

Reactions of the Si–H bonds in tetrakis(dimethylsilyl)methane and silane

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Dedicated to Professor Stanisław Pasynekiewicz on his 70th birthday.

Abstract

(Me₂HSi)₄M (M = C or Si) were used as: (i) branching substrates in the synthesis of hybrid single atom liquid crystal (lc) materials (low-molecular-weight liquid crystal compounds with mesogens attached via flexible spacers to a central single atom) and (ii) free radical reducing agents for organic bromides in processes initiated by UV radiation and ultrasound (US). In the former application, hydrosilylation of the mesogenic terminal alkenes 4'-methoxy-phenyl-4-(alkenyloxy)benzoates and 4'-cyano-4-(10-undecenyloxy)stilbene led to synthesis of a novel class of hybrid liquid crystals with Si or carbon as a tetrahedral centre. The respective silane and methane were found to be efficient reducing agents. For model substrates — benzyl bromide and hexadecyl bromide — all four Si–H bonds in both branched molecules are equally effective in the UV-initiated reactions. The inefficiency of the ultrasound-promoted reductions is ascribed to low volatility of tetrakis(dimethylsilyl)silane and methane. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Branched silanes; Reducing agents; Hydrosilylation; Hybrid liquid crystals

1. Introduction

Over the last 20 years studies of branched, often sterically hindered silanes, have led to the synthesis of a number of novel stable organometallic compounds and, as the result of their unprecedented chemistry, also to the discovery of novel reaction mechanisms [1,2]. There has, however, been little emphasis on the potential use of such compounds and their derivatives in chemical synthesis [3,4]. Recently, tris(trimethylsilyl)methyl substituted alkenes and tris(trimethylsilyl)methyl lithium were successfully applied to the structural modification of, respectively, polysiloxanes and polystyrene copolymers [5]. As a part of our continuing interest in the applied aspects of the chemistry of branched silanes, we carried out reactivity studies of (Me₂HSi)₄M, where

M = C or Si, as substrates for hybrid, tetrahedral liquid crystals as well as free radical reducing agents.

2. Experimental

2.1. General procedures

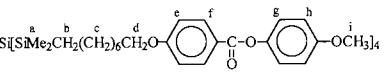
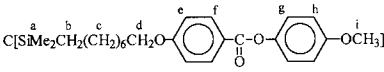
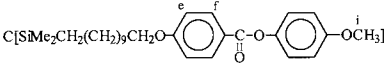
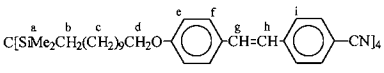
All experiments were carried out using vacuum line techniques under a dry nitrogen atmosphere. Solvents were dried over a sodium mirror. NMR spectra were obtained on Bruker AC 200 and MSL 300 spectrometers in C₆D₆. Mass spectra were obtained by electron impact at 70 eV on a Finnigan MAT95 spectrometer. Microanalyses (C, H, N) were performed on a Carlo Erba CHNS-O EA 1108 elemental analyser. IR spectra were recorded with an ATI Mattson spectrometer. (Me₂HSi)₄C [6], (Me₂HSi)₄Si [3] and mesogenic alkenes, 4'-methoxyphenyl-4-(ω-alkenyloxy)benzoates [7] and 4'-cyano-4-(10-undecenyloxy)stilbene [8], were made by literature methods. The mesomorphism of hybrid liquid

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Table 1
Characteristics of the hybrid single atom liquid crystals

Compound	¹ H NMR (chemical shifts), δ
	a = 0.15 (s), b = 0.74 (m) c = 1.25 (m), d = 3.56 (m) e = 6.40 (m), f = 8.20 (m) g = 7.00 (m), h = 6.70 (m) i = 3.25 (s)
	a = 0.21 (s), b = 0.75 (m) c = 1.26 (m), d = 3.57 (m) e = 6.40 (m), f = 8.20 (m) g = 7.00 (m), h = 6.70 (m) i = 3.25 (s)
	a = 0.21 (s), b = 0.84 (m) c = 1.38 (m), d = 3.49 (m) e = 6.70 (m), f = 8.20 (m) g = 7.10 (m), h = 6.75 (m) i = 3.24 (s)
	a = 0.20 (s), b = 0.61 (m) c = 1.30 (m), d = 3.74 (m) e = 7.20 (m), f = 6.90 (m) g = 6.55 (d) J = 15.9 Hz h = 7.99 (d) J = 15.9 Hz i = 6.80 (m), j = 7.10 (m)

crystal materials has been investigated by X-ray diffraction measurements completed by differential scanning calorimetry and optical microscopy [9].

