Tetrahedron 69 (2013) 5312–5318

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

A new synthetic approach for functional triisopropoxyorganosilanes using molecular building blocks

Yoshifumi Maegawa[a,b,*], Minoru Waki[a], Akinari Umemoto[c], Toyoshi Shimada[c], Shinji Inagaki[a,b]

[a] *Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*
[b] *Japan Science and Technology Agency (JST), ACT-C, Nagakute, Aichi 480-1192, Japan*
[c] *Department of Chemical Engineering, Nara National College of Technology, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan*

ARTICLE INFO

Article history:
Received 19 March 2013
Received in revised form 26 April 2013
Accepted 27 April 2013
Available online 2 May 2013

Keywords:
Organosilica
Alkoxysilane
Molecular building block
Cross-coupling
Sol–gel polymerization

ABSTRACT

We report an efficient synthetic approach for well-designed organic-bridged alkoxysilanes, which allow the formation of highly functional organosilica hybrids under mild sol–gel conditions. A series of molecular building blocks containing a triisopropoxysilyl group were synthesized and used in cross-coupling reactions. The triisopropoxysilyl group showed a good tolerance for various organic transformations. 1,4-Diketo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole-bridged triisopropoxysilane was successfully prepared, allowing rapid formation of organosilica hybrid without loss of functionality under mildly acidic conditions.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Organosilica hybrid materials, such as periodic mesoporous organosilicas (PMOs)[1,2] and polysilsesquioxanes (PSQs)[3,4] have received considerable attention in the fields of catalysis, adsorbents, and optical devices.[5–7] These materials are typically prepared by acid- or base-catalyzed hydrolysis and polycondensation (sol–gel polymerization) of organic-bridged alkoxysilanes ($R[Si(OR')_3]_n$, $n \geq 2$, R: organic group, R′: Me, Et). The $-Si(OMe)_3$ and $-Si(OEt)_3$ groups are most frequently used for alkoxysilane precursors because they are readily hydrolyzed and condensed under mildly acidic or basic conditions to form stable siloxane networks. However, the high reactivity of $Si(OMe)_3$ and $Si(OEt)_3$ has limited the design and synthesis of alkoxysilane precursors with highly functional organic groups (R) and caused formidable problems during work-up and purification using silica gel chromatography.[8–10]

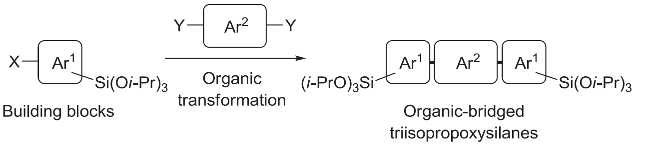
Recently, Shimada et al. found that allylsilyl ($R[Si(CH_2CH{=}CH_2)_m(OEt){=}_{3-m}]_n$; $m=1–3$) groups behaved as the synthetic equivalent of alkoxysilyl groups, and were stable enough to allow purification using silica gel chromatography.[11,12] They also reported the synthesis of a series of molecular building blocks containing allylsilyl groups for synthesis of sol–gel precursors with highly functional organic groups via palladium-catalyzed coupling reactions.[13–15] However, the allylsilyl groups were hydrolyzed and condensed under harsher conditions, such as high temperatures or high concentrations of acid or base, or in the presence of expensive Lewis acids, which sometimes damaged the functional organic groups and/or caused undesired Si–C bond cleavage in the organosilane.[16–18]

Organosilanes with bulky alkoxysilyl groups, such as isopropoxysilyl [$-Si(O\textit{i}\text{-}Pr)_3$] have been used only to a limited extent to date, but have potential as ideal sol–gel precursors because of their medium stability and reactivity due to the steric bulk of the alkoxy group on the silicon atom.[19–21] However, synthetic methodologies have been limited to alkoxy exchange reactions of unstable chlorosilanes and/or less bulky alkoxysilanes.[22] Here, we report the preparation of a series of molecular building blocks containing triisopropoxysilyl groups and the synthesis of highly functional organosilica precursors via cross-coupling reaction of the building blocks (Scheme 1). The isopropoxysilyl group was found to show a good tolerance for various organic transformations. The resulting organosilica precursor was successfully hydrolyzed and condensed to form an organosilica hybrid without loss of functionality under mildly acidic conditions.

