A facile and efficient synthesis of aryltrialkoxy silanes via sonochemical Barbier-type reaction

Adam Shih-Yuan Lee,* Yu-Ting Chang, Shu-Fang Chu and Kuo-Wei Tsao

Department of Chemistry, Tamkang University, Tamsui, Taipei 251, Taiwan

Received 23 June 2006; revised 13 July 2006; accepted 18 July 2006
Available online 14 August 2006

Abstract—A series of aryltrialkoxy silanes was synthesized from the reaction mixture of aryl bromide, Mg powder, 1,2-dibromoethane and tetraethyl orthosilicate in THF under ultrasound. This sonochemical Barbier-type reaction provides a simple and efficient method for preparation of aryltrialkoxy silanes. The Hiyama cross-coupling reaction of phenyltriethoxysilane with bromobenzene was investigated under different palladium catalysts and Pd(PhCN)_2Cl_2 was found to be the best choice.

© 2006 Elsevier Ltd. All rights reserved.

The transition metal catalyzed Stille1–4 and Suzuki–Miyaura5–8 cross-coupling reactions are one of the most extensively employed methods for the synthesis of biologically active compounds and useful synthetic intermediates such as unsymmetric biaryl and alkencyl derivatives. Recently, arylsilane compounds have increasingly played an important role and emerged as a powerful reagent for palladium-catalyzed Hiyama9–18 cross-coupling reactions with conventional organohalides. The arylsiloxane molecules avoid the inherent limitations which are associated with traditional methodologies such as organostannanes (Stille) and byproducts are toxic, and organoboranes (Suzuki) are difficult to be synthesized and purified. The reported synthetic methods of arylsiloxane in the literatures fall into two categories: (1) treatment of organomagnesium (Grignard) reagents or organolithium reagents with silicon compounds19 and (2) silylation of aryl iodides by trialkoxy silane in the presence of palladium catalysts.20,21 The metalloid reaction method is limited by the formation difficulties of arylmetaloids and generally inferior yields of siloxane. The Pd-mediated silylation method is limited due to the difficult synthesis of aryl iodides and only electron rich, para-substituted aryl iodides afford good yield of arylsiloxane. The simple and efficient preparation of aryltrialkoxy silane is a prerequisite for further transformation with a view for the application of Pd-catalyzed Hiyama cross-coupling reactions in organic synthesis. Recently, DeShong’s laboratory have reported the synthesis of aryltrialkoxy silanes from aryl Grignard and organolithium reagents with tetraalkyl orthosilicate.19 The synthesis of arylsiloxanes via Grignard reagent was limited by the formation of diarylated (Ar_2Si(OR)_2) and triarylated silanes (Ar_3Si(OR)). DeShong and co-workers found that Grignard silylation reaction which was proceeded at much lower temperature of −30 °C gave predominately monoaryl siloxanes. Our previous studies have shown that Barbier-type reactions were improved and successfully achieved by introducing ultrasound.22–24 Thus, we investigated the additional reaction of aryl bromide with tetraethyl orthosilicate under sonochemical Barbier-type reaction condition. Herewith, we wish to report a simple and efficient method for synthesis of aryltrialkoxy silanes at room temperature under sonochemical Barbier-type reaction condition (Scheme 1).

To a reaction mixture of magnesium powder (2.5 mmol), 1,2-dibromoethane (1.0 mmol) and tetraethyl orthosilicate in anhydrous THF was added dropwise para-methoxyphenyl bromide (1.0 mmol) under ultrasound and the reaction mixture was continuously sonicated at room temperature for 30 min. The monoarylated product (22%) was obtained with a mixture of polyarylated silanes (Scheme 2). The highest yield (65%) was obtained when less amount of...
1,2-dibromoethane (0.5 equiv) and more amount of tetraethyl orthosilicate (5.0 equiv) were introduced under the reaction condition.

An exothermic phenomenon was observed when 1,2-dibromoethane was introduced to the reaction mixture. Thus, we rearranged the additional order of 1,2-dibromoethane to avoid the suddenly increasing temperature during reaction. To a reaction mixture of magnesium powder (3.0 mmol) and tetraethyl orthosilicate (5.0 mmol) in THF (4 mL) was added dropwise a solution of para-methoxyphenyl bromide (1.0 mmol) and 1,2-dibromoethane (0.5 mmol) in THF (1 mL) under ultrasound and the reaction mixture was continuously sonicated at room temperature for 30 min (Scheme 3). A higher yield (76%) of para-methoxyphenyltriethoxysilane was achieved under this reaction condition. We also found that consequently a stepwise addition of 1,2-dibromoethane and then para-methoxyphenyl bromide improve dramatically the formation yield of para-methoxyphenyltriethoxysilane to 89% yield. To a reaction mixture of Mg (3.0 equiv) and tetraethyl orthosilicate (5.0 equiv) was added 1,2-dibromoethane (0.5 equiv) and then immediately para-methoxyphenyl bromide (1.0 equiv) was added dropwise under ultrasound and the reaction mixture was further sonicated at room temperature for 30 min. Increasing the amount of tetraethyl orthosilicate did not improve the formation of expected monoarylated product.