2.2. Synthesis of (Me₂HSi)₄C- and (Me₂HSi)₄Si-based liquid crystals

The tetrahedral liquid crystals were made via hydrosilylation of mesogenic alkenes 4'-methoxyphenyl-4-(7-octenyloxy)benzoate, 4'-methoxyphenyl-4-(10-undecenyloxy)benzoate and 4'-cyano-4-(10-undecenyloxy)stilbene.

In a typical hydrosilylation reaction tetrakis(dimethylsilyl)methane (0.0702 g, 0.23 mmol) and 4'-methoxyphenyl-4-(7-octenyloxy)benzoate (0.5 g, 1.41 mmol) were dissolved in a Schlenk tube under nitrogen in 10 ml of dry (sodium mirror) toluene in a Schlenk tube. Then a catalyst, 6 μl of 3% PTDD (platinum tetramethyldivinylsiloxane) in xylene, was added (7 × 10⁻⁴ mol Pt per mol of Si-H) and the solution was stirred for 24 h at room temperature. The reaction was

continued after addition of 12 μl of PTDD for 3 days at 60°C (until IR analysis revealed a complete disappearance of the absorption band at 2100 cm⁻¹, characteristic for Si-H). Toluene was removed under vacuum and the crude product was purified by several dissolutions (methylene chloride) and precipitations (methanol) until it was free from the excess of mesogenic alkene (TLC); 0.13 g (32%) of C{SiMe₂[(CH₂)₈OC₆H₄C(O)OC₆H₄OCH₃]}₄. The same procedure was applied to the synthesis of C{SiMe₂[(CH₂)₁₁OC₆H₄C(O)OC₆H₄OCH₃]}₄ (yield 37%), C{SiMe₂[(CH₂)₁₁OC₆H₄CH=CHC₆H₄CN]}₄ (yield 25%) and Si{SiMe₂[(CH₂)₈OC₆H₄C(O)OC₆H₄OCH₃]}₄ (yield 28%). The ¹H-NMR characteristics of the liquid crystalline products are given in Table 1.

2.3. Reduction of organic bromides with (Me₂HSi)₄M (M = C, Si)

The UV-initiated reactions of branched tetrakis(dimethylsilyl)silane and methane with benzyl bromide and hexadecyl bromide were carried out in a quartz tube irradiated with a 50 W UV lamp at 50°C in hexane, as described in Ref. [3]. The reaction progress was followed by GLC using toluene and hexadecane as internal standards.

Reduction of organic halides with acoustic activation (ultrasound) were carried out using either a rectangular Pulsatron 125H ultrasonic cleaner (38 kHz) or a Sonic & Materials VC 300 sonifier, consisting of a 20 kHz ultrasound generator with a variable output up to 300 W. A Suslick cell (15 ml) or a Rosette cell (50 ml) was used [10].

Details of the reaction conditions and results are given in Table 2.

