A New Route to Strained Cyclic Disilanylene–acetylenes (1,2,5,6-Tetrasilacyclo-octa-3,7-diyne)

Takahisa Iwahara*† and Robert West

Department of Chemistry, University of Wisconsin, Madison, WI 53706, U.S.A.

Treatment of 1,2-dichlorodisilanes with di-Grignard reagents of 1,2-diethynyldisilanes leads to high yields of the eight-membered ring compounds (**1a—c**) which have u.v. absorptions near 250 nm indicative of σ–π conjugation.

Conjugation between Si–Si σ bonds and π systems has now been well established for many polysilyl compounds containing unsaturated or aromatic groups.[1] Especially strong effects were found in the strained cyclic disilanyleneacetylene (**1a**), obtained by Sakurai and co-workers from the thermal or photochemical ring contraction of the nine-membered ring compound (**2**).[2]

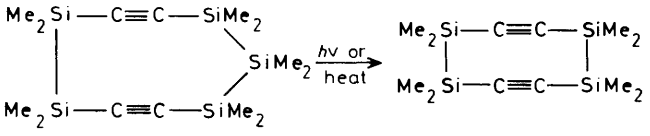
In the course of syntheses of disilanylene–ethynylene polymers, 1,2-dichlorodisilanes were treated with dilute (~0.1 M) solutions of the magnesium derivatives of diacetylenes (**3a,**

† *Permanent address:* Central Research Laboratories, Kanegafuchi Chemical Industry Co., Ltd., 2–80, 1-chome, Yoshida-cho, Hyogo-ku, Kobe 652, Japan.

Table 1. Properties of cyclic disilanylene–diacetylenes.

Compound	% Yield	N.m.r. ^1H[b]	N.m.r. ^{13}C	N.m.r. ^{29}Si	τ/nm[c]
(**1a**)	67	0.25 (s, 24H)	−3.07[b,d]	−33.62[b,d]	213
			119.46		240 (sh)
					249
(**1b**)	73	0.59—0.81 (br.t, 8H)	13.04[e]	−27.04[e]	215
		0.81—1.00 (t, 12H)	13.09		240 (sh)
		1.17—1.50 (m, 16H)	26.83		250
			27.69		
			120.22		
(**1c**)	62	0.24 (s, 12H)	3.07[b]	−27.43[b]	215
		0.61—0.79 (br.t, 4H)	12.56		
		0.79—0.96 (t, 6H)	13.72		250
		1.20—1.50 (m, 8H)	26.45	−33.07	
			27.15		
			118.81		
			120.93		

[a] Satisfactory elemental analyses, (**1b**), or exact mass measurements, (**1a**), (**1c**), were obtained. [b] In $CDCl_3$. [c] In n-hexane. [d] Values in ref. 2. [e] In C_6D_6.

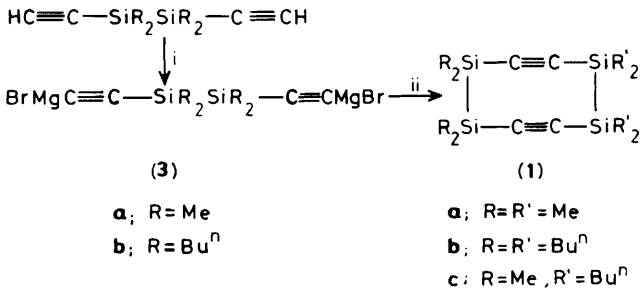


(**2**) (**1a**)

b) in tetrahydrofuran (THF). To our surprise the eight-membered ring diacetylenes (**1a—c**) were produced in 60—75% yield.‡

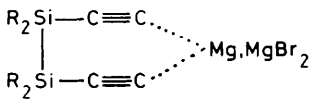
These reactions make these strained-ring compounds easily accessible. Spectroscopic data are in Table 1. The properties of (**1a**) are identical to those of the substance reported earlier.[2] All the compounds show u.v. absorption bands near 250 nm which may be associated with σ–π conjugation. The diethynyldisilane precursors to (**3a, b**) have their longest wavelength absorptions at 217 nm.

Use of dilithium compounds instead of di-Grignard reagents led to ethynylene–disilanylene polymers. § Possible ring closure to give (**1a—c**) may be facilitated by a cyclic structure for the dimagnesium derivative, *i.e.* (**4**). These results suggest that dimagnesium derivatives may be useful in the synthesis of other strained cyclosilane rings, a possibility which is now being explored.



(**3**)
a; R = Me
b; R = Bu^n

(**1**)
a; R = R' = Me
b; R = R' = Bu^n
c; R = Me, R' = Bu^n



(**4**)

Reagents and conditions: i, 2EtMgBr, THF, $-2C_2H_6$; ii, ClSi-$R'_2SiR'_2Cl$.

‡ The synthesis of (**1b**) is typical. To the di-Grignard reagent (**3b**) prepared from $HC{\equiv}CSiBu^n_2SiBu^n_2C{\equiv}CH$ (2.9 mmol) and ethylmagnesium bromide (6.0 mmol) in THF (23 ml), was added 2.7 mmol of $ClSiBu^n_2SiBu^n_2Cl$ (2.7 mmol) in THF (3 ml). A mildly exothermic reaction occurred. The solution was refluxed for 4 h and the THF was pumped off. To the residue was added hexane (30 ml) and then aqueous NH_4Cl (10 ml). After the usual work-up, fractional kugelrohr distillation at a bath temperature of 205—210 °C and 0.45 Torr gave (**1b**) (1.23 g) as a viscous liquid. For (**1c**), kugelrohr distillation was at 144—150 °C. For (**1a**), sublimation at 70 °C and 0.15 Torr gave colourless crystals, m.p. 138—140 °C.

§ The properties of the ethynylene–disilanylene polymers will be described separately. Polymers were also obtained when the reactions between (**3**) and dichlorosilanes were carried out at higher concentrations (~1 M).

Received, 15th March 1988; Com. 8/01055B

References

1 H. Sakurai, *J. Organomet. Chem.*, 1980, **200**, 261; M. Ishikawa, *Pure Appl. Chem.*, 1978, **50**, 11; M. Ishikawa and M. Kumada, *Adv. Organomet. Chem.*, 1981, **19**, 51.
2 H. Sakurai, Y. Nakadaira, A. Hosomi, Y. Eriyama, and C. Kabuto, *J. Am. Chem. Soc.*, 1983, **105**, 3359.