*Journal of Organometallic Chemistry*, 264 (1984) 149–153
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# HEXAMETHYLSILIRANE

## IV *. NUCLEOPHILIC RING OPENING BY ALKYLLITHIUM REAGENTS **

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(Received August 9th, 1983)

### Summary

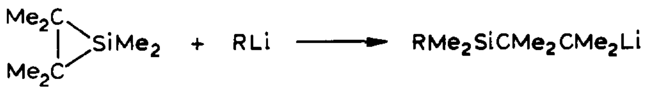
Alkyllithium reagents (methyl-, n-butyl- and t-butyl-) react at 0°C with hexamethylsilirane to give $RSiMe_2CMe_2CMe_2Li$ as the initial product. In a second step this reagent metalates methyl substituents on silicon to give $RSi(CH_3)(CH_2Li)CMe_2CMe_2H$ as the final product.

### Introduction

In a previous paper we have reported the extremely high reactivity of hexamethylsilirane (I) in cleavage reactions by electrophilic and nucleophilic reagents [2]. Noteworthy were the exothermic reactions of hexamethylsilirane with water and methanol. We have also examined the reactions of hexamethylsilirane with alkyllithium reagents. We report here our studies of these reactions which proved not to be straightforward.

### Results and discussion

The expected reaction when hexamethylsilirane is treated with an alkyllithium reagent is that shown in eq. 1. Hydrolysis then should give $RMe_2SiCMe_2CMe_2H$. In our initial experiment it was found that hexamethylsilirane did react with methyllithium in $Et_2O/THF$ medium even at −78°C. The product, obtained after hydrol-



(1)

(I) (II)

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* Part III: ref. 1.

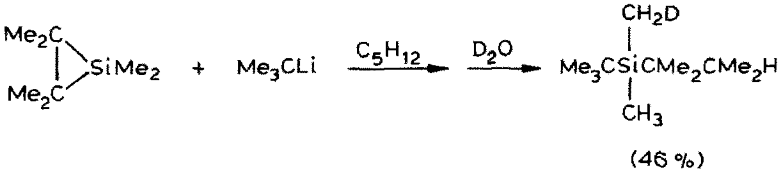
** Dedicated to Professor R. Calas on the occasion of his 70th birthday on April 8, 1984 in recognition of his outstanding research in organosilicon chemistry during the past 30 years.

0022-328X/84/$03.00

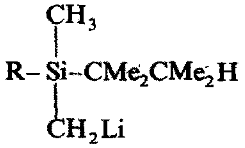
ysis of the reaction mixture, was the expected $Me_3SiCMe_2CMe_2H$, but the yield was only 18%. Also formed in the reaction was a THF-insoluble, apparently polymeric material. The latter could be the product of hexamethylsilirane oligomerization by RLi, $R[Me_2SiCMe_2CMe_2]_xLi$, or could result from reaction of the tertiary lithium reagent, II, with the THF solvent. (It is well-known that tertiary alkyllithium reagents can react with aliphatic ethers [3]). t-Butyllithium and n-butyllithium are supplied in alkane solution, so, if as much of the THF solvent as possible is removed from the hexamethylsilirane, solvent attack should not be a problem with these reagents.

The addition of a pentane solution of hexamethylsilirane to an excess of t-butyllithium in pentane at room temperature gave a clear yellow solution. Upon hydrolysis, the expected $Me_3CSiMe_2CMe_2CMe_2H$ was obtained in 49% yield. Similarly, the cleavage of hexamethylsilirane with n-butyllithium in hexane gave n-$C_4H_9SiMe_2CMe_2CMe_2H$ in 48% yield after hydrolytic work-up. In both cases some organic-insoluble solid was formed, so hexamethylsilirane oligomerization is a possibility.