3. Results and discussion

3.1. Hybrid, silicon-based tetrahedral liquid crystals

Both molecules, containing four reactive Si-H bonds with central carbon or silicon, can be used for the

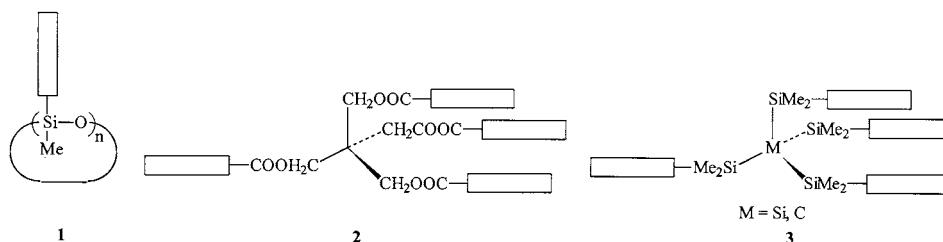
Table 2
Reduction of organic bromides with (Me₂HSi)₄M (M = Si, C)

Initiation	UV				US	
	(Me ₂ HSi) ₄ Si	(Me ₂ HSi) ₄ C	(Me ₂ HSi) ₄ Si	(Me ₂ HSi) ₄ C	(Me ₂ HSi) ₄ Si	(Me ₂ HSi) ₄ C
Organosilicon hydride	C ₆ H ₅ CH ₂ Br	C ₁₆ H ₃₃ Br	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂ Br	C ₆ H ₅ CH ₂ Br
Organic bromide	33	33	33	33	20	25
Temperature (°C)	0.20	0.18	1.4	1.8	15 ^a (<1%) ^b	15 ^a (<1%) ^b
Half life time (h)	1.9 × 10 ⁻³	2.2 × 10 ⁻³	2.8 × 10 ⁻⁴	2.2 × 10 ⁻⁴	2 ^a (0%) ^c	
Rate constant (dm ³ mol ⁻¹ s ⁻¹)						

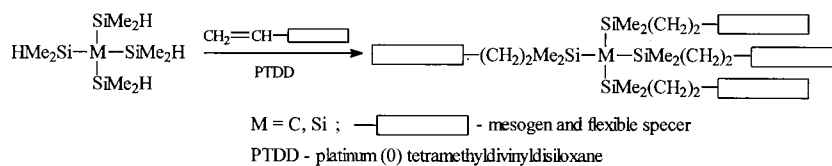
^a Total time of experiment.

^b Ultrasonic cleaner.

^c Sonifier.



Scheme 1.



Scheme 2.

synthesis of tetrahedral liquid crystal structures. The so-called hybrid low-molecular-weight liquid crystal systems that, contrary to side-chain macromolecular liquid crystals, exhibit reduced melt viscosity, are of special interest due to their potential use as thin-film optical elements [11]. One class of such hybrid liquid crystals has been studied in detail and it involves cyclic oligomers — side chain siloxanes **1**, with several side mesogenic moieties [12,13]. The simplest structure can be a single atom molecule, such as **2**. To our knowledge, the only single atom type liquid crystal molecules prepared so far are based on esters of pentaerythritol [14]. The hydrosilylation route offers a simple and effective method for synthesis of almost any architecturally modified hybrid liquid crystal of a single atom (silicon or carbon) of type **3** (Scheme 1).

Four such liquid crystal molecules have been made (Scheme 2, Table 3) with carbon or silicon as the central single atoms in a hybrid structure with mesogenic rods of methoxyphenyl benzoate and cyanostilbene type linked to the tetrahedral centre via alkoxy spacers of different length $[-(\text{CH}_2)_8\text{O}-$ and $-(\text{CH}_2)_{11}\text{O}-$].

All of the hybrid liquid crystals exhibit smectic phase (as shown by X-ray diffraction studies) and in this respect resemble the liquid crystal esters of pentaerythritol with biphenyl, biphenylcyclohexyl and phenylcyclohexyl type mesogens mentioned above [14]. This new type of tetrahedral hybrid liquid crystal shows, however, a much lower temperature (by $\sim 100^\circ\text{C}$) of phase transitions than their ester analogues. The crucial factor is certainly the presence of silicon atoms in the molecules giving higher flexibility to the spacers connecting rigid mesogens with the central atoms [15], as well as the lack of ester bonds in the flexible spacer, which typically lead to higher phase transition temperatures [16].

