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PREPARATION AND REACTIONS OF 1,1,4,4-TETRAKIS(TRIMETHYLSILYL)BUTANE-1,4-DIYL DIANION[1]

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Abstract: Reduction of 1,1-bis(trimethylsilyl)ethylene by alkali metal led to the facile dimerization to the 1,1,4,4-tetrakis(trimethylsilyl)butane-1,4-diyl dianion which has been found to be utilized as a reagent for the Peterson reaction.

Although vinyltriphenylsilane has been reported by Eisch et al.[2] to give the corresponding radical anion followed by the formation of the dimeric dianion by alkali metal reduction, attempts to extend this bimolecular coupling to other silyl-substituted olefins such as vinyltrimethylsilane failed and led to polymerization or cleavage reactions. Under the circumstances, no reaction other than hydrolysis has been investigated about the 1,4-dianion prepared from vinyltriphenylsilane.

Since organodimetallic species are useful intermediates in organic synthesis, we wish herein to report the preparation and some interesting reactions of the 1,4-dianion, **2**, a new entry of the dimeric dianions of olefins.

$(Me_3Si)_2C{=}CH_2$ **1** $[(Me_3Si)_2C{=}CH_2]^{\cdot-}$ **1**$^{\cdot-}$ $[(Me_3Si)_2\bar{C}CH_2\text{-}]_2$ **2**

A mixture of **1** (1.05 g, 6.1 mmol), lithium powder (131 mg, 19 mmol) and THF (20 ml) was stirred for 1 h under argon at room temperature. Titration with butanol by using α,α'-bipyridyl as an indicator revealed that the dianion **2** was formed in 91% yield. After hydrolysis of the solution, 1,1,4,4-tetrakis(trimethylsilyl)butane (**3**)[3] was obtained in 96% yield as determined by glc (15% SE30-celite 545, 1.5 m). The hydrolysis with D_2O gave **3** whose NMR spectrum showed that the deuterium was incorporated in 90.1% at the expected position. These results clearly indicate that the 1,4-dianion can be easily formed by the coupling of the primarily generated radical anion of 1,1-bis(trimethylsilyl)ethylene (**1**$^{\cdot-}$). The driving force should be the anion-stabilizing ability of organosilyl groups at the α-position. Whereas **1** was regenerated from the THF solution of **2** by bubbling oxygen for 3 min in 66% yield, accompanied with 6% of **3**, dianion **2** was rather stable in THF solution under argon.

The dianion **2** was found to be useful as a reagent for the Peterson reactions[4] as demonstrated by following examples. A filtered solution of **2**, prepared from **1** (3.81 mmol) in THF (10 ml), was added to a suspension of paraformaldehyde (600 mg, 20.0 mmol) in THF (2 ml) and the mixture was stirred for 2 h at room temperature and then 6 h under reflux. Usual workup gave 2,5-bis(trimethylsilyl)-1,5-hexadiene (**4a**)[5] in 75% yield. Similarly a mixture of 1,6-diphenyl-2,5-bis(trimethylsilyl)-1,5-hexadiene was obtained in 55% yield by the reaction with benzaldehyde. Attempted reaction of **2** with pivalaldehyde and acetaldehyde gave only 5 - 10% of the desired 1,5-diene. The results are summarized in Table 1.

$$\mathbf{2} \xrightarrow{\mathrm{RCHO}} [\mathrm{RC(OLi)HC(SiMe_3)_2CH_2\text{-}}]_2 \longrightarrow [\mathrm{RCH{=}C(SiMe_3)CH_2\text{-}}]_2 \qquad (1)$$

4a, R=H, 75%
4b, R=Ph, 55%

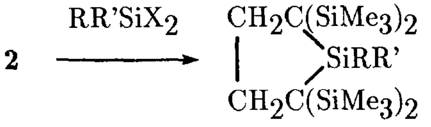
The produced trimethylsilylalkadiene would be a useful synthetic reagent since it has two vinylsilane moieties in a molecule.[6] For instance, **4a** gave easily pure 2,5-dibromo-1,5-hexadiene (**5**)[7] in 44% yield by bromination-debromosilylation sequence.

$$\mathbf{4a} \xrightarrow[\text{2) NaOEt/EtOH}]{\text{1) Br}_2\text{/CCl}_4} \underset{\mathbf{5}}{\mathrm{CH_2{=}CHBrCH_2CH_2CHBr{=}CH_2}} \qquad (2)$$

The dianion **2** reacts with various alkyl halides to give the dialkylated products as shown in eq 3. When bromoform was used as a substrate, halogen-metal exchange occurred preferentially to give 1,4-dibromo-1,1,4,4-tetrakis(trimethylsilyl)butane in 83% yield. The results of the reaction of **2** with various haloalkanes are also listed in Table 1.

