during this tandem reaction process since some small spots could be recognized by TLC plates along with the major products **2**. Their structures were determined by spectroscopic data, HRMS, and microanalyses (see the Supporting Information). Furthermore, the X-ray crystal structure of **2c** was determined and its CIF data and ORTEP drawing are presented in the Supporting Information. A plausible reaction mechanism for the formation of **2** has been outlined in Scheme 2 via intermediates **A**, **B**, and **C** similarly as we reported in the previous paper (also see Scheme 3).[3b] This result suggests that the first aldol-type reaction with allenic ester indeed takes place from the C_α position in intermediate **A** preferentially to afford intermediate **B** and the next aldol-type reaction from the $C_{\alpha'}$ position in intermediate **B** would be favored by the phenyl substituent under thermodynamically controlled conditions (60 °C in DCE). The phenyl substituent at the α′-position can suppress the aromatization process. Therefore, compound **2** could be isolated as the major product.

Interestingly, if we reconsider the reaction mechanism for the formation of 2,3-dihydrobenzofuran-4-ol derivative **3** and dihydrofuro[2,3-*h*]chromen-2-one **4** shown in Scheme 3 in the TMSOTf-mediated reactions of 1-cyclopropyl-2-arylethanone **1** with allenic ester via intermediates **A′**−**G′** in our previous paper,[3b] it is conceivable that using ethyl acetoacetate instead of allenic ester could also afford 2,3-dihydrobenzofuran-4-ol derivative **3** and dihydrofuro[2,3-*h*]chromen-2-one **4** in the TMSOTf-mediated reaction with 1-cyclopropyl-2-arylethanone **1** under identical conditions since the plausible reaction mechanism could be very similar via intermediates

TABLE 3. Generality on the TMSOTf-Mediated Reactions of 2-Aryl-1-(1-phenylcyclopropyl)ethanone 1 with Allenic Ester under Optimal Conditions



1 2

entry	Ar	yield [%][a] of **2**
1	**1b**, *p*-ClC_6H_4	**2b**, 33
2	**1c**, *p*-MeC_6H_4	**2c**, 36
3	**1d**, *p*-BrC_6H_4	**2d**, 54
4	**1e**, *o*-BrC_6H_4	**2e**, 22
5	**1f**, *p*-FC_6H_4	**2f**, 31
6	**1g**, *m*-FC_6H_4	**2g**, 32
7	**1h**, *o*-ClC_6H_4	**2h**, 25

[a] Isolated yields.

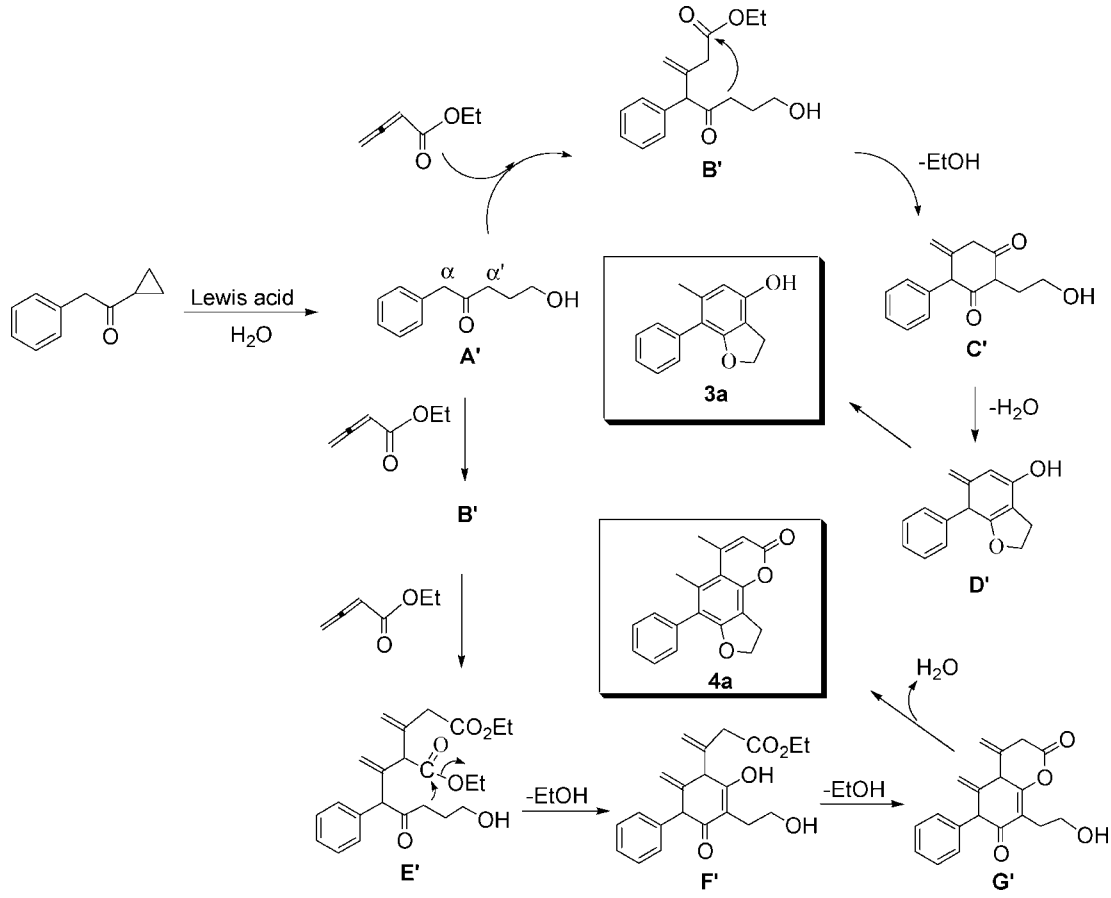
D, **E**, and **F** (Scheme 4 and also see Scheme 5). Therefore, we examined the Lewis acid-mediated reactions of 1-cyclopropyl-2-phenylethanone **1i** with ethyl acetoacetate under the standard conditions. The results of these experiments are summarized in Table 4. Using $SnCl_4$ as a Lewis acid (1.0 equiv) to react with ethyl acetoacetate (1.5 equiv) indeed afforded **3a** in 20% in DCE at 60 °C (Table 4, entry 1). $BF_3 \cdot OEt_2$ did not catalyze this reaction under similar conditions (Table 4, entry 2). Using TMSOTf (1.0 equiv) as a Lewis acid to react with ethyl acetoacetate (1.5 equiv) produced **3a** in 45% yield at 60 °C in DCE, which are the best reaction conditions for the preparation of **3a** as shown in Table 4 since increasing or decreasing the employed amounts of ethyl acetoacetate and TMSOTf did not further improve the yields of **3a** under otherwise identical conditions (Table 4, entries 3−8).