We present here only a preliminary description of this novel class of hybrid liquid crystals and a route for their synthesis utilising the chemistry of bulky, highly branched silanes. It seems, however, worth noting the two factors that seem to determine the liquid crystal properties within this class of molecule. Phase transition temperatures appear to be affected only by the length of an alkoxy spacer and the formation temperature of the smectic mesophase drops significantly (to less than -40°C) on going from $-(\text{CH}_2)_8\text{O}-$ to $-(\text{CH}_2)_{11}\text{O}-$. The type of central atom and the character of bridging, and of end groups, do not seem to introduce large changes in the temperature span of the liquid crystal phase.

3.2. Tetrakis(dimethylsilyl)methane and tetrakis(dimethylsilyl)silane as reducing agents

UV- and ultrasound (US)-initiated reductions of organic halides, using branched silanes, have shown that

Table 3
Phase transition temperatures ($^\circ\text{C}$) for single atom organosilicon hybrid liquid crystals^a

$\text{Si}[(\text{CH}_2)_8\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3]_4$	K 33 S 60 I
$\text{C}[(\text{CH}_2)_8\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3]_4$	K 30 S 70 I
$\text{C}[(\text{CH}_2)_{11}\text{O}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{C}_6\text{H}_4-\text{OCH}_3]_4$	K 44 S 53 I
$\text{C}[(\text{CH}_2)_{11}\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{CN}]_4$	K 44 S 52 I

^a K, crystal phase; S, smectic phase; I, isotropic phase.

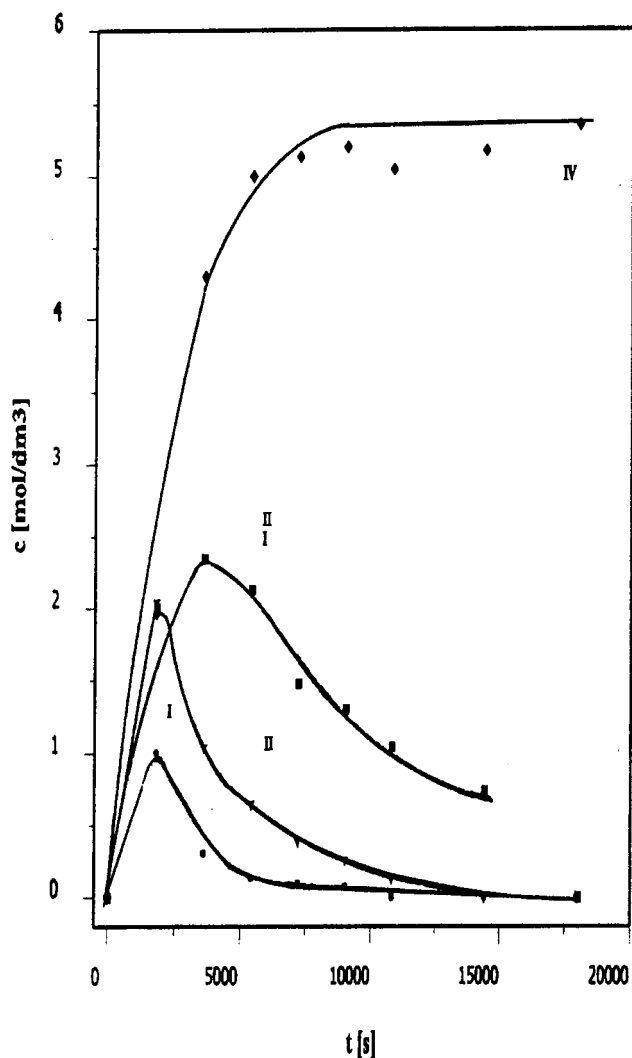


Fig. 1. Progress of the reaction of $C_6H_5CH_2Br$ with $(HMe_2Si)_4C$ (*n*-hexane, $55^\circ C$): (I) $(BrMe_2Si)C(SiMe_2H)_3$; (II) $(BrMe_2Si)_2C(SiMe_2H)_2$; (III) $(BrMe_2Si)_3C(SiMe_2H)$; (IV) $(BrMe_2Si)_4C$.

of the two methods of activation only the UV method is effective in promoting these useful radical processes. We believe that the failure of the silane plus the ultrasound method in the reduction of organic halides is probably due to the very high boiling points (very low volatility of the silanes). This prevents them from entering the cavitation bubbles, where during collapse free radicals are formed. This feature may also make them ineffective in diffusing into the activated liquid shell immediately surrounding the vapour-filled cavity.

