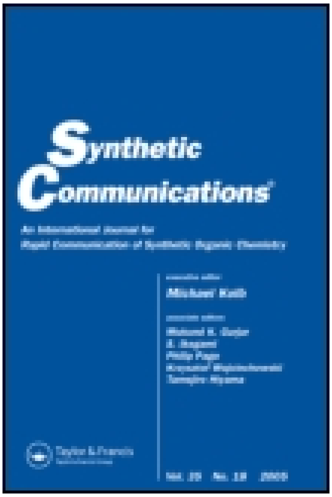


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Tris(dimethylsilyl)methyllithium: A Reagent for the Synthesis of Vinylbis(silanes) Containing Si-H Functional Groups

Kazem D. Safa [a] , Akbar Hassanpour [a] & Shahin Tofangdarzadeh [a]
[a] Organosilicon Research Laboratory, Faculty of Chemistry , University of Tabriz , Tabriz, Iran

To cite this article: Kazem D. Safa , Akbar Hassanpour & Shahin Tofangdarzadeh (2009) Tris(dimethylsilyl)methyllithium: A Reagent for the Synthesis of Vinylbis(silanes) Containing Si-H Functional Groups, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:9, 1601-1610, DOI: 10.1080/00397910802563412

To link to this article: http://dx.doi.org/10.1080/00397910802563412

Synthetic Communications®, 39: 1601–1610, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802563412

Tris(dimethylsilyl)methyllithium: A Reagent for the Synthesis of Vinylbis(silanes) Containing Si–H Functional Groups

Kazem D. Safa, Akbar Hassanpour, and Shahin Tofangdarzadeh
Organosilicon Research Laboratory, Faculty of Chemistry,
University of Tabriz, Tabriz, Iran

Abstract: Reactions between a series of nonenolisable aldehydes and tris(dimethylsilyl)methyllithium, $(HMe_2Si)_3CLi$, are described. The Peterson reaction takes place readily to give vinylbis(silanes). Moreover, styrene and butyl acrylate 1:1 copolymer (P), prepared by use of α,α'-azobis(isobutyronitrile) (AIBN) as an initiator in toluene at $70 \pm 1°C$, was formylated via direct electophilic substitution by methyl dichloromethyl ether (Cl_2CHOMe) in the presence of tin(IV) chloride ($SnCl_4$) in nitrobenzene ($PhNO_2$) as solvent. The reaction of $(HMe_2Si)_3CLi$ with formyl groups on the side chains of the copolymer led to new macromolecules bearing vinylbis(silane) functional groups.

Keywords: Functionalized copolymer, Peterson reaction, Si–H functional group, tris(dimethylsilyl)methyllithium, vinylbis(silanes)

INTRODUCTION

Vinylsilanes are useful reagents in organic synthesis because the C(sp^2)-Si bonds undergo numerous transformations.[1] Vinylbis(silanes), which show a number of similar properties, have received significant attention as potential synthons in organic and organosilicon synthesis.[2] The

Received August 20, 2008.

Address correspondence to Kazem D. Safa, Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran. E-mail: dsafa@tabrizu.ac.ir

potential of the vinylbis(silanes) as precursors for the preparation of ketones and isoxazoline derivatives as well as a variety of important organosilicon reagents, such as acylsilanes, epoxysilanes, and silanols, has stimulated their development. In contrast to vinylsilanes, however, vinylbis(silanes) are relatively unexplored.[3]

Organosilyl groups of various sizes have been incorporated into polymer structures to modify the polymer properties, and this has generated much new research.[4]

Peterson-type olefination is a useful method for the preparation of alkenes from carbonyl compounds.[5] However, no Si–H functionalized vinylbis(silanes) bearing heterocycle rings have hitherto been prepared by this method. In the present work, we describe the synthesis of some vinylbis(silane) derivatives bearing Si–H functional groups, the preparation of acrylic copolymers of styrene bearing –CHO groups, and conversion of these to new copolymers containing vinylbis(silanes).

