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HEXASUBSTITUTED DISILANES FROM CHLOROSILANES AND LITHIUM IN TETRAHYDROFURAN

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SUMMARY

General procedures are provided for the preparation in satisfactory yields of hexamethyl-, hexaethyl- and 1,2-dibenzyl-1,1,2,2-tetramethyldisilane from the corresponding R_3SiCl compounds with lithium metal in THF.

Optimal conditions for the preparation of hexamethyldisilane by this procedure were studied.

Dimethylphenyl- and diethylphenylchlorosilanes gave the corresponding disilanes when treated with one equivalent of lithium in THF; no secondary cleavage of the Si–Si bond occurred under these conditions.

Diethylphenylsilyllithium was obtained by lithium cleavage of the corresponding disilane and characterized by reaction with chlorotriphenylsilane to give 1,1-diethyl-1,2,2,2-tetraphenyldisilane.

INTRODUCTION

It has been reported that silylmetallic compounds may be prepared directly from chlorosilanes and alkali metals in cyclic ethers such as tetrahydrofuran (THF). (For reviews of organometallic chemistry, see ref. 1.) In all of these preparations, the silylmetallic compounds had at least one aryl group attached to silicon. Since silyllithium compounds couple readily with chlorosilanes, even at low temperatures[1], the production of silylmetallic species is thought to involve the lithium cleavage of an intermediate disilane, *e.g.*:

$$2\,Ph_3SiCl + 2\,Li \rightarrow 2\,LiCl + Ph_3Si\text{–}SiPh_3 \xrightarrow{2\,Li} 2\,Ph_3SiLi$$

Hexaalkyldisilanes, in contrast, have not been cleaved by alkali metals under various conditions to give the expected trialkylsilylmetallic species[1,2].

Disilanes are obtainable from the corresponding chlorosilanes by several methods[3]. The action of either magnesium[4] or a Grignard reagent[5] on a chlorosilane in THF gave good yields of the corresponding disilanes. sym-Tetraphenyldisilane[4], hexaphenyldisilane[5] and 1,1,1-trimethyl-2,2,2-triphenyldisilane[5], for example, were prepared by this method. Disilanes have also been prepared from chlorosilanes via a Wurtz-type coupling using sodium in xylene[6] or when trialkylhalosilanes were involved, in the absence of solvent[7]. By this method, hexaaryldisilanes[6a,b,c], sym-dialkyltetraaryldisilanes[7b] and sym-tetraalkyldiaryldisilanes[7b] are formed from the corresponding chlorosilanes and sodium in refluxing xylene.

Two general methods have been applied to the preparation of hexaalkyldisilanes: (1) alkylation of hexahalodisilanes using appropriate organometallic reagents[8]; (2) coupling of trialkylhalosilanes using sodium, potassium or sodium/potassium alloy under various conditions[7,9]. Hexamethyldisilane has also been obtained by oxidation of hexamethyldisilazane[10] and by methylation of the distillation residue from the "direct synthesis" using methylmagnesium bromide[11]. Chlorotriethylsilane did not react with sodium in refluxing xylene[12] nor on treatment with sodium/potassium alloy[13]. Only the use of molten sodium at 140° in the absence of any solvent converted chlorotriethylsilane into hexaethyldisilane[7b]. Similarly, in the present study, benzyldiethylchlorosilane failed to give the corresponding disilane when treated with sodium in refluxing toluene.

The use of lithium sand or more conveniently, finely-cut lithium wire in THF, however, has been found to be a suitable method for preparing disilanes having only alkyl or aralkyl groups attached to silicon. These reactions go to completion apparently because the lithium chloride formed is somewhat more soluble in THF than in toluene or xylene. The reaction stops at the disilane stage because of the apparent resistance of hexaalkyldisilanes to cleavage by alkali metals[2].