In contrast to the ultrasound experiments, the UV initiation leads to high yields of the respective hydrocarbons (toluene and hexadecane). As shown in Fig. 1, the intermediate organosilicon products of reduction reach their maximum concentration after

~ 0.5 h and the conversion is completed, for example, in 5 h for the reduction of benzyl bromide with $C(SiMe_2H)_4$ at $55^\circ C$. What is important, as revealed by the rate studies (Table 2), is that the process follows the second-order rate law throughout reduction (Fig. 2), which means that all intermediate silanes — $C(SiMe_2H)_n(SiMe_2Br)_{4-n}$ ($n = 1, 2, 3$) — are as effective in the splitting off H^\bullet radicals as the starting tetrakis(dimethylsilyl)methane. The same is true for reductions carried out with $(HMe_2Si)_4Si$, as shown in Fig. 3, for the reaction with hexadecyl bromide. Thus, the presence of a variable number of Si–Br bonds in the molecule does not seem to affect the strength of the remaining Si–H bonds to a measurable extent. We do not intend to comment here on the mechanism of the process, but from the synthetic point of view it is a very useful feature as one can make effective use of the four Si–H bonds in one molecule, compared to only one in the widely recommended $(Me_3Si)_3SiH$ [4].

Although the rate of reduction using the tetrakis(dimethylsilyl)silane is roughly one order of magnitude higher than that of its methane analogue, the latter $(HMe_2Si)_4C$ has the advantage that it is relatively simple to prepare, and the final product (in the cases described above $(BrMe_2Si)_4C$) from the reduction of organic halides is air and moisture stable [6]. Moreover, the rate of reduction with $(HMe_2Si)_4C$ can be easily increased by raising the temperature (at $55^\circ C$ the half lifetime in a reaction with benzyl bromide is 0.4 h).

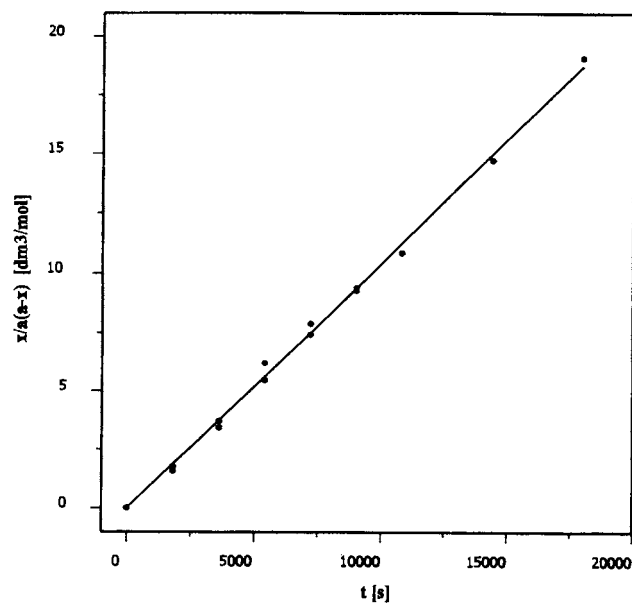


Fig. 2. Second-order rate law dependence for reduction of benzyl bromide with $(HMe_2Si)_4C$.