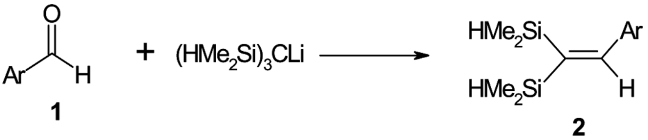
RESULTS AND DISCUSSION

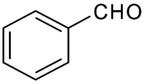
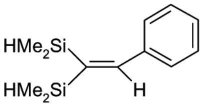
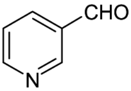
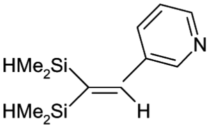
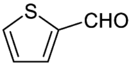
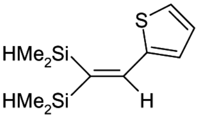
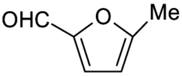
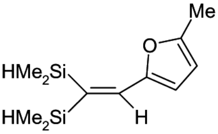
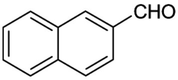
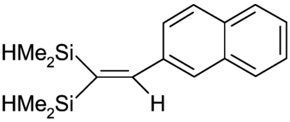
The precursor tris(dimethylsilyl)methane, $(HMe_2Si)_3CH$, has been conveniently prepared by the reaction of $CHBr_3$ and Mg with HMe_2SiCl in tetrahydrofuran (THF). The generation of $(HMe_2Si)_3CLi$ was easily accomplished by deprotonation of $(HMe_2Si)_3CH$ by lithium diisopropylamide (LDA) in THF.[6] The direct reaction of $(HMe_2Si)_3CLi$ with benzaldehyde, 3-pyridinaldehyde, 2-thiophenealdehyde, 5-methylfurfural, 2-naphthaldehyde, cinnamaldehyde, and terephthaldehyde led to the corresponding vinylbis(silanes) (Table 1). The reaction can also be used for the synthesis of a bisaldehyde (entry 7) and a dienylsilane (entry 6).

The Si–H infrared (IR) stretching frequency for **2a** was at $2115\,\text{cm}^{-1}$. The ^1H NMR spectrum of **2a** showed two doublets at 0.19 and 0.31 ppm assigned to the two methyl groups on each silicon atom, one singlet at 7.83 ppm assigned to a proton on the β-carbon, and one septet in the range 4.30–4.34 ppm for the Si–H proton, resulting from vicinal coupling. All these results clearly show the formation of bisvinyl(silane) **2a**.

To study the analogous reaction with copolymer containing formyl groups in the side chain, a random copolymer (**P**) of styrene and butyl acrylate was synthesized by free radical polymerization using a,a-azobis(isobutyronitrile) (AIBN) as an initiator. To introduce formyl groups in the side chain, **P** was treated with methyl dichloromethyl ether (Cl_2CHOMe) in the presence of tin(IV) chloride ($SnCl_4$) (Scheme 1)[7] in CH_2Cl_2 or $PhNO_2$ at room temperature. $PhNO_2$ appears to be more suitable than CH_2Cl_2 because of the completion of the hydrolysis step of the formylation reaction.

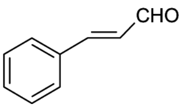
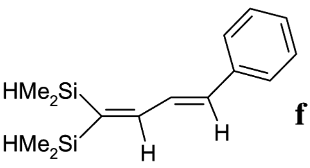
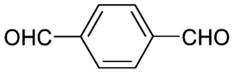
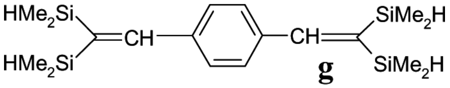
Table 1. Vinylbis(silanes) from aromatic aldehyds



Entry	Substrate	Product	Yield[a] (%)
1		 **a**	74
2		 **b**	59
3		 **c**	62
4		 **d**	70
5		 **e**	63

(*Continued*)

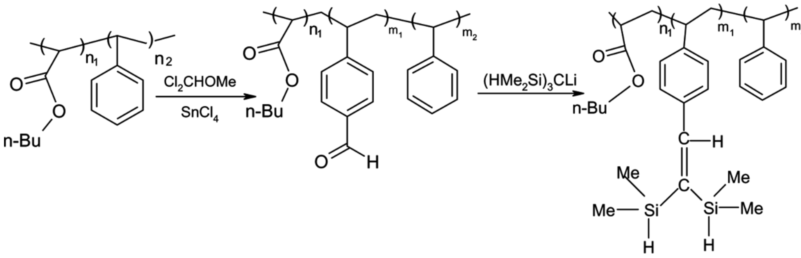
Table 1. Continued

Entry	Substrate	Product	Yield[a] (%)
6		 **f**	68
7		 **g**	58

[a]Yields calculated by GC–mass spectroscopy.