---

[*] Corresponding author. Tel.: +81 561 71 7139; fax: +81 561 63 6507; e-mail address: ymaegawa@mosk.tytlabs.co.jp (Y. Maegawa).

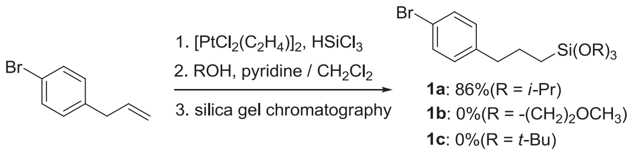
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.04.130



Scheme 1. Synthetic method for functional organic-bridged triisopropoxysilanes using molecular building blocks.

2. Results and discussion

First, we sought a suitable bulky alkoxysilyl group for the building blocks. 2-Methoxyethoxysilyl and *tert*-butoxysilyl groups, in addition to the isopropoxysilyl group, were introduced by hydrosilylation of allylbromobenzene with trichlorosilane in the presence of $[PtCl_2(C_2H_4)]_2$, followed by alkoxylation using appropriate alcohols in the presence of pyridine in CH_2Cl_2 (Scheme 2).[23] The triisopropoxysilyl group was efficiently introduced and showed sufficient stability during general work-up and silica gel chromatography. The bulkier linear tris(2-methoxyethoxy)silyl group was not retained during the reaction and purification, giving a complex mixture that contained none of the target compound. The introduction of the bulkier branched tri(*tert*-butoxy)silyl group failed due to steric hindrance during the alkoxylation reaction.

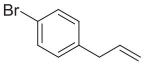
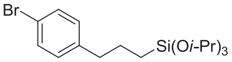
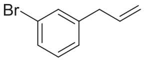
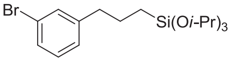
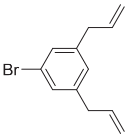
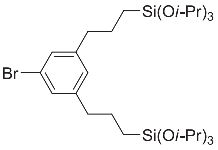
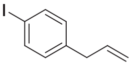
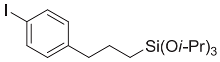
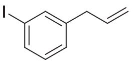
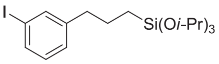
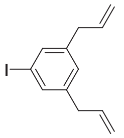
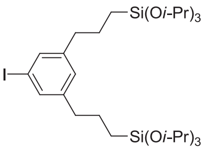


Scheme 2. Synthesis of bromobenzene-based molecular building blocks containing various bulky alkoxysilyl groups.

We then synthesized a variety of halogenated benzene-based building blocks with triisopropoxysilyl groups attached, as shown in Table 1. During this study, we found that allylhalobenzene was readily prepared by halogen–magnesium exchange reaction of bromobenzene derivatives with a mixture of *i*-PrMgCl and *n*-BuLi in cyclopentyl methyl ether followed by allylation with allyl bromide in the presence of CuCN.[24] Both hydrosilylation and isopropoxylation of *p*- and *m*-allylbromobenzene proceeded successfully to give the corresponding building blocks **1a** and **1d** in high yields of 86% and 85%, respectively (Table 1, entries 1 and 2). The bis-silylated building block **1e** could be synthesized from diallylated bromobenzene (Table 1, entry 3). In this case, hydrosilylation proceeded effectively in the presence of $(Bu_4N)_2PtCl_6$ as a catalyst.[25] A series of iodobenzene building blocks, **1f**–**h**, were also obtained under same reaction conditions (Table 1, entries 4–6).