A series of aryl bromides was investigated under this sonochemical Barbier-type reaction condition and the results are shown in Table 1. The typical procedure for synthesis of an aryltriethoxysilane is as follows: To a reaction mixture of magnesium powder (3.0 mmol) and tetraethyl orthosilicate (5.0 mmol) in dry THF was added dropwise 1,2-dibromoethane (0.5 mmol) and then aryl bromide (1.0 mmol) was immediately added dropwise under ultrasound. The reaction mixture was continuously sonicated at room temperature for 30 min. After the sonication, hexane (10 mL) was added and then an aqueous NH₄Cl (5%) solution was added to the reaction mixture. The mixture was further sonicated at room temperature for 30 min. Increasing the amount of tetraethyl orthosilicate did not improve the formation of expected monoarylated product.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>Products</th>
<th>Yield a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>Si(OEt)₃</td>
<td>91</td>
</tr>
<tr>
<td>2</td>
<td>MeO</td>
<td>MeO</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>Cl</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>F₂C</td>
<td>F₂C</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td>O</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Br</td>
<td>Br</td>
<td>63</td>
</tr>
<tr>
<td>7</td>
<td>Br</td>
<td>Br</td>
<td>42</td>
</tr>
<tr>
<td>8</td>
<td>Br</td>
<td>Br</td>
<td>59</td>
</tr>
<tr>
<td>9</td>
<td>Br</td>
<td>(EtO)₃Si</td>
<td>49</td>
</tr>
<tr>
<td>10</td>
<td>S</td>
<td>S</td>
<td>91</td>
</tr>
<tr>
<td>11</td>
<td>Br</td>
<td>(EtO)₃Si</td>
<td>62</td>
</tr>
<tr>
<td>12</td>
<td>N</td>
<td>N</td>
<td>N.R. b</td>
</tr>
</tbody>
</table>

Table 1. Synthesis of aryltriethoxysilanes

a The yields were determined after chromatographic purification.
b No reaction and recovery of starting material.

The experimental results showed that the formation yield of aryltriethoxysilane by this sonochemical Barbier-type reaction is generally higher than the yield produced by Grignard addition reaction. The electron-withdrawing group attached to the aryl bromide usually gave a lower yield of aryltriethoxysilane (Table 1, entries 3, 4 and 9). Polyaromatic bromides were converted to their corresponding triethoxysilanes under the reaction condition (Table 1, entries 6–8). It should be noted
that 2-bromofluorene was transformed to the corresponding triethoxysilane without blocking the acidic protons which were easily deprotonated by Grignard reagent (Table 1, entry 8). The dibromides such as 1,4-dibromobenzene and 2,5-dibromothiophene were successfully transformed to their bis(triethoxysilane) compounds which were the important synthetic intermediates for material science (Table 1, entries 9 and 11). 2-Bromopyridine was resistant under the reaction condition (Table 1, entry 12).

The previous studies in the literatures28–35 have shown that aryltrialkoxysilanes undergo palladium-catalyzed, fluoride-mediated coupling reactions with various aromatic compounds. Among these reported reaction procedures, aryliethoxyxilanes are generally selected and investigated for Hiyama cross-coupling reaction. Therefore, we further investigated the coupling reaction of bromobenzene with phenyltriethoxysilane under different palladium catalysts (Table 2). A reaction mixture of 3 mol% palladium catalyst, tetrabutylammonium fluoride (TBAF), phenyltriethoxysilane and bromobenzene in toluene was refluxed for 23 h. The results showed that the Pd(PhCN)₂Cl₂ was the best choice of catalyst for the coupling reaction.

In conclusion, this reaction condition provides a simple method for the preparation of aryliethoxysilane which is the important synthetic intermediate for biologically active compounds and organic materials. The synthetic application of aryliethoxysilane for Hiyama cross-coupling reaction was studied and the proper Pd-catalyzed reaction condition was established.

Acknowledgements

We thank the National Science Council in Taiwan (NSC 94-2113-M-032-004) and Tamkang University for financial support.

References and notes

25. Lai, Y.-H. Synthesis 1991, 585. The addition of 1,2-dibromoethane was used for the activation of metal and it reacted with Mg powder in situ to generate Lewis acid MgBr₂ and ethene.
26. All aryl bromides and reagents were purchased from Aldrich and Riedel-deHaen and all were used directly without further purification.
27. The ultrasonic cleaning bath (Elma-T490DH, 50 kHz) should be filled with water containing some 3–5% detergent. In our laboratory, we used Decon 90 which permits much more even cavitation in bath water.