A Facile Synthesis of 1,1-Disilylethenes via Me_3MgLi-Induced Monomethylation of Dibromodisilylmethanes

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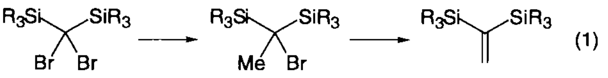
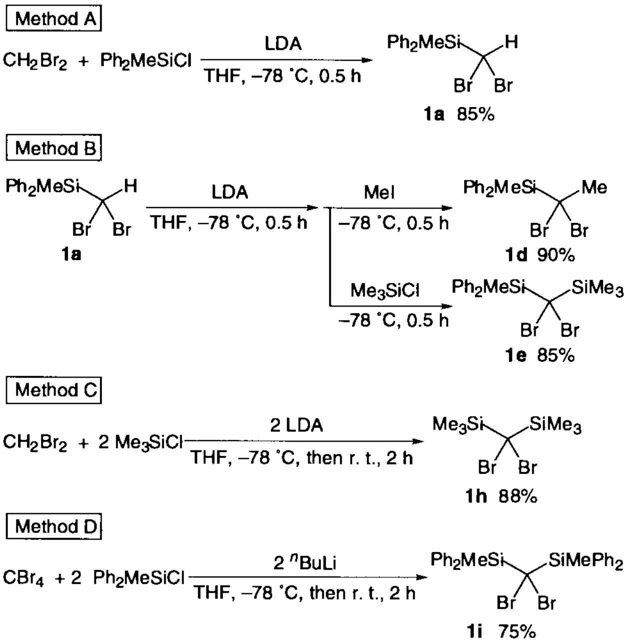
Lithium trimethylmagnesate (Me_3MgLi) induces monomethylation of dibromodisilylmethanes in excellent yields. Subsequent dehydrobromination of the resulting 1-bromo-1,1-disilylethanes with DBU affords 1,1-disilylethenes in good yields.

The vinylsilane chemistry has been well-established because of its great importance in organic synthesis, and a number of preparative methods and widespread application of vinylsilanes have been reported.[1] In contrast to vinylsilanes, however, the utility of 1,1-disilylalkenes remains still unexplored, although one can expect that 1,1-disilylalkenes possess similar versatility to vinylsilanes.[2,3] 1,1-Bis(trimethylsilyl)ethene is easily prepared by the reaction of tris(trimethylsilyl)methyllithium and paraformaldehyde.[2a,b] However, this method lacks generality due to the difficulty in the preparation of tris(trialkylsilyl)methyllithium, and development of alternative routes is hence required. We have undertaken a new preparative route to 1,1-disilylethenes as outlined in eq 1. We have chosen dibromodisilylmethanes, which can be easily prepared from commercially available materials in one step, as starting substrates (*vide infra*). The introduction of the methyl group and the subsequent dehydrobromination reaction with a base would lead to 1,1-disilylethenes.


(1)

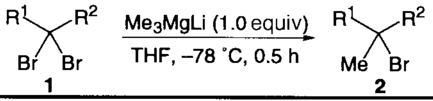
Metal–halogen exchange of one of the two bromines and the subsequent addition of methyl iodide did not give satisfactory results presumably because of the steric hinderance of silyl groups. During our study on the reaction of organomagnesium ate complexes with *gem*-dibromo compounds,[4] we have found that monomethylation of dibromomethylsilanes ($R_3SiCHBr_2$)[5a] occurred by the action of trimethylmagnesate reagent (Me_3MgLi).[6] This procedure proved to be applicable for monomethylation of dibromodisilylmethanes.

Starting *gem*-dibromo compounds are prepared by several procedures (methods A, B, C, and D) shown in Scheme 1.[5] To a THF solution of lithium trimethylmagnesate (Me_3MgLi), prepared by mixing methylmagnesium bromide and methyllithium in a 1:2 ratio, was added *gem*-dibromo compounds **1** at –78 °C and the mixture was stirred for 0.5 h. Aqueous workup followed by purification afforded monomethylation products **2** in good to excellent yields (Table 1).[7]



Scheme 1.

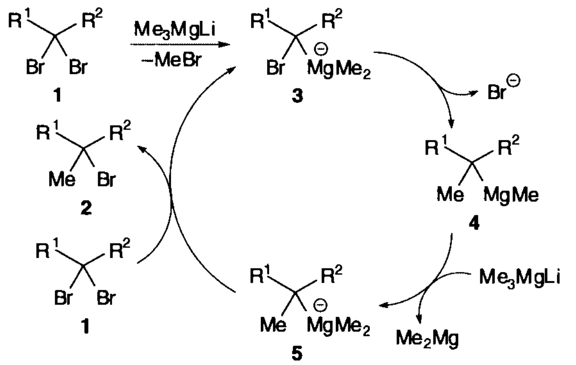
Table 1. Monomethylation of dibromodisilylmethanes with Me_3MgLi[a]