Magnesium-containing building blocks were obtained from the iodobenzene-based building blocks (Table 2, entries 1–3). A Grignard exchange reaction of **1f** with *i*-PrMgCl·LiCl in a mixture of 1,4-dioxane/tetrahydrofuran (THF) (1:10 v/v) proceeded effectively at −40 °C for 4 h and gave the magnesium-containing building block **2a** quantitatively. It is notable that the triisopropoxysilyl group was stable towards *i*-PrMgCl·LiCl and the resulting magnesium reagent, owing to its bulky structure. Interestingly, no reaction occurred in the absence of 1,4-dioxane, and unreacted **1f** was recovered. This may be attributed to the formation of a magnesium complex between *i*-PrMgCl and the triisopropoxysilyl group. Indeed, the use of excess *i*-PrMgCl in THF gave the corresponding **2a**. The addition of 1,4-dioxane affects the dissociation of the magnesium complex, as reported by Knochel's group.[26] *m*-Silylated (**2b**) and bis-silylated (**2c**) Grignard reagents were also successfully obtained from corresponding iodo-building blocks under the same reaction conditions.

Table 1
Synthesis of halogen-substituted molecular building blocks containing one or two triisopropoxysilyl groups[a]

Entry	Substrate	Product		Yield %
1			**1a**	86
2			**1d**	85
3[b]			**1e**	83
4			**1f**	86
5			**1g**	85
6[b]			**1h**	84

[a] Reagents and conditions: (i) allylhalobenzene (1 equiv), $HSiCl_3$ (3.3 equiv), $[PtCl_2(C_2H_4)]_2$ (0.25 mol % Pt), rt, overnight, (ii) *i*-PrOH (4.5 equiv), pyridine (4.5 equiv), CH_2Cl_2, 0 °C–rt, 6 h.

[b] $[(Bu_4N)_2PtCl_6]$ (0.1 mol % Pt) was used as a catalyst.

The magnesium-containing building blocks successfully underwent transmetallation upon treatment with other metal reagents. The transmetallation of **2a** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in a mixture of 1,4-dioxane/THF (1:10 v/v) gave the borylated building block **2d** in 93% yield (Table 2, entry 4). The reaction of **2a** with trimethyltin chloride afforded the trimethylstannylated building block **2e** in a high yield of 87% (Table 2, entry 5).

With key building blocks in hand, we then examined the utility of the molecular building blocks as cross-coupling partners. The halogen-substituted building blocks can be used as coupling reagents for Suzuki–Miyaura[27] and Sonogashira–Hagihara cross-coupling reactions.[28] Suzuki–Miyaura coupling between **1f** and 2-thiophenboronic acid in the presence of $Pd(PPh_3)_4$ as a catalyst gave the thiophene-substituted building block **2f** in 71% yield (Table 2, entry 6). Notably, in the reaction, the use of a basic aqueous solution did not affect the hydrolysis of the triisopropoxysilyl group. The α-proton on thiophene ring in **2f** was readily brominated using *N*-bromosuccinimide (NBS) to afford the bromothiophene building block **2g** in 81% yield (Table 2, entry 7). The resulting **2g** is a useful coupling partner for the construction of π-conjugated thiophene bridging groups. Sonogashira–Hagihara coupling between **1a** and 2-methyl-3-butyn-2-ol in the presence of $PdCl_2(PPh_3)_2$/CuI as a catalyst gave the ethynylated compound **2h** in 86% yield (Table 2, entry 8). The resulting **2h** can easily be deprotected using NaH to afford the terminal ethyne-substituted building block **2i** in 71% yield without decomposition of the triisopropoxysilyl group (Table 2, entry 9). The obtained **2i** can then be used as a coupling partner for Sonogashira–Hagihara coupling and/or click reactions with azide compounds.[29]

Materials based on 1,4-diketo-3,6-dithienylpyrrolo[3,4-*c*]pyrrole (DTDPP) have attracted tremendous attention in the fields of solar cells and field effect transistors because of their promising optical and electrical properties.[30,31] DTDPP-bridged silane

Download English Version:

https://daneshyari.com/en/article/5218759

Download Persian Version:

https://daneshyari.com/article/5218759

Daneshyari.com