Under these optimal conditions, we next examined many other 1-cyclopropyl-2-arylethanones **1j**−**o** with ethyl acetoacetate and the results of these experiments are outlined in Table 5. As can be seen from Table 5, the corresponding 2,3-dihydrobenzofuran-4-ol derivatives **3** were obtained in moderate yields, although as for 1-cyclopropyl-2-arylethanones **1n** and **1o** bearing an electron-donating group on the benzene ring, the corresponding 2,3-dihydrobenzofuran-4-ol derivatives **3f** and **3g** were obtained in 22% and 20% yields, respectively, presumably due to the electron-rich aromatic moiety not favoring the aldol-type reaction of the key intermediate **A′** with ethyl acetoacetate shown in Scheme 4 (Table 5, entries 6 and 7).

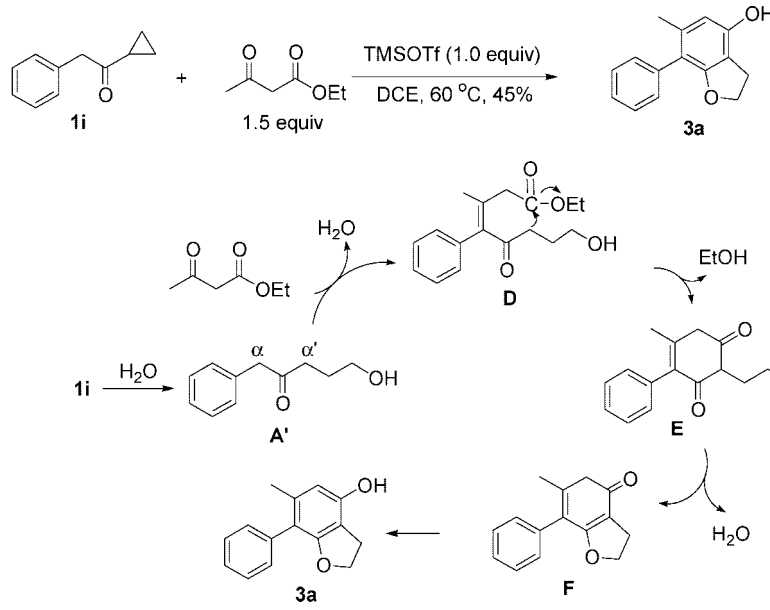
When using a large excess amount of ethyl acetoacetate (4.5 equiv) in this reaction under identical conditions, the corresponding dihydrofuro[2,3-*h*]chromen-2-one derivative **4a** was formed in 24% yield along with the formation of **3a** in 36% yield (Scheme 5). The structure of **4a** was further confirmed by an X-ray diffraction. Its CIF data and ORTEP drawing are presented in the Supporting Information. A plausible mechanism has been also shown in Scheme 5 via intermediates **D**, **G**, **H**, and **I**, which is very similar as the plausible mechanism shown in Scheme 3 in the TMSOTf-mediated reactions of 1-cyclopropyl-2-arylethanones **1** with allenic ester.

