

# An Efficient Bismuth(III) Chloride-Catalyzed Synthesis of 1,1-Diaryllkenes *via* Friedel–Crafts Reaction of Acyl Chloride or Vinyl Chloride with Arenes

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**Abstract:** In the presence of catalytic amount of bismuth(III) chloride, the reactions of acyl chlorides or vinyl chlorides with arenes afforded 1,1-diaryllkenes in 25–82 % isolated yield. In the case of the reaction of acyl chlorides with arenes, the procedure includes an initial Friedel–Crafts acylation, subsequent formation of vinyl chlorides and final Friedel–Crafts-type vinylation of another arene molecule

with vinyl chloride. This paper reports the first Lewis acid-catalyzed cleavage of the C–Cl bond of vinyl chloride and its application in the synthesis of multiply substituted alkenes.

**Keywords:** acyl chlorides; arenes; bismuth(III) chloride; 1,1-diaryllkenes; Friedel–Crafts reaction; vinyl chlorides

## Introduction

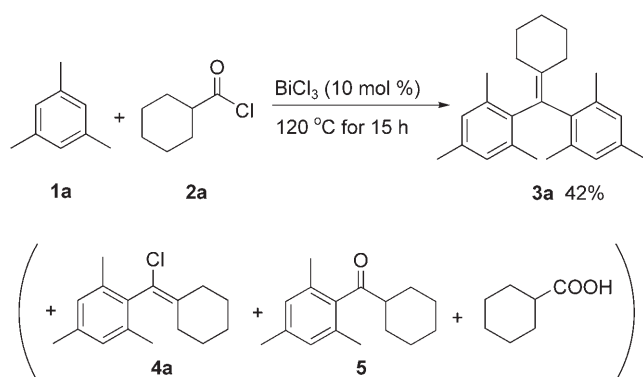
1,1-Diaryllkenes are an important class of organic compounds, which are useful intermediates in organic synthesis, particularly in the preparation of fluorescent materials.<sup>[1]</sup> Some of 1,1-diaryllkene moiety-containing compounds have physiological and biological activities.<sup>[2]</sup> 1,1-Diaryllkenes are usually synthesized through multistep reactions, thus the development of simple, efficient methods is still an interesting and significant subject of organic synthesis.

Because bismuth(III) salts such as BiCl<sub>3</sub>,<sup>[3]</sup> BiBr<sub>3</sub>,<sup>[4]</sup> Bi(OTf)<sub>3</sub>,<sup>[5]</sup> and Bi(NO<sub>3</sub>)<sub>3</sub><sup>[6]</sup> are stable in air, relatively non-toxic and inexpensive when compared with transition metal complexes, in recent years the diverse applications of bismuth(III) salts as catalysts in organic synthesis have been reported. In this work, with the purpose of developing new synthetic methods for 1,1-diaryllkenes from simple and easily available starting materials, we investigated the reactions of acyl chlorides with arenes in the presence of catalytic amounts of BiCl<sub>3</sub>, in which 1,1-diaryllkenes were obtained instead of normal Friedel–Crafts acylation products. The results reported in this paper disclose an unprecedented Friedel–Crafts-type vinylation of arenes in which the C–Cl bond of vinyl chlorides is catalytically

cleaved by Lewis acids (BiCl<sub>3</sub>). To the best of our knowledge, there has been no report on a Lewis acid-catalyzed cleavage of the C–Cl bond of vinyl chloride for Friedel–Crafts-type vinylation, although the transition metal-catalyzed cleavage of the C–Cl bond and its application in C–C bond formation have been well documented.<sup>[7]</sup>