Entry	Substrate	R^1	R^2	Product	Yield/%
1	**1a**	Ph_2MeSi	H	**2a**	98
2	**1d**	Ph_2MeSi	Me	**2d**	89
3	**1e**	Ph_2MeSi	Me_3Si	**2e**	93
4	**1f**	Et_3Si	Et_3Si	**2f**	90
5	**1g**	^{t}BuMe$_2$Si	Me_3Si	**2g**	82
6	**1h**	Me_3Si	Me_3Si	**2h**	89
7	**1i**	Ph_2MeSi	Ph_2MeSi	**2i**	90

[a] **1** (10 mmol) was treated with Me_3MgLi, prepared by mixing MeMgBr (THF solution, 10 mmol) and MeLi (Et_2O solution, 20 mmol), for 0.5 h in THF at –78 °C.

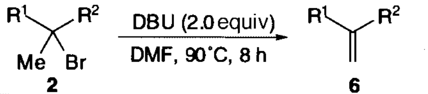
Substrates such as dibromomethylsilane (entry 1), 1,1-dibromoethylsilane (entry 2) and dibromodisilylmethanes (entries 3–7) can be converted into the corresponding monomethylated compounds in good yields regardless of the bulkiness of silyl substituents. The use of other reagents such as $^nBu_3MgLi$ did not give the monoalkylated products.[4] Although the reaction pathway of this methylation is not clear at present, we assume the following mechanism involving the formation of the ate-type carbenoid species **3** via bromine–magnesium exchange reaction[8] (Scheme 2). The 1,2-migration of one of the methyl groups on magnesium provides **4** with concomitant elimination of the bromide anion. One of methyl groups in Me_3MgLi was transferred to **4** to form the ate complex **5**, which is more reactive than Me_3MgLi for the bromine–magnesium exchange reaction. The complex **5** abstracts the bromine atom from **1** to yield the monobromo compound **2** and the carbenoid **3**.



Scheme 2.

We then investigated the dehydrobromination reaction of **2**. After several attempts, we found that treatment of the methylation products **2** with 2.0 equiv of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in DMF at 90 °C for 8 h provided 1,1-disilylethenes **6**.[9] Table 2 summarizes the results. In each case, the desired product is obtained in good yield. The reaction of **2** with ^{n}BuLi or ^{i}PrMgBr also provided **6** in moderate yields. The use of ^{t}BuOK as a base caused decomposition of substrates **2i** to yield methyldiphenylsilanol (Ph$_2$MeSiOH) and 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane (Ph$_2$MeSi OSiMePh$_2$).

Table 2. Dehydrobromination of **2** with DBU^a



Entry	Substrate	R^1	R^2	Product	Yield/%
1	**2e**	Ph$_2$MeSi	Me$_3$Si	**6e**	98
2	**2f**	Et$_3$Si	Et$_3$Si	**6f**	98
3	**2g**	^{t}BuMe$_2$Si	Me$_3$Si	**6g**	85
4	**2h**	Me$_3$Si	Me$_3$Si	**6h**	83
5	**2i**	Ph$_2$MeSi	Ph$_2$MeSi	**6i**	89

^{a}A solution of **2** (9.0 mmol) and DBU (18.0 mmol) in DMF (30 mL) was stirred for 8 h at 90 °C.

In summary, we have developed a new efficient route to 1,1-disilylethenes via Me$_3$MgLi-induced monomethylation of dibromodisilylmethanes and the subsequent dehydrobromination reaction. This new facile method provided us with a synthetic route to various 1,1-disilylethenes.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

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7 To a solution of **1i** (5.66 g, 10 mmol) in THF (50 mL) was added a solution of lithium trimethylmagnesate, prepared by mixing methylmagnesium bromide (10.8 mL, 0.93 M solution in THF, 10 mmol) and methyllithium (17.5 mL, 1.14 M solution in Et$_2$O, 20 mmol) in THF (15 mL), at –78 °C under argon atmosphere. After stirring for 0.5 h at –78 °C, the mixture was poured into 1 M HCl carefully and extracted with AcOEt. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated *in vacuo*. Washing the residual colorless solid with pentane provided 1-bromo-1,1-bis(methyldiphenylsilyl)ethane (**2i**, 4.51 g, 9.0 mmol) in 90% yield.

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9 A solution of **2i** (4.51 g, 9.0 mmol) and DBU (2.7 mL, 18.0 mmol) in DMF (40 mL) was stirred for 8 h at 90 °C. The mixture was poured into 1 M HCl carefully and extracted with AcOEt. The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated in vacuo. Washing the residual colorless solid with cold hexane provided 1,1-bis(methyldiphenylsilyl)ethene (**6i**, 3.37 g, 8.0 mmol) in 89% yield.