To confirm the reaction intermediate **A** or **A′** involved in the above reactions as shown in Schemes 2–5, we attempted to directly prepare 5-hydroxy-1-phenylpentan-2-one (intermediate **A′**) by another synthetic method and utilize it as the substrate

SCHEME 3. Reaction Mechanism on the Formation of Dihydrofuro[2,3-*h*]chromen-2-one and 2,3-Dihydrobenzofuran-4-ol Derivatives in the Reaction of 1-Cyclopropyl-2-arylethanones with Allenic Ester



SCHEME 4. TMSOTf-Mediated Reaction of 1-Cyclopropyl-2-arylethanone 1i with Ethyl Acetoacetate and the Plausible Reaction Mechanism



under these reaction conditions. According to the previous literature,[4] we first prepared 2-benzylidenetetrahydrofuran from lithiation of 2,3-dihydrofuran with *n*-butyllithium in THF and its reaction with benzyl bromide (Scheme 6). The obtained 2-benzylidenetetrahydrofuran (30% yield) was hydrolyzed by aqueous hydrochloric acid (20% w/w) to afford 5-hydroxy-1-phenylpentan-2-one in 95% yield (Scheme 6). The control experiment indicated that when using 5-hydroxy-1-phenylpen-

(4) Helma, M. B.; Alex, B. S.; Jan, C. *Tetrahedron* **1995**, *51*, 7495.

SCHEME 5. Reaction of 1i with Ethyl Acetoacetate (4.5 equiv) in the Presence of TMSOTf and the Plausible Reaction Mechanism

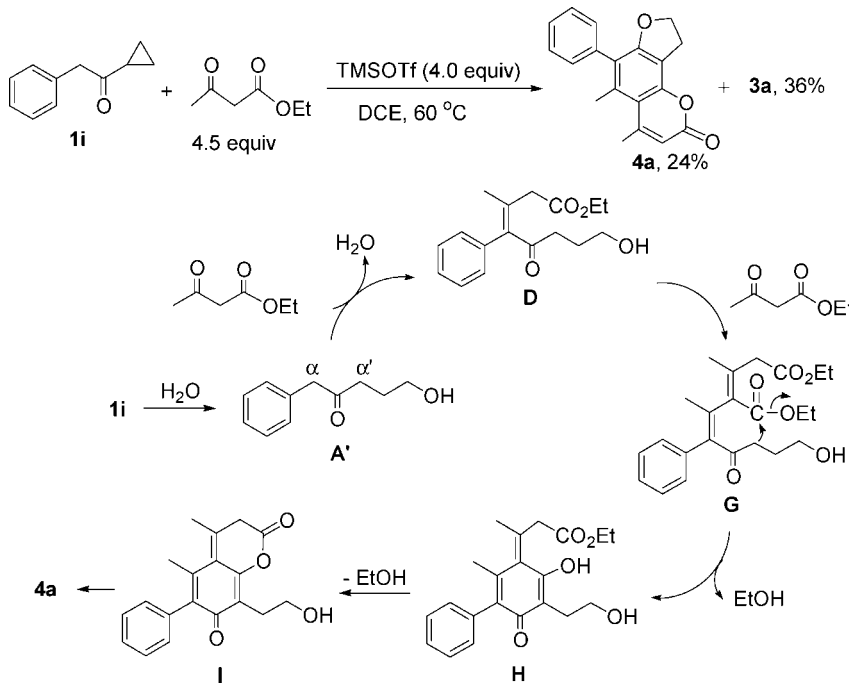
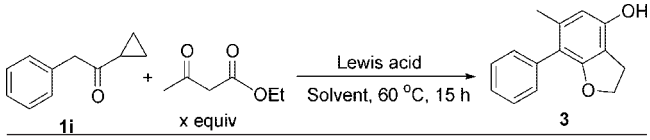


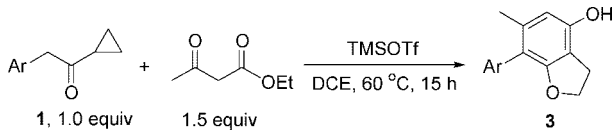
TABLE 4. Lewis Acid-Mediated Reactions of 1-Cyclopropyl-2-arylethanone 1i with Ethyl Acetoacetate



entry	*x*	Lewis acid	solvent	yield [%][a] of **3**
1	1.5	$SnCl_4$ (1.0 equiv)	DCE	20
2	1.5	$BF_3 \cdot Et_2O$ (1.0 equiv)	DCE	0
3	1.5	TMSOTf (1.0 equiv)	DCE	45
4	1.5	TMSOTf (1.0 equiv)	toluene	22
5	1.0	TMSOTf (2.0 equiv)	DCE	30
6	2.0	TMSOTf (2.0 equiv)	DCE	37
7	4.5	TMSOTf (4.0 equiv)	DCE	37
8	0.5	TMSOTf (1.0 equiv)	DCE	30

[a] Isolated yield.

