Preliminary communication

Organylsilatranes from the reaction of tetraorganylsilanes with triethanolamine

Vladimir Gevorgyan, Larisa Borisova, Edmunds Lukevics *

Latvian Institute of Organic Synthesis, Aizkraukles 21, Riga, LV-1006, Latvia

Abstract

Triethanolamine selectively cleaves Si–C bonds in heterylsilanes (3) under basic/nucleophilic catalysis, leading to organylsilatranes (4) with good to excellent yields.

Keywords: Silatrane; Triethanolamine; Nucleophilic; Basic; Catalysis; Silane

1. Introduction

Since silatranes were first synthesized by Frye et al. [1], they have been extensively studied and well documented in several hundreds of papers, including review articles [2–11]. Owing to their intriguing structural [6,7,9,10], spectroscopic [3,5,6,12–15], and biological [3,16–19] properties, silatranes have been in the focus of interest of several research groups in the last three decades; nevertheless, only a few methods of silatrane ring formation have been developed [4]. The key step of all known methods is the cleavage of three Si-hetero-atom bonds in hydro-, alkoxy-, acyloxy-, or halosilanes (1) by triethanolamine or by its derivatives [1] followed by the formation of three Si–O bonds of silatranes (2) (Scheme 1).

Herein we report a new and effective method of synthesis of organyl silatranes (4) based on the unprecedented mild and selective cleavage of Si–C bonds in heterylsilanes (3) by triethanolamine (Scheme 2).

2. Results and discussion

Recently, we have reported that Si–C bond in dihydrofuryl-, furyl-, and dihydropyranylsilanes and Ge–C bond in dihydrofurylgermanes undergo mild and selective cleavage by H- [23,24] and C-nucleophiles [25],

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* Corresponding author.
[1] Some examplary data concerning preparation of silatranes by reaction of alkoxysilanes with boratrane have been reported [20–22].

leading to the corresponding hydro- and carbosilanes and -germanes (some data regarding cleavage of heteryl groups by O- and N-nucleophiles have been found, see Ref. [26]). Cleavage of the Si–C bond in 2-furyl- and (2-thienyl)trialkylsilanes by MeONa in MeOH has also been reported [27].
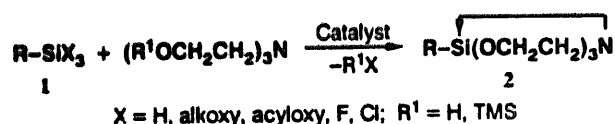
The results obtained prompted us to test whether these heterylsilanes (-germanes) are able to react in the same manner with triethanolamine. Thus, we have tested the reactivity of tris(2-furyl)phenyl- (3a), tris(2-thienyl)phenyl- (3b), tris[2-(4,5-dihydrofuryl)]phenyl- (3c), tris[2-(5,6-dihydro-4H-pyranyl)]phenyl- (3d), tetrakis(2-furyl- (3e), tetrakis(2-thienyl)silane (3f), and tetrakis(2-thienyl)germane (3g) in this reaction (Scheme 2, Table 1).

We have found that triethanolamine in the presence of catalytic amount (5 mol%) of base (KOH, NaOEt) or CsF easily substitutes three furyl- (entries 1, 2), dihydrofuryl- (entry 5), and thienyl groups (entry 3) in tris(heteryl)phenylsilanes 3a-c, leading to phenylsilatrane 4a with 68–95% yields (Table 1).
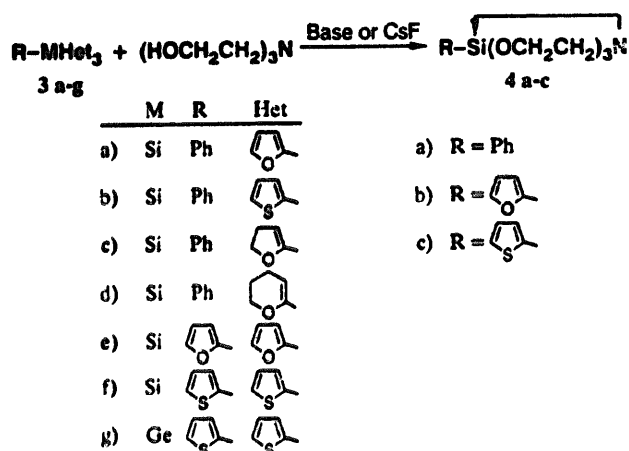
Unexpectedly, the dihydropyranyl group in 3d appeared to be the worst leaving group among all heteryl groups tested. (The leaving ability of 2-(5,6-dihydro-4H-pyranyl) group towards H and C nucleophiles was found to be comparable with that of 2-(4,5-dihydrofuryl)-, and 2-furyl groups [24,25].) Thus, the prolonged heating with NaOEt (70 h at 80°C) did not cause any noticeable reaction (entry 6), and only in the presence of CsF (18 h at 80°C) did it succeed in converting 3a into 4a with 32% yield (entry 7).