The percentage of formyl groups on copolymer $\mathbf{P}_{\mathrm{CHO}}$ was determined from the ^{1}H NMR spectrum (Fig. 1a).[8] The molar fraction of the formylated styrene was calculated from the ratio of the peaks at 9.89 ppm assigned to aldehyde groups to the total area between 6.59 and 7.51 ppm, attributed to the nine aromatic protons of the formylstyrene and styrene. The molar composition of copolymer **P** was determined by the same method. The results are listed in Table 2.

A solution of copolymer $\mathbf{P}_{\mathrm{CHO}}$ was treated with an excess of $(HMe_2Si)_3CLi$ in THF. As for simple aromatic aldehydes, Peterson olefination gave a new macromolecule bearing Si–H functional and reactive groups (Scheme 1). The spectroscopic results indicate that the



Scheme 1.

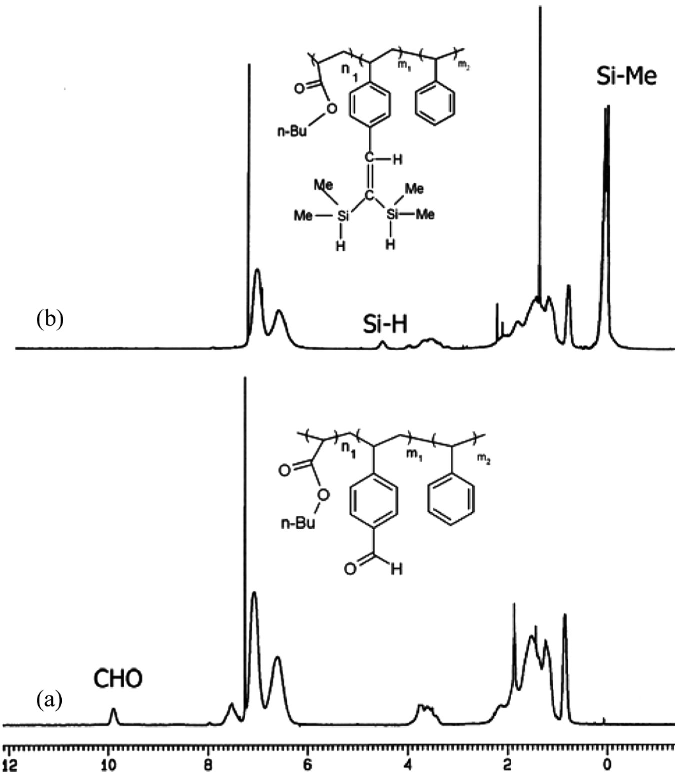


Figure 1. ^{1}H NMR spectra: (a) formylated copolymer $\mathbf{P}_{\mathrm{CHO}}$ and (b) Si–H bearing copolymer $\mathbf{P}_{\mathrm{SiH}}$.

conversion of carbonyl groups into vinylbis(silane) on the side chain of the $\mathbf{P}_{\mathrm{CHO}}$ was complete (see Fig. 1b). It is also noteworthy that because of high reactivity of the formyl group, the carbonyl group of the ester remained unchanged during the reaction.

Table 2. Molar composition of all copolymers

Sample	BuAc (%)[a]	St (%)	St-$_{\mathrm{CHO}}$ (%)	St-$_{\mathrm{SiH}}$ (%)
P	26	74	—	—
P_{CHO}	26	61.5	12.5	—
$P_{\mathrm{Si\text{-}H}}$	26	61.5	—	12.5

[a] All the molar compositions were calculated from the corresponding ^{1}H NMR spectra.

EXPERIMENTAL

Solvents and Reagents

Reactions involving organolithium reagents were carried out under dry argon. Solvents were dried by standard methods. Substrates for preparation of tris(dimethylsilyl)methyllithium, namely $HSiMe_2Cl$ (Merck), Mg (Merck), $CHBr_3$ (Merck), all aldehydes (Merck), Cl_2CHOMe (Merck), and $SnCl_4$ (Merck), were used as received. For the synthesis of LDA, n-BuLi (Fluka 1.6 M) was titrated by diphenylacetic acid.