TABLE 5. TMSOTf-Mediated Reactions of Various 1-Cyclopropyl-2-arylethanones 1 with Ethyl Acetoacetate



entry	Ar	yield [%][a] of **3**
1	**1i**, C_6H_5	**3a**, 45
2	**1j**, *p*-ClC_6H_4	**3b**, 49
3	**1k**, *p*-BrC_6H_4	**3c**, 40
4	**1*l***, *m*-BrC_6H_4	**3d**, 37
5	**1m**, *m*-FC_6H_4	**3e**, 33
6	**1n**, *m*-MeC_6H_4	**3f**, 22
7	**1o**, *p*-MeC_6H_4	**3g**, 20

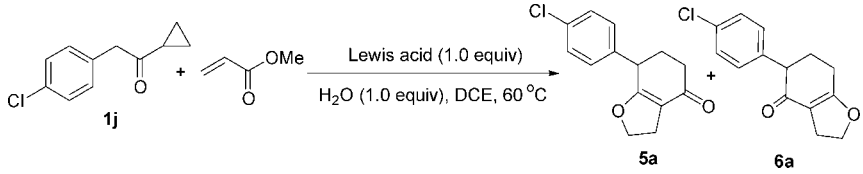
[a] Isolated yield.

tan-2-one (intermediate **A′**) as the substrate to react with allenic ester under the standard reaction conditions, the corresponding products **3a** and **4a** were indeed formed in 6% and 24% yields, respectively, suggesting that 5-hydroxy-1-phenylpentan-2-one (intermediate **A′**) could be the reaction intermediate in the above reactions shown in Schemes 2–5 (Scheme 6).

On the basis of these control experiments, we can conclude that the tandem reaction pathways shown in Schemes 2–5 for the formation of 6-methyl-3a,7-diphenyl-3,3a-dihydro-2*H*-benzofuran-4-one, dihydrofuro[2,3-*h*]chromen-2-one, and 2,3-dihydrobenzofuran-4-ol derivatives are reasonable and the Lewis acid-mediated ring-opening reaction of 1-cyclopropyl-2-arylethanone, intermolecular and intramolecular aldol reactions as well as aromatization are responsible for these transformations.

Moreover, we also attempted to explore the Lewis acid-mediated reactions of 1-cyclopropyl-2-arylethanones **1j**−**o** with methyl acrylate since we envision that a similar reaction pathway might be able to take place to provide interesting cyclized products as well. Using 1-cyclopropyl-2-(*p*-chlorophenyl)ethanone **1j** as the substrate, we initially examined the reactions with methyl acrylate in the presence of various Lewis acids to find out the best one in this transformation and the results of these experiments are summarized in Table 6. As can be seen, 7-(*p*-chlorophenyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one **5a** and 5-(*p*-chlorophenyl)-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one **6a** were obtained in 88% total yield as mixtures of regioisomers in the presence of $Bi(OTf)_2Cl$ (1.0 equiv) in DCE at 60 °C without addition of extra water (Table 6, entry 5). Other Lewis acids such as $Bi(OTf)_3$, $Gd(OTf)_3$, $Nd(OTf)_3$, and TMSOTf and Brønsted acid HOTf are not as effective as $Bi(OTf)_2Cl$ under identical conditions even in the presence of water (Table 6, entries 1−6). $BF_3 \cdot OEt_2$, $La(OTf)_3$, $Cu(OTf)_2$, and $AlCl_3$ did not catalyze this reaction under the standard conditions (Table 6, entries 7−10). To further optimize the reaction conditions, we next examined the solvent effects using $Bi(OTf)_2Cl$ as a Lewis acid, and the results of these experiments are shown in Table 7. As can be seen, when the reaction was carried out in

TABLE 6. Lewis Acid-Mediated Reactions of 1-Cyclopropyl-2-(*p*-chlorophenyl)ethanone 1j with Methyl Acrylate



entry	Lewis acid	yield [%][a] of (**5a**:**6a**)
1	$Bi(OTf)_3 \cdot 9H_2O$	76[c] (3.1:1)
2	HOTf	59 (3.9:1)
3	$Gd(OTf)_3$	44 (1.8:1)
4	$Nd(OTf)_3$	15[b]
5	$Bi(OTf)_2Cl$	88[c] (5.1:1)
6	TMSOTf	55 (1.7:1)
7	$BF_3 \cdot Et_2O$	0
8	$La(OTf)_3$	0
9	$Cu(OTf)_2$	0
10	$AlCl_3$	0

[a] Isolated yields. [b] Trace of 6a was obtained. [c] No water was added.