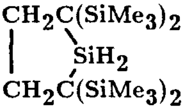
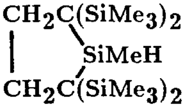
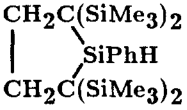
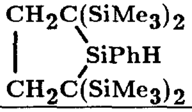
Silacyclopentane derivatives were prepared by the reaction of **2** with dihalosilanes. The reactions of **2** with dichlorosilane and methyldichlorosilane gave the corresponding silacyclopentanes, **7a** and **b**, in 41 and 34% yields, respectively.[8] Trichlorosilane and tetrachlorosilane did not give the expected cyclization products by the reaction with **2**. The former gave only **3**, suggesting the high acidity of the hydrogen in trichlorosilane. Both phenylsilane and diphenylsilane reacted with **2** to give the same silacyclopentane, **7c**, in 42 and 5% yields, respectively.[8] It may be important to note that two very crowded alkyl substituents can be introduced to the ring silicon atom by the present method. The silacyclopentane **7a** is easily derived to the corresponding 1,1-dichlorosilacyclopentane (**8**)[9] by the reaction with chlorine in 97% yield. Further related works are in progress.

$$\mathbf{2} \xrightarrow{\mathrm{R'X}} \underset{\mathbf{6}}{\mathrm{(Me_3Si)_2CR'CH_2CH_2CR'(SiMe_3)_2}} \qquad (3)$$



7a, R = R'= H, 41%;
7b, R = Me, R'= H, 34%;
7c, R = Ph, R'= H.
(4)

Table 1. Reaction of 1,1,4,4-Tetrakis(trimethylsilyl)butane-1,4-diyl Dianion with Various Substrates in THF.

Substrate	Conditions	Product	Yield/%
HCHO	rt, 2 h, then reflux 6 h	$[CH_2{=}C(SiMe_3)CH_2\text{-}]_2$	75
PhCHO	−78 °C ⟶ rt, 6 h	$[PhCH{=}C(SiMe_3)CH_2\text{-}]_2$	55
t-BuCHO	−78 °C ⟶ rt, 6 h	$[t\text{-}BuCH{=}C(SiMe_3)CH_2\text{-}]_2$	—[a]
CH_3CHO	−78 °C ⟶ rt, 6 h	$[CH_3CH{=}C(SiMe_3)CH_2\text{-}]_2$	—[a]
CH_3I	rt, 12 h	$[(Me_3Si)_2C(CH_3)CH_2\text{-}]_2$	83
CH_3OCH_2Cl	−78 °C, 1 h ⟶ rt, 1 h	$[(Me_3Si)_2C(CH_2OCH_3)CH_2\text{-}]_2$	73
$CH_2{=}CHCH_2Br$	−110 °C, 1 h ⟶ rt, 1 h	$[(Me_3Si)_2C(CH_2CH{=}CH_2)CH_2\text{-}]_2$	64
$CHBr_3$	−110 °C, 1 h ⟶ rt, 1 h	$[(Me_3Si)_2CBrCH_2\text{-}]_2$	83
H_2SiCl_2	−78 °C, 0.5 h ⟶ 0 °C, 3 h		41
$HMeSiCl_2$	reflux, 24 h		34
$PhSiH_3$	rt, 16 h		42
Ph_2SiH_2	reflux, 17 h		5

a) Yield was not determined.

References

1. Chemistry of Organosilicon Compounds. 250.
2. J. J. Eisch and R. J. Beuhler, J. Org. Chem., **28**, 2876 (1963); J. J. Eisch and G. Gupta, J. Organomet. Chem., **50**, C23 (1973); **168**, 139 (1979).
3. **1** was prepared by the reaction of tris(trimethylsilyl)methyllithium and paraformaldehyde in THF: B. T. Grobel and D. Seebach, Chem. Ber., **110**, 852 (1977).
   3: ^1H NMR ($CDCl_3$) δ −0.37 ~ −0.21 (2H, m) 0.10 (36H, s), −1.43 ~ 1.59 (4H, m); ^{13}C NMR ($CDCl_3$) δ 0.5 (q), 15.6 (d), 30.5 (t); ^{29}Si NMR ($CDCl_3$) δ 2.8; MS (12 eV)

m/z (rel intensity) 346 (M^+, 0.4), 243 (53), 173 (100), 85 (79), 73 (23). Found: m/z 346.236. Calcd for $C_{16}H_{42}Si_4$: M, 346.236.