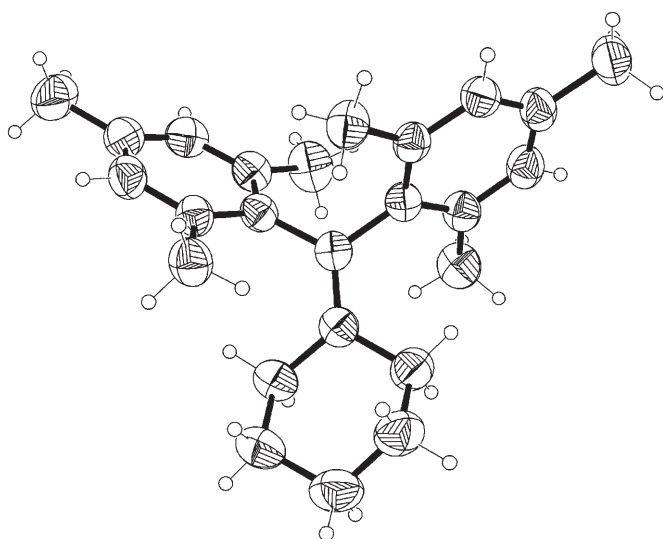
## Results and Discussion

Friedel–Crafts acylation is an important reaction for the preparation of aryl ketones. In the course of our study on the development of the BiCl<sub>3</sub>-catalyzed Friedel–Crafts acylation of mesitylene (**1a**) with cyclohexanecarbonyl chloride (**2a**) (Scheme 1), we have found that when a mixture of **1a** (4.0 mmol), **2a** (2.0 mmol) and BiCl<sub>3</sub> (0.2 mmol) was heated at 120 °C with stirring for 16 h, the reaction produced an unidentified compound **3a** as major product, along with the formation of a small amount of [chloro-(2,4,6-trimethylphenyl)-methylene]-cyclohexane (**4a**) (<5%), a trace amount of the expected cyclohexylmesitylmethanone (**5**), and a considerable amount of cyclohexanecarboxylic acid as confirmed by GC and GC-MS analyses. Compound **3a** was isolated in 42 % yield,<sup>[8]</sup> and



Scheme 1.

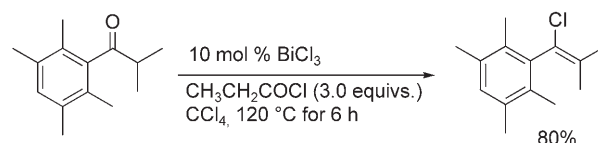
showed a molecular ion peak at  $m/z=332$ . Both  $^{13}\text{C}$  NMR and IR spectra indicate that **3a** does not contain a ketone group. The structure of **3a** was finally determined by X-ray crystallography and shown in Figure 1.<sup>[9]</sup> A noteworthy feature in the conformation of **3a** is that the two aryl groups are not coplanar.

Figure 1. Crystal structure of **3a**.

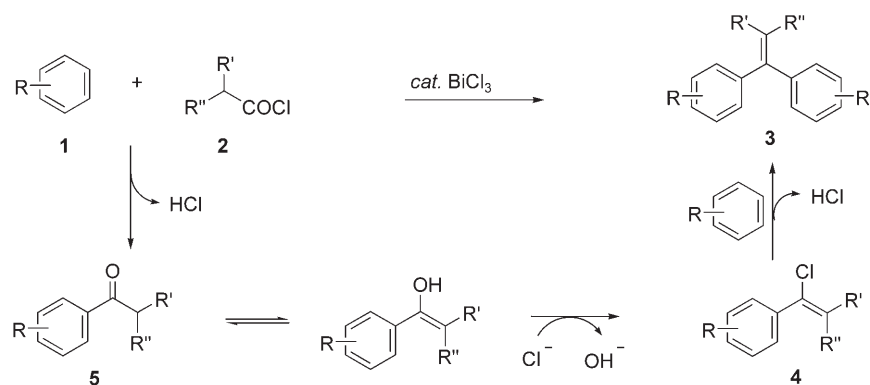
In order to elucidate the route of the formation of **3a**, under the same reaction conditions, the reaction of **1a** with **5** was examined, and **3a** was not formed at all, both **1a** and **5** were recovered completely. Furthermore, we also carried out the reaction of **1a** with **2a** in a sealed tube with an HCl saturated solution at 120 °C for 10 h, the formation of **3a** could not be detected by GC and GC-MS.