SCHEME 6. A Control Experiment

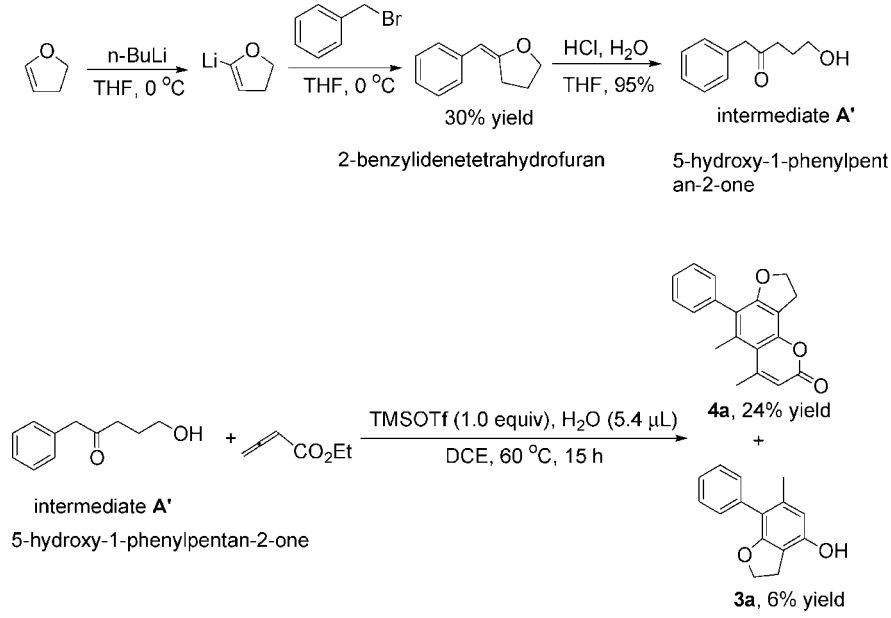
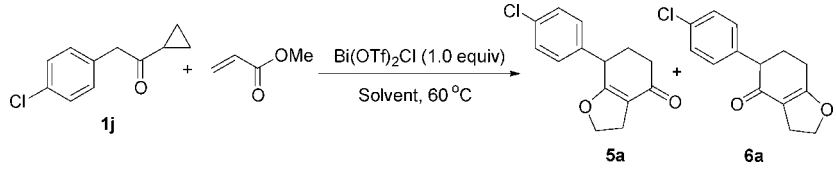


TABLE 7. Solvent Effects in the $Bi(OTf)_2Cl$-Mediated Reactions of 1-Cyclopropyl-2-phenylethanone 1j with Methyl Acrylate



entry	solvent	yield [%][a] of (**5a**:**6a**)
1	toluene	73 (2.9:1)
2	MeCN	no reaction
3	chlorobenzene	42 (5.2:1)
4	hexane	61 (2.6:1)
5	DCM	32[b]
6	toluene	45[c] (5.6:1)
7	THF	no reaction

[a] Isolated yields. [b] Trace of **6a** was obtained. [c] The reaction temperature was raised to 110 °C.

toluene, chlorobenzene, hexane, or DCM, **5a** and **6a** were obtained in lower yields (Table 7, entries 1 and 3−5). Using acetonitrile (MeCN) or tetrahydrofuran (THF) as the solvent, no reaction occurred (Table 7, entries 2 and 7). Even in toluene under reflux, **5a** and **6a** were obtained in 45% total yield (Table 7, entry 6). Therefore, the best conditions are to conduct the reaction in DCE using $Bi(OTf)_2Cl$ as a Lewis acid at 60 °C without addition of extra water.

