Tetrahedron Letters,Vol.30,No.45,pp 6195-6198,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

PREPARATION AND REACTIVITY OF BIS(BROMOMAGNESIO)BIS(TRIMETHYLSILYL)METHANE

M. Hogenbirk, N.J.R. van Eikema Hommes, G. Schat,
O.S. Akkerman, F. Bickelhaupt*, G.W. Klumpp*

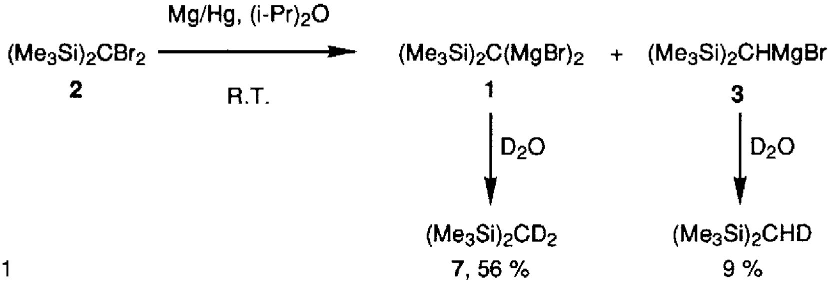
Scheikundig Laboratorium, Vrije Universiteit
De Boelelaan 1083, NL-1081 HV Amsterdam, The Netherlands

Abstract: The preparation of the title compound (**1**) by three different routes is described. The compound was found to be remarkably unreactive towards electrophiles.

As part of our research aimed at new di-Grignard compounds[1], and to extend previous work on silicon substituted dimetallomethanes[2,3], we studied the preparation and reactivity of bis(bromomagnesio)bis(trimethylsilyl)methane (**1**). This compound is a potentially interesting reagent for the preparation of metallacycles[4] or metalla-alkenes[5] from transition metal or main group halides. Furthermore, **1** was expected to react with aldehydes and ketones in a Wittig type reaction[2,7] to furnish bis(trimethylsilyl) substituted alkenes[8].

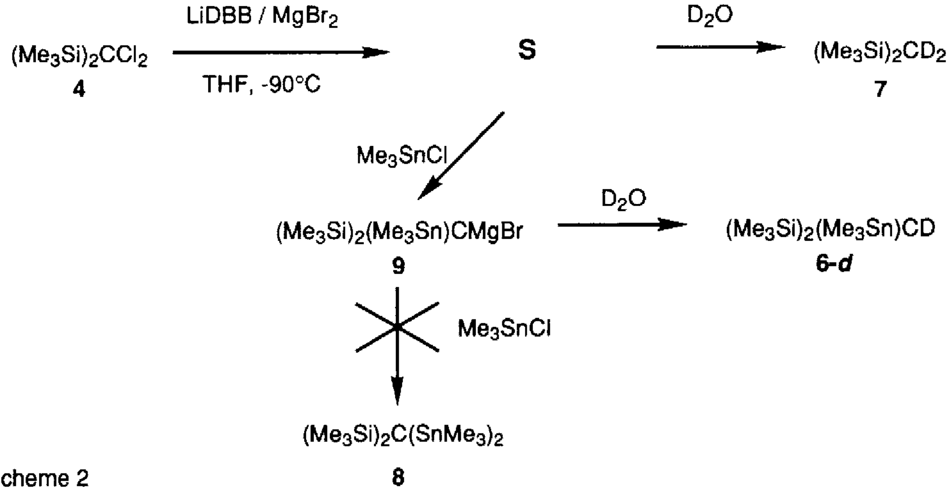
The title compound (**1**) was prepared in three ways: I, the "amalgam procedure"; II, the transmetalation procedure; and III, the "normal" Grignard procedure. These methods will be described and compared.

Method I. Following our standard procedure for the preparation of di-Grignard reagents [2,4] 1.9 g (5.6 mmol) of dibromobis(trimethylsilyl)methane[9] (**2**) was stirred with magnesium amalgam (0.84 g (35 mmol) Mg in 6 ml Hg) in diisopropyl ether (90 ml) for 48 h at 20 °C. Contrary to bis(bromomagnesio)methane [4] and bis(bromomagnesio)trimethylsilylmethane[2], which are insoluble in diisopropyl ether, **1** did not precipitate and could therefore not be separated from the mono-Grignard reagent bis(trimethylsilyl)methylmagnesium bromide (**3**) by simple decantation. Reaction with D_2O showed **1** and **3** to be formed in 56% and 9 % yield respectively as derived from titration and GCMS analysis[10a]. (Scheme 1)