Therefore, the present one-pot formation of **3a** from the reaction of **1a** with **2a** indicates the generation of the vinyl chloride in the reaction mixture, and the proposed reaction route is shown in Scheme 2. It involves the initial Friedel–Crafts acylation of arene with acyl chloride to produce aryl ketone (**5**), and then HCl or acyl chloride converts this to the vinyl chloride (**4**), and the final Friedel–Crafts-type vinylation of **4** with another arene molecule to afford **3**. This new catalytic procedure disclosed two interesting transformations: (1) the formation of vinyl chloride from a ketone; (2) the Friedel–Crafts-type vinylation of an arene in the presence of  $\text{BiCl}_3$ .

It had been reported that aryl ketones could be converted into vinyl chlorides by the reactions of aryl ketones with acetyl chloride in the presence of silica gel-supported  $\text{ZnCl}_2$ .<sup>[10]</sup> In order to get the substantial evidence to confirm the formation of vinyl chlorides in the present  $\text{BiCl}_3$ -catalyzed reaction, we have also examined the reaction of aryl ketones with acyl chlorides, and disclosed that  $\text{BiCl}_3$  is an efficient catalyst for the transformation of aryl ketones into vinyl chlorides. For example, when 2,3,5,6-tetramethyl-isobutyrophenone and propionyl chloride in  $\text{CCl}_4$  were heated at 120 °C for 6 h in the presence of  $\text{BiCl}_3$ , the corresponding vinyl chloride was obtained in good yield (Scheme 3).

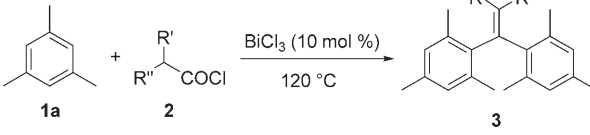


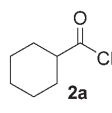
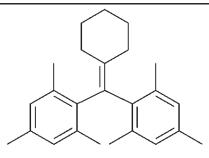

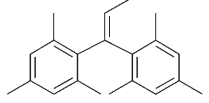
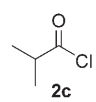
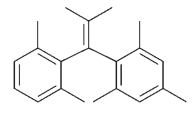
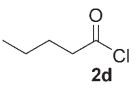
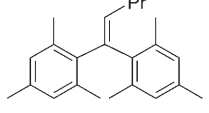
Scheme 3.

Scheme 2. Proposed mechanism for the formation of **3**.

In order to determine the scope and limitation of this new catalytic reaction, the reactions of **1a** with several acyl chlorides **2** were examined. The reaction progress was monitored by GC, and the time indicated in Table 1 was the optimal reaction time. As

**Table 1.** BiCl<sub>3</sub>-catalyzed reaction of mesitylene with acyl chlorides.<sup>[a]</sup>



Entry	Acyl chloride	Time [h]	Product <b>3</b>	Isolated yield [%] <sup>[b]</sup>
1		16		42
2		10		62
3 <sup>[c]</sup>	<b>2b</b>	10	<b>3b</b>	61
4		12		25 (34)
5		14		63

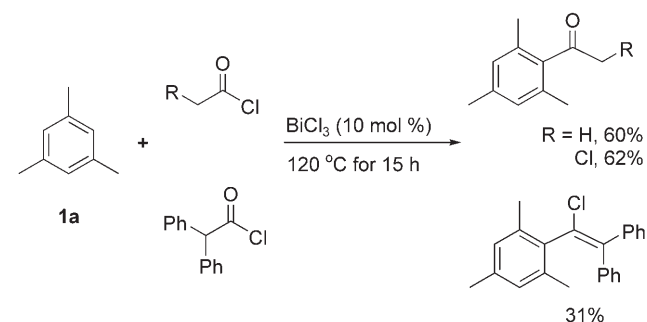
<sup>[a]</sup> Reactions were carried out using 4 mmol of **1a**, 2 mmol of **2** and 0.2 mmol of catalyst.

<sup>[b]</sup> Based on the amount of **2** used. Values in parentheses are GC yields.

<sup>[c]</sup> BiBr<sub>3</sub> was used as catalyst.