SCHEME 7. A plausible Mechanism on the Formation of 5 and 6

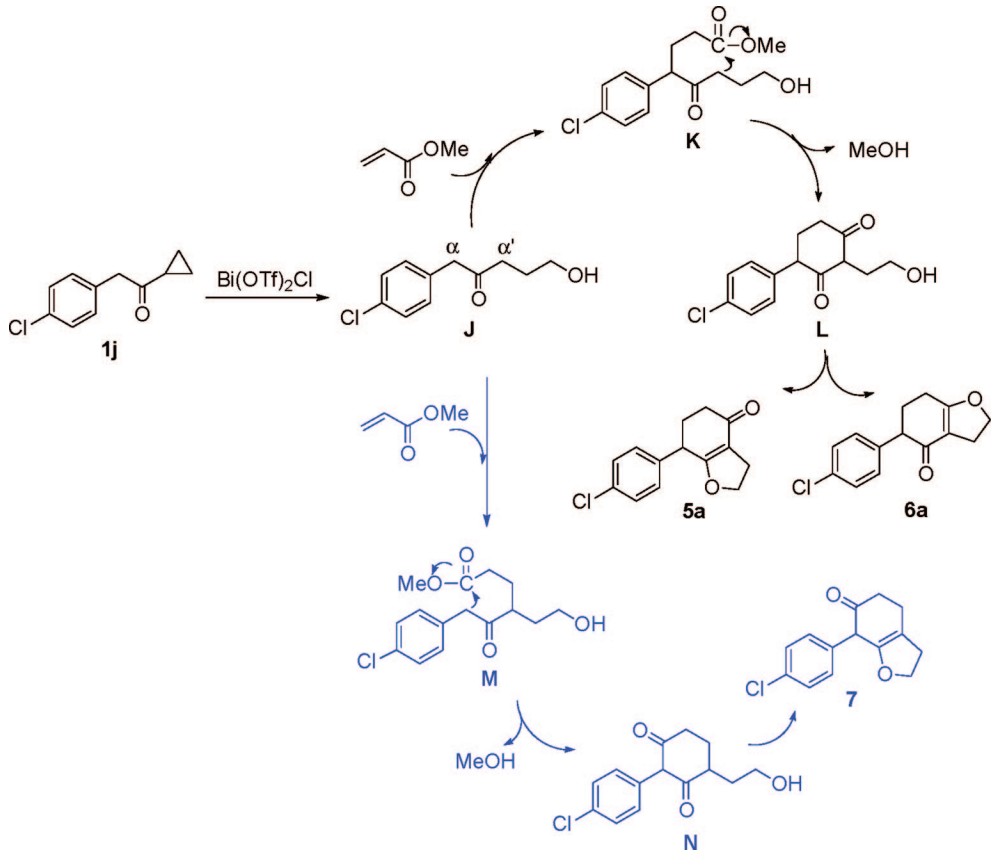
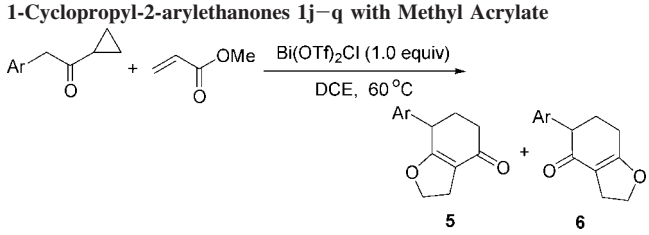


TABLE 8. $Bi(OTf)_2Cl$-Mediated Reactions of 1-Cyclopropyl-2-arylethanones 1j−q with Methyl Acrylate



entry	Ar	yield [%][a] (5:6)
1	**1i**, C_6H_5	83 (**5b**:**6b** = 1.2:1)
2	**1k**, *p*-BrC_6H_4	96 (**5c**:**6c** = 2.7:1)
3	**1l**, *m*-BrC_6H_4	84 (**5d**:**6d** = 2.6:1)
4	**1m**, *m*-FC_6H_4	60 (**5e**:**6e** = 0.7:1)
5	**1n**, *m*-$CH_3C_6H_4$	50 (**5f**:**6f** = 3.5:1)
6	**1o**, *p*-$CH_3C_6H_4$	48 (**5g**:**6g** = 2.3:1)
7	**1p**, *o*-BrC_6H_4	87 (**5h**:**6h** = 3.4:1)
8	**1q**, *m*-Cl, *p*-ClC_6H_3	98 (**5i**:**6i** = 3.2:1)

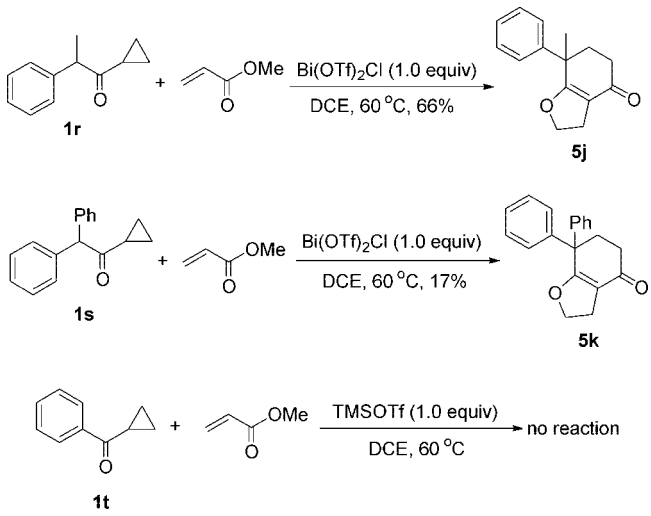
[a] Isolated yields.