4. D. J. Peterson, J. Org. Chem., **33**, 780 (1968).

5. **4a**: ^{1}H NMR ($CDCl_3$) δ 0.16 (18H, s), 2.27 (4H, s), 5.36 (2H, d, J= 3 Hz), 5.61 (2H, d, J= 3 Hz); ^{13}C NMR ($CDCl_3$) δ 1.4 (q), 35.6 (t), 123.8 (t), 152.3 (s); ^{29}Si NMR ($CDCl_3$) δ −4.8; MS (70 eV) m/z (rel intensity) 153 (M^+−15, 25), 152 (13), 123 (11), 78 (13), 73 (100), 59 (11). Found: C, 63.45; H, 11.87%. Calcd for $C_{12}H_{26}Si_2$: C, 63.63; H, 11.57%.

6. See for the synthetic utility of vinylsilanes; E. Colvin, "Silicon in Organic Synthesis," Butterworths, London, 1981; W. P. Weber, " Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin, 1983.

7. **5** has been obtained by the bromination-dehydrobromination of 1,5-hexadiene followed by fractional distillation of the product mixture: D. Shehan, Ph.D. Dissertation, Yale University, **1964** . We thank Prof. A. J. Asche III for his comment about this point. See also, A. J. Asche III, C. M. Kausch, and O. Eisenstein, Organometallics, **6**, 1185 (1987).

8. **7a**: mp 95 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (36H, s), 1.87 (4H, m), 4.19 (2H, s); ^{13}C NMR ($CDCl_3$) δ 2.0 (q), 4.1 (s), 33.6 (t); ^{29}Si NMR ($CDCl_3$) δ −15.0, 3.7; IR (KBr) 2130 cm^{-1}(Si-H); MS (70 eV) m/z (rel intensity) 359 (M^+−15, 13), 300 (15), 227 (17), 73 (100). Found: C, 51.05; H, 11.47%. Calcd for $C_{16}H_{42}Si_5$: C, 51.26; H, 11.29.
   7b: mp 43-44 °C; ^{1}H NMR ($CDCl_3$) δ 0.18 (36H, m); 0.49 (3H, d, J= 4.5 Hz), 1.97 (4H, m), 4.45 (1H, q, J= 4.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.4 (q), 2.2 (q), 3.5 (q), 6.7 (q), 33.0 (t); ^{29}Si NMR ($CDCl_3$) δ 2.8, 3.7, 8.7; IR (KBr) 2110 cm^{-1} (Si-H); MS (70 eV) m/z (rel intensity) 338 (M^+, 0.16), 373 (17), 314 (14), 299 (14), 240 (21), 73 (100). Found: m/z 388.2313. Calcd for $C_{17}H_{44}Si_5$: 388.2290.
   7c: mp 95-96 °C; ^{1}H NMR (CCl_4) δ 0.10 (18H, s), 0.18 (18H, s), 1.93 ~ 2.11 (4H,m), 4.90 (1H, s), 7.15 ~ 7.75 (5H, m); ^{13}C NMR ($CDCl_3$) δ 2.2 (q), 3.7 (q), 7.5 (s), 33.2 (t), 127.4 (d), 129.3 (s), 135.8 (d), 136.2 (d); ^{29}Si NMR ($CDCl_3$) δ 2.2, 4.6, 8.7; IR (KBr) 2100 (Si-H). Found: C, 58.37; H, 10.25%. Calcd for $C_{22}H_{46}Si_5$: C, 58.59; H, 10.28%.

9. **8**: mp 170 °C; ^{1}H NMR (CCl_4) δ 0.30 (36H, s), 2.18 (4H, s); ^{13}C NMR ($CDCl_3$) δ 3.9 (q), 17.6 (s), 31.8 (t). Found: C, 43.09; H, 8.92%. Calcd for $C_{16}H_{40}Cl_2Si_5$: C, 43.30; H, 9.08%.

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