The results of the MeLi and t-BuLi experiments were taken as clear evidence that the cleavage had occurred as shown in eq. 1 and that it was the hydrolysis of organolithium reagents of type II which produced the observed products. Experiments in which the lithium reagent formed in the t-BuLi cleavage of hexamethylsilirane was treated with $D_2O$ gave at first sight surprising results and showed that the reaction course was more complicated (eq. 2). That a deuterium atom had been incorporated into a methylsilyl group and that a $CMe_2CMe_2H$ (not a $CMe_2CMe_2D$) substituent was present on silicon was shown clearly by the 60 MHz $^1H$ NMR spectrum of the product: δ 0.06 (s, 5H, Si-methyl), 0.84 (d, *J* 6 Hz, 6H, $\mathrm{CH(C}\mathit{H}_3)_2$), 0.86 (s; 6H, $C(CH_3)_2$), 0.95 (s, 9H, $(CH_3)_3C$), 1.61–2.06 ppm (septet, *J* 6 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_3)_2}$ (in $CCl_4$). A 250 MHz $^1H$ NMR spectrum (in $CDCl_3$) gave better evidence of the presence of a $CH_2D$ substituent on silicon, showing a triplet (*J* 2 Hz) at δ −0.05 for Si-$CH_2D$ and a singlet at δ −0.03 for Si-$CH_3$, as well as the septet at 1.77–1.93 ($J = 6.6$ Hz) for $\mathrm{C(CH_3)_2}\mathit{H}$.



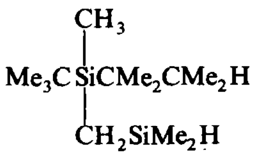
Further confirmation that the lithium reagent which was ultimately produced was III, not II, was given by a reaction in which the t-BuLi/hexamethylsilirane reaction



$$\mathrm{R{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2Li}{Si}}{-}CMe_2CMe_2H}$$

(III)

mixture was treated with $Me_2SiHCl$. The product which was isolated was IV, not V. A similar result was obtained when hexamethylsilirane was cleaved with n-butyllithium and the reaction mixture was quenched with $Me_2SiHCl$.



$$Me_3C\overset{CH_3}{\underset{CH_2SiMe_2H}{Si}}CMe_2CMe_2H$$

(IV)

$Me_3CSiMe_2CMe_2CMe_2SiMe_2H$

(V)

It is clear that in these reactions II, the organolithium which must have been formed initially by nucleophilic cleavage of hexamethylsilirane, reacts, either intra- or inter-molecularly, to metalate methyl substituents on silicon to give III. This reaction is readily understood in terms of known reactivity patterns. First, tertiary alkyllithiums are the most basic (compared with primary and secondary alkyllithiums) and they show high reactivity in the deprotonation of weakly acidic C–H bonds [4]. Then also, $\alpha$-lithio substituents in alkylsilanes appear to enjoy special stabilization and $\alpha$-lithioalkylsilanes are readily formed [5]. For example, the action of t-butyllithium on various methylsilicon compounds ($Me_4Si$, $(Me_3Si)_2O$, $Me_3SiOEt$) results in methyl group lithiation [6]. Thus the chemistry which we have observed is not altogether surprising.

## Experimental

### *General comments*

Hexamethylsilirane was prepared as described in detail in Part I of this series [7]. The general comments of previous papers of this series [1,2,6] are applicable. The high reactivity of hexamethylsilirane toward atmospheric oxygen and moisture requires special precautions to exclude air and moisture during all steps in which this compound is prepared, handled and utilized. Organolithium reagents were obtained from Alfa Products of Thiokol/Ventron.