Scheme 1

Method II. Using the previously described *in situ* transmetalation procedure[11], we hoped to obtain **1**, free from **3**, by reacting 225 μl (1 mmol) dichlorobis(trimethylsilyl)methane[12] (**4**) with 4 mmol lithium 4,4'-di-*tert* -butylbiphenyl[13] (LiDBB) in the presence of 2 mmol of magnesium bromide in THF (20 ml, –90 °C). Deuterolysis of the reaction mixture at room temperature gave exclusively bis(trimethylsilyl)dideuteromethane (**7**). Contrary to bis(trimethylsilyl)dilithiomethane which is not stable in THF at room temperature, the organometallic species (**S**, vide infra) resulting from this procedure exhibits a surprisingly low degree of reactivity. The mixture reacted very sluggishly with trimethyltin chloride to give, after 3.5 h at room temperature and subsequent deuterolysis and GCMS analysis, only 58% of the monotin derivative **6**, 47% of which was deuterated. Bis(trimethylsilyl)dideuteromethane (**7**) was also formed (40%), showing that a large amount of unreacted dianionic material was still present in the solution. The unobserved ditin derivative **8** is a known stable compound and has been obtained by quenching bis(trimethylsilyl)dilithiomethane with trimethyltin chloride[15]. (Scheme 2)



Scheme 2

An obvious disadvantage of this method is the presence of 4,4'-di-*tert* -butylbiphenyl (DBB) in the reaction mixture; a route to pure **1** would be preferable.

Method III. To our surprise, the normal procedure for the preparation of Grignard reagents, which had failed for other geminal dihalides[2,6], was successful in the case of **2**. When **2** was stirred with an excess of magnesium (triply sublimed) in diethyl ether in a sealed glass system[14], deuterolysis of the resulting solution followed by GCMS analysis indicated that **1** and **3** had been formed in 60% and 20% yield, respectively. Upon concentration and cooling of the solution, **1** crystallized as colorless rectangular crystals in an overall yield of about 35%[10b]. (Scheme 3)

$$\underset{\mathbf{2}}{(Me_3Si)_2CBr_2} \xrightarrow[\text{R.T.}]{\text{Mg, Et}_2\text{O}} \underset{\substack{\mathbf{1}\\60\ \%}}{(Me_3Si)_2C(MgBr)_2} + \underset{\substack{\mathbf{3}\\20\ \%}}{(Me_3Si)_2CHMgBr}$$

Scheme 3

The reactivity of **1** obtained in this way was found to be extremely low. It did not react either with an excess of trimethylgermanium chloride or with trimethyltin chloride in THF within 24 h. In diethyl ether, however, trimethyltin chloride gave, after more than 40 h and after D_2O quench, a mixture of five compounds, the composition of which was obtained by GCMS analysis[10c]: **7**[10a] (29%), **6-*d*** (8%), and the not fully characterized compounds **A** (23%, highest m/z 501, containing Sn_2 and Si_2), **B** (38%, presumably $(Me_3Si)_2C(SnMe_3)(SnClMe_2)$), and **C** (2%, presumably $(Me_3Si)_2C(SnMe_3)(SnBrMe_2)$. Apparently, **B** and **C** were formed from **8** by methyl-halogen exchange. Thus, under certain conditions **1** can react with 2 equivalents of an electrophile.

For the preparation of **1**, method III is clearly preferable, as it furnishes pure **1** in a reasonable yield by a convenient procedure.

The difference in reactivity towards trimethyltin chloride of the reagents formed in procedures II and III suggests that two different dimetallomethanes are formed. By method III, only **1** or a related dimagnesium compound can be formed. The somewhat higher reactivity of the reaction mixture obtained by method II suggests that besides **1**, **S** contains the lithium-magnesium compound $(SiMe_3)_2CLi(MgBr)$.

From the reactivity of **1** towards D_2O and Me_3GeCl or Me_3SnCl we conclude that **1** is a strong nucleophile towards protons but a weak one towards Me_3SnCl or Me_3GeCl. Two effects may be responsible: as observed for $CH_2(MgBr)_2$[1,16] and $Me_3SiCH(MgBr)_2$[2], polysubstitution with electropositive elements (Mg, Si) seems to reduce the nucleophilic reactivity; in the case of **1**, steric hindrance also plays an important role: both the two trimethylsilyl groups and the two magnesium atoms carrying two ether groups cause considerable congestion around the carbon atom[17].

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10. (a) **7**: M.S.: m/z (%) = 147 (100) [M - Me], 73 (79) ; (b) **1**: ^{1}H NMR (90 MHz, [D_8]THF) : $\delta = 0.11$ ppm (s, 18 H); **1**: ^{13}C NMR (62.89 MHz, [D_8]THF): $\delta = 2.64$ ppm (central C), 9.99 ppm (q, $^1J(CH) = 115.6$ Hz, methyl C); ^{13}C NMR (62.89 MHz, Et_2O / C_6D_6 (1:1)): $\delta = 5.42$ ppm (s, central C), 9.75 ppm (q, $^1J(CH) = 114.7$ Hz, methyl C); (c) **6**: M.S.: m/z (%) = 309 (100) [M - Me], 129 (76), 73 (13); **A**: M.S.: m/z (%) = 501 (100), 165 (14), 73 (29); **B**: M.S.: m/z (%) = 491 (100) [M - Me], 193 (61), 73 (100); **C** : M.S.: m/z (%) = 535 (9) [M - Me], 193 (84), 73 (100). All compounds showed the expected isotope patterns.

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(Received in UK 21 September 1989)