Spectra

The ^1H NMR and ^{13}C NMR were recorded on a Bruker Fourier transform (FT) 400-MHz spectrometer at room temperature with $CDCl_3$ as a solvent. The mass spectra were obtained with a GC-Mass Agilent quadrupole mode 5973 N instrument, operating at 70 eV. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with an Elementar Vario EL III instrument.

Preparation of the Formylated Polymers (P_{CHO})

The dissolved polymer in nitrobenzene was treated with Cl_2CHOMe in the presence of $SnCl_4$ (molar ratio 1:1:2, 20–25 °C, 3 h). After hydrolysis and washing with water–1,4-dioxane–HCl, the organic layer was poured into cooled methanol to precipitate the formylated polymer $\mathbf{P}_{CHO}$.

FT-IR (KBr, cm^{-1}), 3033 (HC =), 2837, 2730 (CHO), 1690 (HCO), 1730 (O–CO); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.84–2.12 (aliphatic), 3.5–3.7 (OCH_2) 6.60–7.51 (aromatic), 9.89 (CHO).

Preparation of Polymer Bearing Vinylbis(silanes) ($P_{Si–H}$)

$(HMe_2Si)_3CLi$ (15.8 mmol) was added dropwise with stirring to a solution of copolymer $\mathbf{P}_{CHO}$ (14 mmol) in THF at room temperature. The reaction was quenched by adding a small amount of acidic methanol after 2 h, and the reaction mixture was poured into cooled acidic methanol to precipitate the polymer $\mathbf{P}_{Si–H}$. FT-IR (KBr, cm^{-1}), 3035 (HC =), 2108 (Si–H), 1251, 895 (Si–CH_3); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.15–0.26 ($SiMe_2$), 0.85–2.27 (aliphatic), 3.62 (OCH_2), 4.03–4.11 (Si–H), 6.65–7.26 (aromatic).

General Procedure for Synthesis of Vinylbis(silanes)

A mixture of tris(dimethylsilyl)methyllithium (15.8 mmol) and aldehyde (15 mmol) in ether (10 ml) was heated under reflux for 2 h, then poured into water and extracted into ether. The organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated to give a liquid, which was separated by preparative thin-layer chromatography (TLC) in n-hexane to give the 1,1-bis(silyl)-1-alkene.

Reaction of $(HMe_2Si)_3CLi$ with Benzaldehyde (2a)

Colorless oil: $R_f = 0.95$ (n-hexane); yield = 74%; FT-IR (KBr, cm^{-1}), 2114 (Si–H), 1251, 898 (Si–CH_3); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.19 (d, 6H, $^3J_{HH} = 3.82$ Hz, $SiMe_2$), 0.31 (d, 6H, $^3J_{HH} = 3.68$ Hz, $SiMe_2$), 4.30–4.34 (septet, 2H, $^3J_{HH} = 3.71$, Si–H) 7.30–7.34 (m, 5H, Ph), 7.83 (s, 1H, HC=); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −4.2, −3.3 ($SiMe_2$), 125.3, 126.5, 127.1, 139.6, 140.0, 154.9 (Ph, C = C); m/z (EI): 220 (15%, $[M]^+$), 205 (32%, $[M\text{-}Me]^+$), 161 (70%, $[M–SiMe_2H]^+$), 143 (100%, $[M–Ph]^+$), 59 (18%, $[SiMe_2H]^+$). Anal. calc. for $C_{12}H_{20}Si_2$: C, 65.4; H, 9.1. Found: C, 65.7; H, 9.3.