### *Reaction of hexamethylsilirane with methyllithium*

A solution containing 4 ml of 2.5 *M* MeLi/LiBr in diethyl ether (10 mmol) and 15 ml of dry THF was cooled to −78°C in a 50 ml one-necked flask equipped with a magnetic stir-bar and a no-air stopper holding an argon needle inlet. Subsequently, a solution of 1.3 mmol of hexamethylsilirane in THF was added by syringe during the course of 3 min. The resulting yellow solution was stirred at −78°C for 15 min and then hydrolyzed with aqueous HCl. The solution was allowed to warm to room temperature, diluted with 10 ml of hexane and extracted with 10 ml of water. An amorphous white solid (56 mg) which precipitated from the organic layer was filtered. The organic phase was dried and concentrated at reduced pressure. The residue was examined by GLC (20% UC-W98 silicone on Chromosorb W at a column temperature of 100°C) and showed the presence of $Me_3SiCMe_2CMe_2H$ in 18% yield. A pure sample, $n_D^{25}$ 1.4345, was isolated by GLC. Found: C, 68.35; H, 14.21. $C_9H_{22}Si$ calcd.: C, 68.25; H, 14.01%. 60 MHz $^1H$ NMR ($CCl_4$): $\delta$ 0.033 (s, 9H, $Me_3Si$), 0.83 (s, 6H, $CMe_2$), 0.89 (d, $J$ 6 Hz, $CH(CH_3)_2$, 1.17–1.67 ppm (heptet, $J$ 6 Hz, 1H, $CH(CH_3)_2$).

### *Reaction of hexamethylsilirane with t-butyllithium*

*(a) $H_2O$ quench.* A solution containing 1.92 mmol of hexamethylsilirane in 4 ml of pentane was added to 10 ml of 1.2 *M* (12 mmol) of t-butyllithium in pentane at

0°C. The clear yellow reaction mixture was stirred for 30 min at room temperature. The cloudy solution which resulted was cooled to 0°C and treated with 5 ml of saturated $NH_4Cl$ solution which discharged the yellow color. The organic layer was dried and concentrated at reduced pressure. Trap-to-trap distillation of the residue (40°C at 0.02 mmHg) was followed by GLC analysis of the distillate. The product was identified as $Me_3CSiMe_2CMe_2CMe_2H$ (49% yield), $n_D^{25}$ 1.4615. Found: C, 72.21; H, 14.02. $C_{12}H_{28}Si$ calcd.: C, 71.90; H, 14.08%. 60 MHz $^1H$ NMR ($CCl_4$): $\delta$ 0.00 (s, 6H, $Me_3Si$), 0.89 (d, $J$ 6 Hz, 6H, $CH(CH_3)_2$), 0.90 (s, 6H, $CMe_2$), 0.98 (s, 9H, $CMe_3$) and 1.67–2.04 (heptet, $J$ 6 Hz, 1H, $CH(CH_3)_2$).

*(b) $D_2O$ quench.* A similar procedure was followed, except that the reaction mixture resulting from the addition of 1.61 mmol of hexamethylsilirane to 12 mmol of t-butyllithium at 0°C was quenched with 6 ml of $D_2O$ to which 0.1 ml of $SiCl_4$ had been added to give an acidic solution. A white precipitate formed which was filtered. The organic layer was dried and concentrated using a 10 cm Vigreux column. The residue was trap-to-trap distilled at 0.03 mmHg. GLC analysis (15% SE-30, 155°C) showed the presence of 2-(2,3-dimethylbutyl)-t-butyldimethylsilane in 35% yield, $n_D^{20}$ 1.4628. NMR analysis (Bruker WM 250 spectrometer, in $CDCl_3$ solution) showed the product to be $Me_3CSi(CH_3)(CH_2D)CMe_2CMe_2H$: $\delta$ – 0.05 (t, $J$ 2 Hz, 2H, $SiCH_2D$), –0.03 (s, 3H, $SiCH_3$), 0.85 (d, $J$ 6.6 Hz, $CH(CH_3)_2$), 0.86 (s, 6H, $CMe_2$), 0.94 (s, 9H, $CMe_3$) and 1.77–1.93 (septet, $J$ 6.6 Hz, $CH(CH_3)_2$).