With these optimal conditions in hand, we next examined the generality of this reaction with a variety of 1-cyclopropyl-2-arylethanones **1i** and **1k−q** and the results of these experiments are outlined in Table 8. The corresponding products **5** and **6** were obtained in moderate to high total yields whether there was an electron-withdrawing or an electron-donating group on the benzene ring of **1** (Table 8, entries 1−8). Adding a moderately electron-donating methyl group on the benzene ring of **1n** and **1o** afforded the products in moderate yields (Table 8, entries 5 and 6). The structures of **5** and **6** were determined by ^1H and ^{13}C NMR spectroscopic data and HRMS analytic data (Supporting Information). Moreover, the structure of **5c** was determined unambiguously by X-ray diffraction. Its CIF data and ORTEP drawing are also presented in the Supporting Information.

A plausible mechanism for the formation of **5** and **6** is outlined in Scheme 7 with **1j** as a model. Similarly, the reaction of **1j** with a trace of ambient water generates 1-(4-chlorophenyl)-5-hydroxypentan-2-one intermediate **J** in the presence of Lewis acid.[3] Michael addition of intermediate **J** from the C_α-position with methyl acrylate in the presence of Lewis acid produces intermediate **K**. The subsequent intramolecular aldol reaction from the $C_{\alpha'}$-position affords intermediate **L**. Intramolecular cyclization with two different carbonyl groups and the subsequent dehydration produce compounds **5a** and **6a**, respectively. On the other hand, it should be noted that 7-(4-chlorophenyl)-3,4,5,7-tetrahydro-2*H*-benzofuran-6-one **7** could not be detected in this reaction via intermediates **M** and **N**, suggesting that Michael addition from the $C_{\alpha'}$-position is unable to take place, presumably due to a reactive enol from the $C_{\alpha'}$ position being hard to form in the presence of Lewis acid under these reaction conditions (Scheme 7).

To clarify the reaction mechanism, several control experiments were carried out under the standard conditions (Scheme 8). We found that in the reaction of 1-cyclopropyl-2-phenylpropan-1-one **1r** and 1-cyclopropyl-2,2-diphenylethanone **1s** having a substituent at the C_α-position with methyl acrylate, the corresponding products **5j** and **5k** were obtained in 66% and 17% yields, respectively, indicating that Michael addition of intermediate **A** in Scheme 2 or intermediate **J** in Scheme 7 from the C_α-position with methyl acrylate is a preferred process in this transformation and a sterically bulky sub-

SCHEME 8. Control Experiment



stituent at the C_α-position of **1r** and **1s** can partially retard the reaction rate to give the corresponding products in low yields. Moreover, by using cyclopropylphenylmethanone **1t** as the substrate under the standard conditions, no reaction occurred, suggesting that a methylene or methine moiety between the aromatic group and the carbonyl group is required (Scheme 8).

In conclusion, we have found a reaction process involving the sequential ring-opening reaction of cyclopropyl alkyl ketones by H_2O, followed by one intermolecular aldol-type reaction with allenic esters and two intramolecular aldol-type reactions, a cyclic transesterification along with a dehydration and aromatization mediated by Lewis acids, which affords an efficient synthetic protocol for the preparation of dihydrofuro[2,3-*h*]-chromen-2-one derivatives. Further work directed at elucidation of the detailed mechanisms of this process and the application of it to the synthesis of dihydrofuro[2,3-*h*]chromen-2-one containing natural products is currently in progress.

Experimental Section

General Procedure for the Reaction of 2-Phenyl-1-(1-phenylcyclopropyl)ethanone with Ethyl Buta-2,3-dienoate. 2-Phenyl-1-(1-phenylcyclopropyl)ethanone **1a** (71 mg, 0.3 mmol), ethyl buta-2,3-dienoate (50.4 mg, 0.45 mmol), TMSOTf (54 μL, 0.3 mmol), and DCE (3.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C for 12 h. The solvent was removed under reduced pressure and then the residue was purified by a flash column chromatography (Table 1, entry 1).

6-Methyl-3a,7-diphenyl-3,3a-dihydrobenzofuran-4(2*H*)-one 2a. A yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.85 (d, 3H, J = 0.9 Hz), 2.56−2.61 (m, 2H), 3.96 (dd, 1H, J = 15.8 Hz, J = 9.0 Hz), 4.34−4.40 (m, 1H), 5.58 (d, 1H, J = 0.9 Hz), 7.34−7.47 (m, 8H), 7.62 (dd, 2H, J = 8.0 Hz, J = 1.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 22.4, 35.4, 63.2, 70.9, 110.5, 117.3, 126.4, 127.4, 128.3, 128.4, 128.9, 130.2, 134.4, 137.0, 159.0, 166.4, 199.5; IR (CH_2Cl_2) ν 3057, 2924, 2851, 1674, 1537, 1492, 1380, 1265, 991 cm^{-1}; MS (EI) *m*/*z* (%) 302 [M$^+$] (100), 303 (26.9), 274 (23.3), 259 (21.0), 231 (32.0), 129 (28.8), 128 (24.0), 115 (33.5); HRMS (EI) calcd for $C_{21}H_{18}O_2$ (M$^+$) requires 302.1307, found 302.1306.