Reaction of $(HMe_2Si)_3CLi$ with 3-Pyridinaldehyde (2b)

Yellow oil: $R_f = 0.65$ (n-hexane); yield = 59%; FT-IR (KBr, cm^{-1}), 2112 (Si–H), 1255, 835 (Si–CH_3); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.09 (d, 6H, $^3J_{HH} = 3.72$ Hz, $SiMe_2$), 0.21 (d, 6H, $^3J_{HH} = 3.69$ Hz, $SiMe_2$), 4.17–4.24 (m, 2H, Si–H), 7.15–7.18 (dd, 1H, $^3J_{HH} = 4.84$ Hz, aromatic), 7.50 (d, 1H, $^3J_{HH} = 7.81$ Hz, aromatic), 7.63 (s, 1H, HC=), 8.43 (d, 1H, $^3J_{HH} = 4.75$ Hz, aromatic), 8.47 (s, 1H, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.3, −3.7 ($SiMe_2$), 121.4, 133.9, 134.8, 14.1, 147.3, 148.1, 150.5 (aromatic, C = C); m/z (EI): 222 (13%, $[M]^+$), 221 (100%, $[M-1]^+$), 207 (5%, $[M–Me]^+$), 163 (15%, $[M\text{-}SiMe_2H]^+$), 59 (20%, $[SiMe_2H]^+$).). Anal. calc. for $C_{11}H_{19}Si_2N$: C, 59.5; H, 8.6; N, 6.3. Found: C, 59.7; H, 8.8; N, 6.2.

Reaction of $(HMe_2Si)_3CLi$ with 2-Thiophenealdehyde (2c)

Dark brown oil: $R_f = 0.65$ (n-hexane); yield = 62%; FT-IR (KBr, cm^{-1}), 2113 (Si–H), 1250, 833 (Si–CH_3); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.33 (d, 6H, $^3J_{HH} = 3.67$ Hz, $SiMe_2$), 0.37 (d, 6H, $^3J_{HH} = 3.85$ Hz, $SiMe_2$), 4.32–4.38 (septet, 1H, $^3J_{HH} = 3.67$ Hz, Si–H), 4.64–4.70 (septet, 1H, $^3J_{HH} = 3.85$ Hz, Si–H), 7.07–7.09 (dd, 1H, $^3J_{HH} = 3.64$ Hz, aromatic), 7.18 (d, 1H, $^3J_{HH} = 3.56$ Hz, aromatic), 7.38 (d, 1H, $^3J_{HH} = 4.10$ Hz, aromatic), 7.79 (s, 1H, HC =); ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.9, −3.8 ($SiMe_2$), 125.1, 125.9, 128.0, 137.4, 143.2, 145.3 (aromatic, C = C); m/z (EI): 226 (30%, $[M]^+$), 211 (45%, $[M\text{-}Me]^+$), 167 (72%, $[M\text{-}SiMe_2H]^+$), 143 (100%, $[M\text{-}C_4H_3O]^+$), 59 (16%, $[SiMe_2H]^+$). Anal. calc. for $C_{10}H_{18}Si_2S$: C, 53.1; H, 8.0. Found: C, 53.4; H, 7.7.

Reaction of $(HMe_2Si)_3CLi$ with 5-Methylfurfural (2d)

Brown oil: $R_f = 0.77$ (n-hexane); yield = 70%; FT-IR (KBr, cm^{-1}), 2106 (Si–H), 1253, 896 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.27 (d, 6H, $^3J_{HH} = 3.52$ Hz, $SiMe_2$), 0.35 (d, 6H, $^3J_{HH} = 3.76$ Hz, $SiMe_2$), 2.34 (s, 3H, CH_3), 4.26–4.31 (septet, 1H, $^3J_{HH} = 3.36$ Hz, Si–H), 4.37–4.43 (septet, 1H, $^3J_{HH} = 3.73$ Hz, Si–H), 6.05 (d, 1H, $^3J_{HH} = 3.04$ Hz, aromatic), 6.29 (d, 1H, $^3J_{HH} = 3.17$ Hz, aromatic), 7.29 (s, 1H, HC=); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.2, −3.8 ($SiMe_2$), 106.9, 111.7, 120.9, 131.8, 152.6 (aromatic, C = C); m/z (EI): 224 (55%, $[M]^+$), 209 (100%, $[M\text{-}Me]^+$), 165 (85%, $[M\text{-}SiMe_2H]^+$), 143 (40%, $[M\text{–}C_5H_5O]^+$), 59 (50%, $[SiMe_2H]^+$). Anal. calc. for $C_{11}H_{20}Si_2O$: C, 58.9; H, 8.9. Found: C, 59.2; H, 9.1.