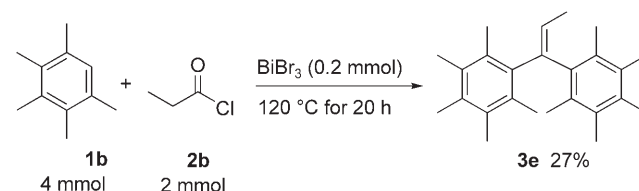
shown in Table 1,  $\alpha$ -monosubstituted acyl chlorides showed higher reactivity than  $\alpha,\alpha$ -disubstituted ones. Thus the reaction of **1a** with **2b** afforded **3b** in 62 % yield (Table 1, entry 2). Repeating the same reaction using BiBr<sub>3</sub> as catalyst resulted in the similar result, indicating that both BiCl<sub>3</sub> and BiBr<sub>3</sub> displayed the similar catalytic activity (Table 1, entry 3). In the case of isobutyryl chloride (**2c**), the corresponding tetra-substituted alkene **3c** was obtained in only 25 % (34 % GC yield, Table 1, entry 4). As expected, **2d** showed reactivity similar to that of **2b** to produce **3d** in 63 % yield (Table 1, entry 5). The formation of **3b** and **3d** in higher yields was considered to be due to the lower steric hindrance of their structures.

In addition, we have performed the reactions of **1a** with acetyl chloride, chloroacetyl chloride, and diphenylacetyl chloride. However, acetyl chloride and chloroacetyl chloride proceeded by the normal Friedel–Crafts acylation to give the corresponding acyl ketones in 60 % and 62 % isolated yields, respectively, and the reaction of diphenylacetyl chloride produced the vinyl chloride-type compound as major product (31 % isolated yield). Only trace amounts of **3**-type compounds were found in the reaction mixtures (Scheme 4).



**Scheme 4.**

Pentamethylbenzene (**1b**) is a more nucleophilic substrate than **1a**, but unexpectedly, the reaction of **1b** with **2b** in the presence of BiBr<sub>3</sub> at 120 °C for 20 h gave the product **3e** in only 27 % yield (Scheme 5).

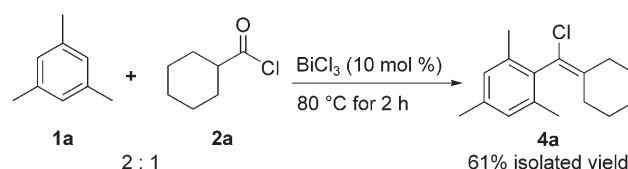


**Scheme 5.**

Furthermore, under the reaction conditions as indicated in Table 1, the reactions of a variety of other arenes such as 2-bromomesitylene, 1,2,4,5-tetramethylbenzene, *m*-xylene and toluene could not produce the corresponding 1,1-diarylalkenes **3** at all.

Although many attempts including changing the ratio of reactants, performing the reactions at different temperatures and using different bismuth salts as catalysts have been made with the purpose to improve the yield of **3** in the reactions included in Table 1, little improvement was achieved. Therefore, we next turned our attention to the reaction of vinyl chloride **4** with arenes to develop the Friedel–Crafts-type vinylation and the general synthetic method to make 1,1-diarylalkenes **3** in the presence of BiCl<sub>3</sub>.

We initiated our studies on the synthesis of vinyl chloride **4** with the same reaction as described above by changing the reaction conditions. Fortunately, when the reaction of **1a** with **2a** was carried out at a lower temperature (at 80 °C) and a shortened reaction time (2 h), **4a** was formed as a major product and could be isolated from the reaction mixture in 61 % yield (Scheme 6). Next, we investigated the reactions of **4a** with a variety of arenes (4.0 equivs.) in the presence of BiCl<sub>3</sub>. As shown in Table 2, the reaction of **4a** with **1a** in the presence of BiCl<sub>3</sub> at 120 °C for 16 h afforded **3a** in a good isolated yield (62 %, Table 2, entry 1). However, the reaction of **4a** with **1b** gave **3f** also in a low yield (Table 2, entry 2), similar to the re-



Scheme 6.

action shown in Scheme 5. The reaction of **4a** with **1c** produced a mixture of **3g** and **3g'** in a ratio of 84:16 (Table 2, entry 3).<sup>[11]</sup> Notably, in the cases of **1d–g** used, the reactions proceeded with high selectivity to generate the 1,1-diaryl alkenes **3h–k** in good yields (Table 2, entries 4–7). In the reaction of **4a** with **1h**,