Using this procedure hexamethyl-, hexaethyl- and 1,2-dibenzyl-1,1,2,2-tetramethyldisilane were prepared in satisfactory yields. It was also found that the reaction could be stopped at the disilane stage, even when an aryl group was attached to silicon, if only one equivalent of the metal was employed. Thus, 1,1,2,2-tetramethyl- and 1,1,2,2-tetraethyl-1,2-diphenyldisilane were prepared in 75 and 80.5% yields, respectively, by this procedure. The chlorosilanes having mixed substituents were prepared by reacting an excess of either dimethyl- or diethyldichlorosilane with the appropriate Grignard reagent in ether. The coupling of the various R_3SiCl compounds described herein is summarized in Table 1.

TABLE 1

HEXASUBSTITUTED DISILANES FROM R_3SiCl AND LITHIUM IN THF

R_3SiCl	Form of lithium	Lithium to R_3SiCl ratio	Reaction time (h)	Product (%)
Me_3SiCl	Li sand	Excess	12	Me_6Si_2, 68
Me_3SiCl^a	High-sodium	1.0	60	Me_6Si_2, 36.4
Me_3SiCl^a	Low-sodium	1.0	60	Me_6Si_2, 53.2
Me_3SiCl^b	Low-sodium	1.7	17	Me_6Si_2, 0
Me_3SiCl^c	Low-sodium	1.7	80	Me_6Si_2, 17.3
Me_3SiCl^a	Low-sodium	1.7	30	Me_6Si_2, 65.6
Me_3SiCl^a	Low-sodium	1.7	60	Me_6Si_2, 76
Et_3SiCl	Li sand	4.3	12	Et_6Si_2, 62.5
$Me_2PhSiCl$	Low-sodium	1.0	12	$[Me_2PhSi]_2$, 75
$Et_2PhSiCl$	Low-sodium	1.0	12	$[Et_2PhSi]_2$, 80.5
$Me_2(C_6H_5CH_2)SiCl$	Low-sodium	5.8	4	$[Me_2(C_6H_5CH_2)Si]_2$, 79

[a] These reactions were carried out using chlorotrimethylsilane (0.3 mole) in THF (40 ml). [b] Solvent was diethyl ether (40 ml). [c] Mixed solvent of THF (20 ml) and ether (20 ml).

Incidental to studies concerned with optimum conditions necessary for the formation of hexamethyldisilane from chlorotrimethylsilane and finely-cut lithium wire in THF, the following observations were made: (1) Lithium of low sodium content ($< 1\%$) gave higher yields. (2) A molar ratio of chlorotrimethylsilane to lithium of 1/1.7 gave satisfactory yields of hexamethyldisilane. (3) The efficiency of stirring had a marked influence on the coupling reaction of chlorotrimethylsilane to hexamethyldisilane: a Hershberg or nichrome-wire stirrer operating at high speeds gave best results. This factor has the effect of activating the lithium metal surface. (4) Higher temperatures (reflux temperature of THF) had a slightly beneficial effect on the yields of hexamethyldisilane.

As part of this study, 1,1,2,2-tetraethyl-1,2-diphenyldisilane was cleaved by lithium in THF to give the previously unreported silyllithium compound, diethylphenylsilyllithium. When titration of an aliquot indicated that cleavage was complete, the mixture was derivatized with chlorotriphenylsilane to obtain a 40.4% yield of 1,1-diethyl-1,2,2,2-tetraphenyldisilane together with 44.5% of triphenylsilanol. The low yield of the disilane may be due to cleavage of the solvent by the silyllithium reagent[14]; however, no attempt was made to isolate this cleavage product.

EXPERIMENTAL

All reactions employing Grignard reagents or chlorosilanes were carried out under an atmosphere of dry, oxygen-free nitrogen. THF was dried by refluxing over sodium for at least 24 h, followed by distillation under nitrogen into a refluxing suspension of lithium aluminum hydride in THF and distillation from this suspension immediately before use. Other solvents employed were sodium-dried. Petroleum ether used had b.p. 60–70°. Melting and boiling points are uncorrected. Some products were characterized by a comparison of their physical data with the reported values.