General Procedure for the Reaction of 1a with Ethyl Acetoacetate (Ethyl 3-Oxobutanoate). 1-Cyclopropyl-2-phenylethanone **1i** (48 mg, 0.3 mmol), ethyl acetoacetate (ethyl 3-oxobutanoate) (58.5 mg, 0.45 mmol), TMSOTf (54 μL, 0.3 mmol), and DCE (3.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C for 15 h. The solvent was removed under reduced pressure and then the residue was purified by flash column chromatography (Table 5, entry 1).

6-Methyl-7-phenyl-2,3-dihydrobenzofuran-4-ol (3a). A yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.11 (s, 3H), 3.17 (t, J = 8.6 Hz, 2H), 4.56 (t, J = 8.6 Hz, 2H), 4.92 (s, 1H), 6.28 (s, 1H), 7.26−7.33 (m, 3H), 7.38−7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 20.0, 27.0, 71.7, 109.3, 109.7, 117.4, 126.8, 128.1, 130.2, 136.4, 137.3, 151.0, 159.4; IR (CH_2Cl_2) ν 3411, 2957, 2856, 1706, 1619, 1453, 1421, 1306, 1126, 1048, 702 cm^{-1}; MS (EI) *m*/*z* (%) 226 (100) [M$^+$], 225 (32.2), 211 (26.5), 227 (17.6), 197 (14.9), 165 (10.8), 183 (10.4), 115 (10.2); HRMS (EI) calcd for $C_{15}H_{14}O_2$ (M$^+$) requires 226.0994, found 306.0996.

General Procedure for the Lewis Acid-Catalyzed Reaction of 1-Cyclopropyl-2-arylethanone 1 with Methyl Acylate. 1-Cyclopropyl-2-phenylethanone **1i** (48 mg, 0.3 mmol), methyl acylate (129 mg, 1.5 mmol), $Bi(OTf)_2Cl$ (162.6 mg, 0.3 mmol), and DCE (3.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C for 12 h. The solvent was removed under reduced pressure and then the residue was purified by flash column chromatography (Table 8, entry 1).

7-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one, 5b. A yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.02−2.17 (m, 1H), 2.34−2.51 (m, 3H), 2.86−2.03 (m, 2H), 3.81−3.83 (m, 1H), 4.57 (t, J = 9.3 Hz, 2H), 7.22 (d, J = 7.2 Hz, 2H), 7.26−7.38 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 26.0, 31.4, 35.0, 41.1, 73.2, 114.7, 127.4, 127.7, 128.8, 138.9, 177.9, 195.4; IR (CH_2Cl_2) ν 2953, 2926, 1732, 1651, 1599, 1494, 1409, 1235, 1078, 964, 820 cm^{-1}; MS (EI) *m*/*z* (%) 214 [M$^+$] (39.8), 186 (40.9), 110 (100.0), 105 (68.6), 77 (50.7), 55 (22.1), 51 (26.3), 43 (17.3); HRMS (EI) calcd for $C_{14}H_{14}O_2$ (M$^+$) requires 214.0994, found 214.1010.

5-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one, 6b. A yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 2.23−2.39 (m, 2H), 2.47−2.52 (m, 2H), 2.88−2.95 (m, 2H), 3.58 (dd, J = 9.0 Hz, J = 7.8 Hz, 1H), 4.63 (t, J = 9.6 Hz, 2H), 7.17−7.25 (m, 2H), 7.30−7.35 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ 22.8, 26.1, 30.0, 51.7, 73.4, 113.9, 126.8, 128.3, 128.5, 139.9, 177.6, 195.0; IR (CH_2Cl_2) ν 2961, 2853, 1738, 1683, 1597, 1495, 1407, 1262, 1079, 961, 820 cm^{-1}; MS (EI) *m*/*z* (%) 214 [M$^+$] (30.1), 186 (11.8), 110 (100), 77 (10.9), 57 (15.6), 54 (10.9), 52 (11.5), 43 (13.3); HRMS (EI) calcd for $C_{14}H_{14}O_2$ (M$^+$) requires 214.0994, found 214.1010.

Acknowledgment. We thank the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005) and the National Natural Science Foundation of China for financial support (20472096, 203900502, 20672127, and 20732008).

Supporting Information Available: Spectroscopic data of all new compounds, detailed descriptions of experimental procedures, and the X-ray data for compounds **2c**, **4a**, and **5c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800608H