Table 2. BiCl<sub>3</sub>-catalyzed Friedel–Crafts-type vinylation of arenes.<sup>[a]</sup>

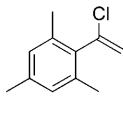
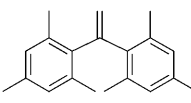
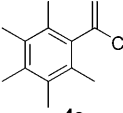
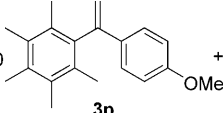
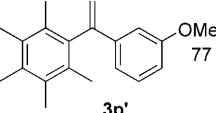
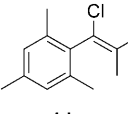
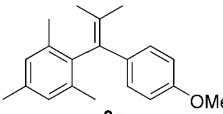
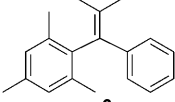
Entry	Arene	Time [h]	Aryl	Isolated yield (GC) [%] <sup>[b]</sup>	
1	<b>1a</b>	16		62(71)	
2	<b>1b</b>	24		29(37)	
3	<b>1c</b>	18	<b>3g</b>	56 ( <b>3g</b> : <b>3g'</b> = 84:16)	
4	<b>1d</b>	20		72	
5	<b>1e</b>	6		72 (selectivity: 98%)	
6	<b>1f</b>	10		67	
7	<b>1g</b>	13		74 (selectivity: 92%)	
8	<b>1h</b>	10	<b>3l</b>	69 ( <b>3l</b> : <b>3l'</b> = 79:21)	
9 <sup>[c]</sup>	<b>1i</b>	16		64	
10	<b>1j</b>	10	<b>3n</b>	80 ( <b>3n</b> : <b>3n'</b> = 55:45)	

<sup>[a]</sup> Reactions were carried out using 4 mmol of **1a**, 2 mmol of **2** and 0.2 mmol of catalyst.

<sup>[b]</sup> Based on the amount of **4a** used. Values in parentheses are GC yields. Selectivity is the ratio of the major product to the other product(s) in the reaction mixture.

<sup>[c]</sup> At 150 °C in a sealed glass tube using 0.5 mL of benzene.

**Table 3.** BiCl<sub>3</sub>-catalyzed Friedel–Crafts-type vinylation of arenes.<sup>[a]</sup>

Entry	Vinyl chloride	Arene	Time [h]	Product <b>3</b>	Isolated yield <sup>[b]</sup>
1		<b>1a</b>	16		80
2		<b>1e</b>	10	 +  3p:3p' = 79:21	77
3		<b>1e</b>	10		77 (selectivity: 95%)
4 <sup>[c]</sup>	<b>4d</b>	<b>1i</b>	24		82

<sup>[a]</sup> Reactions were carried out using 4 mmol of **1a**, 2 mmol of **2** and 0.2 mmol of catalyst.

<sup>[b]</sup> Based on the amount of **4** used. Selectivity is the ratio of the major product to the other product(s) in the reaction mixture.

<sup>[c]</sup> At 150 °C in a sealed glass tube using 0.5 mL of **1i**.

two isomers were formed in a ratio of 79:21 (Table 2, entry 8), the structure of **3p'** was tentatively assigned by compared with the results of the reaction of  $\alpha$ -chloro-2,3,4,5,6-pentamethylstyrene (**4c**) with **1e** (vide Table 3, entry 2). In addition, the reactions of **4a** with the electron-neutral arenes also occurred smoothly. Thus, benzene (**1i**) reacted with **4a** to give **3m** in 64 % yield (Table 2, entry 9), and naphthalene (**1j**) afforded the corresponding vinyated products, **3n** and **3n'**, in 80 % yield in a ratio of 55:45 (Table 2, entry 10). Because attempts to separate **3n** and **3n'** failed, again, we tentatively assigned the  $\beta$ -substituted naphthalene **3n** as the major product on the basis of the higher reactivity of the  $\beta$ -position of naphthalene in Friedel–Crafts alkylation.

It should be noted that, under the present reaction conditions, the electron-deficient arenes could not undergo a similar vinylation reaction.