Reaction of $(HMe_2Si)_3CLi$ with 2-Naphthaldehyde (2e)

Pale yellow oil: $R_f = 0.78$ (n-hexane); yield = 63%; FT-IR (KBr, cm^{-1} 2108 (Si–H), 1252, 825 (Si-CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 0.4 (d, 6H, $^3J_{HH} = 3.83$ Hz, $SiMe_2$), 0.51 (d, 6H, $^3J_{HH} = 3.68$ Hz, $SiMe_2$), 4.54–4.61 (septet, 2H, $^3J_{HH} = 3.75$, Si–H), 7.59–7.63 (m, 3H, aromatic), 7.93–7.98 (m, 4H, aromatic), 8.14 (s, 1H, HC =); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ −3.8, −3.1 ($SiMe_2$), 125.0, 125.1, 125.3, 126.3, 126.4, 126.6, 127.1, 131.7, 131.9, 137.2, 140.6, 155.0 (aromatic, C = C); m/z (EI): 270 (42%, $[M]^+$), 255 (20%, $[M\text{-}Me]^+$), 211 (71%, $[M\text{–}SiMe_2H]^+$), 195 (100%, $[M\text{-}Me\text{-}SiMe_2H]^+$), 127 (35%, $[M\text{-}C_{10}H_7]^+$), 59 (25%, $[SiMe_2H]^+$). Anal. calc. for $C_{16}H_{22}Si_2$: C, 71.1; H, 8.1. Found: C, 71.5; H, 8.3.

Reaction of $(HMe_2Si)_3CLi$ with Cinnamaldehyde (2f)

Yellow oil: $R_f = 0.65$ (n-hexane); yield = 68%; FT-IR (KBr, cm^{-1}), 2115 (Si–H), 1258, 896 (Si–CH_3); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): *δ* 0.31 (d, 6H, $^3J_{HH} = 3.75$ Hz, $SiMe_2$), 0.38 (d, 6H, $^3J_{HH} = 3.80$ Hz, $SiMe_2$), 4.29–4.35 (septet, 1H, $^3J_{HH} = 3.68\,Hz$, Si–H), 4.58–4.64 (septet, 1H, $^3J_{HH} = 3.86\,Hz$, Si–H), 6.72-7.52 (m, 8H, aromatic, C = C); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.1, −3.4 ($SiMe_2$), 125.7, 127.1, 127.6, 127.9, 132.4, 135.5, 135.9, 140.0, 144.7, 153.2 (aromatic, C = C); m/z (EI): 246 (50%, $[M]^+$), 231 (100%, $[M\text{-}Me]^+$), 187 (15%, $[M\text{-}SiMe_2H]^+$), 59 (52%, $[SiMe_2H]^+$). Anal. calc. for $C_{14}H_{21}Si_2$: C, 68.3; H, 8.9. Found: C, 68.5; H, 8.6.

Reaction of $(HMe_2Si)_3CLi$ with Terephthaldehyde (2g)

Pale yellow oil: $R_f = 0.71$ (n-hexane); yield = 58%; FT-IR (KBr, cm^{-1}), 2110 (Si–H), 1251, 832 ($Si\text{-}CH_3$); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 0.23 (d, 12H, $^3J_{HH} = 3.83\,Hz$, $SiMe_2$), 0.33 (d, 12H, $^3J_{HH} = 3.68\,Hz$, $SiMe_2$), 4.32–4.38 (m, 4H, Si–H), 7.32 (s, 4H, aromatic), 7.82 (s, 1H, HC=); ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.9, −3.3 ($SiMe_2$), 126.8, 139.0, 140.4, 154.5 (aromatic, C = C); m/z (EI): 362 (25%, $[M]^+$), 347 (15%, $[M\text{-}Me]^+$), 303 (30%, $[M\text{-}SiMe_2H]^+$), 219 (40%, $[M\text{-}C_6H_{15}Si_2]^+$), 143 (30%, $[C_6H_{15}Si_2]^+$), 59 (50%, $[SiMe_2H]^+$). Anal. calc. for $C_{18}H_{34}Si_4$: C, 59.7; H, 9.4. Found: C, 59.6; H, 9.5.

ACKNOWLEDGMENT

We thank Dr. J. D. Smith for helpful comments.