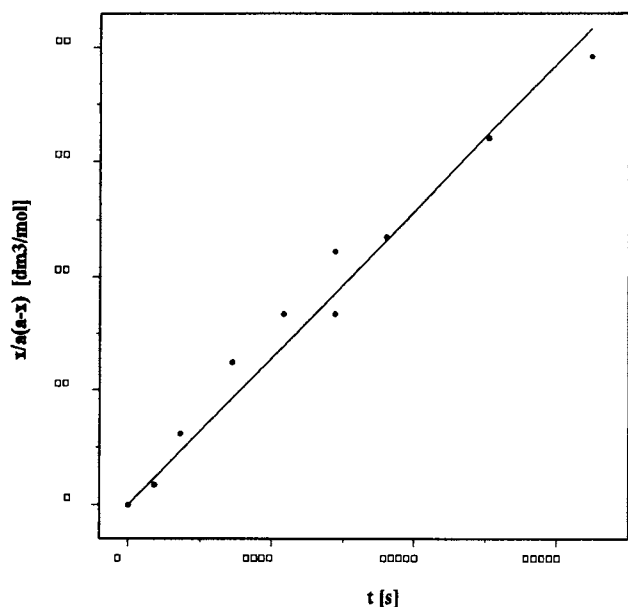


Fig. 3. Second-order rate law dependence for reduction of hexadecyl bromide with $(\text{HMe}_2\text{Si})_4\text{Si}$.

4. Conclusions

The present study clearly shows that the rich chemistry of sterically bulky, branched organosilicon compounds can be successfully applied to a wide range of diverse fields of chemistry ranging from organic synthesis and materials chemistry, in addition to previously known modification of polymer properties [5]. Tetrakis(dimethylsilyl)silane and methane proved to be useful substrates for the synthesis of a novel class of hybrid liquid crystals, as well as effective free radical reducing agents exhibiting equal reactivity for all the Si–H bonds throughout the processes of halide reduction.

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References

- [1] C. Eaborn, J.D. Smith, *Coord. Chem. Rev.* 154 (1996) 125.
- [2] C. Eaborn, K. Izod, J.D. Smith, *J. Organomet. Chem.* 500 (1995) 89.
- [3] P. Kulpiński, P.D. Lickiss, W. Stańczyk, *Bull. Pol. Acad. Sci. Chem.* 40 (1992) 21.
- [4] C. Chatgililoglu, D. Griller, M. Lessage, *J. Org. Chem.* 53 (1988) 3641.
- [5] A. Kowalewska, W.A. Stańczyk, S. Boileau, L. Lestel, J.D. Smith, *Polymer* 40 (1999) 813.
- [6] C. Eaborn, P.D. Lickiss, *J. Organomet. Chem.* 294 (1985) 305.
- [7] M. Mausac, F. Hardouin, H. Richard, M.F. Archard, G. Sigaud, H. Gasparoux, *Eur. Polym. J.* 22 (1986) 137.
- [8] G. Subramaniam, R.K. Gilpin, *Macromolecules* 23 (1990) 693.
- [9] I. Śledzińska, T. Ganicz, J. Przedmojski, J. Sołtysiak, W. Stańczyk, in: J. Żmija, Z. Raszewski, J. Zieliński (Eds.), *Liquid Crystals: Materials Science and Applications*, Proc. SPIE, vol. 2372, 1995, p. 196.
- [10] P.D. Lickiss, R. Lucas, *J. Organomet. Chem.* 510 (1996) 167.
- [11] T.J. Bunning, F.H. Kreuzer, *Trends Polym. Sci.* 3 (1995) 318.
- [12] W. Stańczyk, A. Kowalewska, E. Bialecka-Florjańczyk, I. Śledzińska, J. Sołtysiak, in: J. Żmija, Z. Raszewski, J. Zieliński (Eds.), *Liquid Crystals: Materials Science and Application*, Proc. SPIE, vol. 2372, 1995, p. 262.
- [13] F.H. Kreuzer, Ch. Brauchle, A. Miller, A. Petri, in: V.P. Shibaev (Ed.), *Polymers as Electrooptical and Photooptical Active Media*, Springer-Verlag, Berlin, 1996 (Chapter 3).
- [14] R. Eidenschink, F.-H. Kreuzer, W.H. De Jeu, *Liq. Cryst.* 8 (1990) 879.
- [15] T. Ganicz, W.A. Stańczyk, E. Bialecka-Florjańczyk, I. Śledzińska, *Polymer* 40 (1999) 4733.
- [16] D. Demus, *Mol. Cryst. Liq. Cryst.* 165 (1988) 45.