Furthermore, three other vinyl chlorides were prepared and their reactivity with arenes were also examined. As demonstrated in Table 3, the reaction of  $\alpha$ -chloro-2,4,6-trimethylstyrene (**4b**) with **1a** afforded **3o** in 80 % isolated yield (Table 3, entry 1). The formation of **3o** in a higher yield (80 %) than **3a** (62 %) by the reaction of **4a** with **1a** might be due to the lower steric hindrance of **3o** (Table 3, entry 1 vs. Table 2, entry 1). The reaction of **4c** or 1-chloro-1-mesityl-2-methylpropene (**4d**) with **1e** displayed significantly different selectivity. The former afforded a mixture of

products **3p** and **3p'** in a ratio of 79:21 in 77 % total yield (Table 3, entry 2), while the latter gave **3q** in a high selectivity (Table 3, entry 3). These results indicated that in the case of the trisubstituted vinyl chloride (e.g., **4d**) used, the formation of **3p'**-type compound was unfavorable due to the steric hindrance. Compound **3p** and **3p'** could be separated by careful two-fold preparative TLC separation, and the structure of **3p'** obtained from the vinylation of the *meta*-position of **1e** with **4c** was confirmed by its <sup>1</sup>H NMR spectroscopic data (see Supporting Information). In addition, in a sealed tube, **4d** reacted with **1i** at an elevated temperature (150 °C) in the presence of BiBr<sub>3</sub> resulting in the formation of **3r** in 82 % yield (Table 3, entry 4).

## Conclusions

In conclusion, we investigated the reactions of arenes with acid chlorides or with vinyl chlorides in the presence of BiCl<sub>3</sub>. The present catalytic procedure provides a one-pot synthetic method for the synthesis of various 1,1-diaryllkenes. The reaction includes both the unusual formation of vinyl chlorides and the Friedel–Crafts-type vinylation of arenes catalyzed by BiCl<sub>3</sub>. Further studies to develop another new catalytic C–C bond formation using bismuth(III) salts as catalysts are now in progress.



## Experimental Section

### General Methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL JNM-ECA 300 spectrometer at 300 MHz and 75 MHz, respectively. The chemical shifts ( $\delta$ ) were referenced to TMS or internal solvent resonance. GC-MS was obtained on a Hewlett Packard Series II 5890 GC/MS spectrometer. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer in the Department of Chemistry of Beijing University. GC analyses were performed on an Agilent Technologies 1790 GC instrument. All reactions were carried out under air. Solvents and all reagents were used as received.

### Typical Procedure for the Synthesis of 1,1-Diaryllkenes from the Reaction of Arenes with Acyl Chlorides: Formation of **3a** (Table 1, entry 1)

A mixture of mesitylene (**1a**) (480.0 mg, 4.0 mmol), cyclohexanecarbonyl chloride (**2a**) (293.0 mg, 2.0 mmol) and  $\text{BiCl}_3$  (63.0 mg, 0.2 mmol) was heated with stirring at 120 °C for 16 h. After cooling to room temperature, cyclohexane (15 mL) was added and the insoluble materials were filtered out. Removal of the solvent and volatiles under reduced pressure afforded a viscous residue, which was dissolved in  $\text{CH}_2\text{Cl}_2$  (3.0 mL), and the resulting solution was subjected to preparative TLC (silica) separation using a mixture of diethyl ether and cyclohexane (2:100 v/v) to afford **3a** as a white solid; yield: 269.0 mg (0.84 mmol, 42.0%). Recrystallization of **3a** from hot ethanol gave crystals suitable for X-ray diffraction analysis.

### Typical Procedure for Friedel–Crafts-Type Vinylation: Reaction of **1a** with **4a** Affording **3a** (Table 2, entry 1)

A mixture of vinyl chloride (**4a**, 248.0 mg, 1.0 mmol), **1a** (480.0 mg, 4.0 mmol) and  $\text{BiCl}_3$  (32.0 mg, 0.1 mmol) was heated with stirring at 120 °C for 16 h. After treatment as described above, **3a** was obtained in 62% yield.

Characterization data of **3a–r** and **4a–d** are given in the Supporting Information.

## Acknowledgements

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