*(c) Dimethylchlorosilane quench.* A reaction was carried out as described above between 2.91 mmol of the silirane and 12.2 mmol of t-butyllithium in pentane. To the yellow reaction mixture then was added, at 0°C, 1.7 g (18 mmol) of $Me_2SiHCl$ in 2 ml of diethyl ether. An exothermic reaction resulted. The mixture was filtered to remove a white precipitate and the filtrate was trap-to-trap distilled at high vacuum. The distillate was concentrated and the residue was examined by GLC (15% SE-30, 200°C). Only one product, $Me_3CSi(CH_3)(CH_2SiHMe_2)CMe_2CMe_2H$, $n_D^{20}$ 1.4790, was present (46% yield). Found: C, 65.01; H, 13.17. $C_{14}H_{34}Si_2$ calcd.: C, 65.03; H, 13.25%. 90 MHz $^1H$ NMR ($CDCl_3$): $\delta$ –0.24 (d, $J$ 3.9 Hz, 2H, $SiCH_2Si$), 0.05 (s, 3H, $SiCH_3$) 0.09 (d, $J$ 3.4 Hz, 6H, $HSiMe_2$), 0.86 (d, $J$ 6.4 Hz, 6H, $CH(CH_3)_2$), 0.87 (s, 6H, $CMe_2$), 0.94 (s, 9H, $CMe_3$), 1.72–2.03 (septet, $J$ 6.4 Hz, 1H, $CH(CH_3)_2$) and 3.77–4.10 ppm (m, 1H, SiH).

### *Reaction of hexamethylsilirane with n-butyllithium*

*(a) $H_2O$ quench.* A reaction was carried out using the procedure above between 2.61 mmol of hexamethylsilirane and 14.3 mmol of n-butyllithium in pentane at 0°C. Hydrolysis with 6 ml of water was followed by the usual work-up. GLC analysis (15% SE-30 at 170°C) showed the presence of $n\text{-}C_4H_9SiMe_2CMe_2CMe_2H$ in 48% yield. Found: C, 71.80; H, 14.03. $C_{12}H_{28}Si$ calcd.: C, 71.90; H, 14.08%. 90 MHz $^1H$ NMR ($CDCl_3$): $\delta$ –0.06 (s, 6H, $Me_2Si$), 0.45–0.60 (m, 2H, $SiCH_2CH_2$), 0.79 (s, 6H, $CMe_2$), 0.83 (d, $J$ 6.8 Hz, 6H, $CH(CH_3)_2$), 0.79–1.58 (m, 7H, $CH_2CH_2CH_3$) and 1.77–1.93 ppm (septet, $J$ 6.8 Hz, 1H, $CH(CH_3)_2$).

*(b) Dimethylchlorosilane quench.* The procedure used in the t-butyllithium reaction (using 2.90 mmol of the silirane and 17.8 mmol of n-butyllithium in pentane, followed by 17.1 mmol of $Me_2SiHCl$) gave $n\text{-}C_4H_9Si(CH_3)(CH_2SiHMe_2)CMe_2\text{-}CMe_2H$. Found: C, 64.97; H, 13.22. $C_{14}H_{34}Si_2$ calcd.: C, 65.03; H, 13.25%. 90 MHz $^1H$ NMR ($CDCl_3$): $\delta$ –0.26 (d, $J$ 3.9 Hz, 2H, $SiCH_2Si$), 0.07 (d, $J$ 5.9 Hz, 6H, $HSi(CH_3)_2$), 0.11 (s, 3H, $SiCH_3$), 0.45–0.60 (m, 2H, $SiCH_2CH_2$), 0.80 (s, 6H,

$CMe_2$), 0.84 (d, *J* 6.8 Hz, 6H, $CH(CH_3)_2$), 0.79–1.58 (m, 7H, $CH_2CH_2CH_3$), 1.55–1.77 (septet, *J* 6.8 Hz, 1H, $CH(CH_3)_2$) and 3.90–4.04 (m, 1H, SiH).

## Acknowledgment

The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this work.

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