REFERENCES

1. (a) Pawluc, P.; Hreczycho, G.; Marciniec, B. A new selective approach to 1,1-bis(silyl)-2-arylethenes and 1,1-bis(silyl)-1,3-butadienes via sequential silylative coupling–Heck coupling reactions. *J. Org. Chem.* **2006**, *71*, 8676–8679; (b) Mise, T.; Takaguchi, Y.; Wakatsuki, Y.; Takaguchi, Y.; Umemiya, T.; Shimizu, S.; Wakatsuki, Y. Ruthenium-catalyzed ring-closing reaction of α,ω-bis(vinylsilyl) compounds via a silyl transfer mechanism. *Chem. Commun.* **1998**, *6*, 699–700.
2. (a) Atsushi Inoue, A.; Kondo, J.; Shinokubo, H.; Oshima, K. A facile synthesis of 1,1-disilylethenes via Me_3MgLi-induced monomethylation of dibromodisilylmethanes. *Chem. Lett.* **2001**, 956–961; (b) Safa, K. D.; Paymard Samani, S.; Tofangdarzadeh, S.; Hassanpour, A. Study of the reaction of 1,1-bis-(trimethylsilyl)-2-phenylethylene with some acyl chlorides in the presence of $AlCl_3$. *J. Organomet. Chem.* **2008**, *693*, 2004–2008.
3. (a) Hodgson, D. M.; Comina, P. J.; Drew, M. G. B. Chromium(II)-mediated synthesis of vinylbis(silanes) from aldehydes and a study of acid- and base-induced reactions of the derived epoxybis(silanes): A synthesis of acylsilanes.

J. Chem. Soc., Perkin Trans. 1 **1997**, 2279–2290: (b) Pawluc, P.; Marcinic, B.; Dudziec, B.; Hreczycho, G.; Kubicki, M. Novel highly stereoselective approach toward (Z)-1,2-bis(silyl)ethenes. *Synthesis* **2006**, 3739–3745.

4. (a) Safa, K. D.; Nasirtabrizi, M. H. One-pot, novel chemical modification of glycidyl methacrylate copolymers with very bulky organosilicon side chain substituents. *Eur. Polym. J.* **2005**, *41*, 2310–2319; (b) Safa, K. D.; Babazadeh, M. Glass transition temperature modification of acrylic and dienic type copolymers of 4-chloromethyl styrene with incorporation of $(Me_3Si)_3C$– groups. *Eur. Polym. J.* **2004**, *40*, 1659–1669; (c) Safa, K. D.; Babazadeh, M.; Namazi, H.; Mahkam, M.; Asadi, M. G. Synthesis and characterization of new polymer systems containing very bulky tris(trimethylsilyl)methyl substituents as side chains. *Eur. Polym. J.* **2004**, *40*, 459–466.
5. (a) Schubert, H. H.; Stang, P. J. Application of the Peterson olefination to the preparation of substituted triafulvenes from methoxycyclopropenylium triflates. *J. Org. Chem.* **1984**, *49*, 5087–5090; (b) Barrett, A. G. M.; Flygare, J. A. Triply convergent, stereospecific alkene formation via Peterson olefination. *J. Org. Chem.* **1991**, *56*, 638–642.
6. Hawrelak, E. J.; Ladipo, F. T.; Sata, D.; Braddock-Wilking, J. Synthesis, characterization, and reactivity of $[LiC(SiMe_2H)_3]\cdot 2THF$: Formation of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(dimethylsilyl)-1,3-disilacyclobutane, $[Me_2SiC(SiMe_2H)_2]_2$. *Organometallics* **1999**, *18*, 1804–1807.
7. Kahovec, J. Aldehyde functionalization of styrene polymers. *Polym. Bull.* **1981**, *4*, 731.
8. (a) Kowalewska, A.; Stańczyk, W. A.; Boileau, S.; Lestel, L.; Smith, J. D. Novel polymer systems with very bulky organosilicon side chain substituents. *Polymer* **1999**, *40*, 813–818; (b) Kim, Y. H.; Kwon, S.-K.; Choi, S. K. Synthesis and properties of poly (1,6-heptadiyne) having a bulky siloxy group. *Macromolecules* **1997**, *30*, 6677–6679.