R–SiX$_3$ + (R^{1}OCH$_2$CH$_2$)$_3$N $\xrightarrow[-R^1X]{\text{Catalyst}}$ R–Si(OCH$_2$CH$_2$)$_3$N

1   **2**

X = H, alkoxy, acyloxy, F, Cl; R^1 = H, TMS

Scheme 1. Traditional methods of synthesis of silatranes

R–MHet$_3$ + (HOCH$_2$CH$_2$)$_3$N $\xrightarrow{\text{Base or CsF}}$ R–Si(OCH$_2$CH$_2$)$_3$N

3 a–g   **4 a–c**

	M	R	Het		
a)	Si	Ph	(2-furyl)	a)	R = Ph
b)	Si	Ph	(2-thienyl)	b)	R = (2-furyl)
c)	Si	Ph	(2-furyl)	c)	R = (2-thienyl)
d)	Si	Ph	(pyranyl)		
e)	Si	(furyl)	(furyl)		
f)	Si	(thienyl)	(thienyl)		
g)	Ge	(thienyl)	(thienyl)		

Scheme 2. Organylsilatranes from tetraorganylsilanes.

Table 1
Reaction of heterylsilanes with triethanolamine[a]

Entry	Substrate R (M = Si)	Het	Catalyst	Time/Temp (h/°C)	Yield of 4[b] (%)
1	3a Ph	(2-furyl)	KOH	1/80	4a 95
2	3a Ph	(2-furyl)	CsF	1/20	4a 91
3	3b Ph	(2-thienyl)	NaOEt	3/80	4a 92
4	3c Ph	(2-furyl)	KOH	24/25	4a 25[c]
5	3c Ph	(2-furyl)	CsF	1/80	4a 68
6	3d Ph	(pyranyl)	NaOEt	70/80	4a traces[d]
7	3d Ph	(pyranyl)	CsF	18/80	4a 32[e]
8	3e	(furyl)(furyl)	CsF	3/80	4b 91
9	3f	(thienyl)(thienyl)	CsF	8/80	4c 95
10	3g	(thienyl)(thienyl) (M = Ge)	NaOEt	20/100	no reaction[f]

[a] All reactions were carried out with 1.0 mmol of 3 in dry DMF (0.1 M) with 5 mol% of catalyst with respect to 3, [3]:[triethanolamine] = 1:1.5; [b] isolated yield; [c] elevation of reaction temperature leads to total decomposition of 3c; [d] recovery of 3d > 95%; [e] Recovery of 3d = 65%; [f] recovery of 3g > 95%.

2-Furyl and 2-thienyl groups were found to be the best leaving groups also in tetrakis derivatives **3e** and **3f**. They were converted under CsF catalysis into 2-furyl- (**4b**) and 2-thienylsilatrane (**4c**) with 91% and 95% isolated yields respectively (entries 8, 9). This method is of a preparative value for the synthesis of hetarylsilatranes because it gives (i) high yields, (ii) hydrolytically and chromatographically stable starting materials R$_4$Si, and, moreover, (iii) they are more easily obtainable compared with RSiX$_3$ **1**.

In contrast, Ge–C bonds in thienylgermane **3g** were not reactive towards triethanolamine at all, and starting **3g** was quantitatively recovered from the reaction mixture after 20 h heating at 100 °C (entry 10).

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