Hexamethyldisilane

In a preliminary experiment, an exothermic reaction occurred when a 1.5 molar solution of chlorotrimethylsilane in THF was added with stirring to an excess of lithium sand (prepared as described below). After stirring for 12 h at reflux temperature, followed by filtration, hydrolysis and fractionation, the yield of hexamethyldisilane was 68%, b.p. 111–112°, n_D^{25} 1.4200.

A series of experiments was then carried out using lithium wire of low and high sodium content to determine optimum conditions for this reaction. In an optimal run, a solution of chlorotrimethylsilane (32.4 g, 0.3 mole) in THF (40 ml) was added to finely-cut lithium (low sodium content) (3.5 g, 0.5 g-atom) in a 250 ml flask. The mixture was stirred vigorously with a high-speed nichrome-wire or Hershberg stirrer at room temperature for approximately 60 h. A precipitate gradually formed and the mixture became dark-brown in color. The mixture was filtered to remove unreacted lithium, the filtrate fractionated and the fraction b.p. 80–135° collected. This fraction was extracted with concentrated sulfuric acid at 0° until the organic layer solidified and was free of THF and hexamethyldisiloxane. The organic layer was separated, washed several times with water and dried. Fractionation on a spinning-band column gave hexamethyldisilane (16.6 g, 76%), b.p. 112–113°, n_D^{25} 1.4200.

Other experiments, in which variables such as reaction time, type of metal (lithium of low or high sodium content or pure sodium), solvent and speed of stirring were altered, including those listed in Table 1, gave reduced yields of hexamethyldisilane.

Hexaethyldisilane

The lithium sand used in this preparation was obtained by shaking a suspension of lithium wire (9.3 g, 1.34 g-atoms) in mineral oil at 200°. The oil was decanted from the lithium through a stopcock of a separatory funnel. After washing several times with benzene, the lithium was washed with ether and then transferred to the reaction flask with THF.

A solution of chlorotriethylsilane (46.5 g, 0.31 mole) in THF (220 ml) was added dropwise to the finely-divided lithium. The mixture was stirred for 12 h and then filtered through glass wool. The filtrate was hydrolyzed, extracted with ether and the organic layer washed several times with water to remove most of the THF. Two distillations of the material which remained after removal of the solvent gave hexaethyldisilane (20.8 g, 62.5%), b.p. 120–122°/10 mm, n_D^{20} 1.4789.

Dimethylphenylchlorosilane

Dimethylphenylchlorosilane (157 g, 84%), b.p. 198–201°, was obtained from the reaction of phenylmagnesium bromide (1.1 moles) and dimethyldichlorosilane (193.5 g, 1.5 moles) in ether (950 ml). (Found: Cl, 19.9. $C_8H_{11}ClSi$ calcd.: Cl, 20.8%.)

Diethylphenylchlorosilane

Similarly, diethylphenylchlorosilane, b.p. 238–240°, was obtained in 80.5% yield from phenylmagnesium bromide (1.1 moles) and diethyldichlorosilane (235 g, 1.5 moles) in ether (1000 ml). (Found: Cl, 17.28. $C_{10}H_{15}ClSi$ calcd.: Cl, 17.87%.)

Benzyldimethylchlorosilane

A solution of benzylmagnesium chloride [prepared from benzyl chloride (139.1 g, 1.1 moles) and excess magnesium in ether (1000 ml)] was added dropwise to dimethyldichlorosilane (193.5 g, 1.5 moles) without added solvent. After heating at reflux for 2 h, Color Test I[15] was negative. The solvent and excess dimethyldichlorosilane were removed by distillation and the residual oil taken up in hot petroleum ether. The suspension was filtered under nitrogen and the magnesium salts washed thoroughly with the same solvent. The filtrate was distilled to afford benzyldimethylchlorosilane (156.9 g, 76%), b.p. 205–207°. (Found: Cl, 19.18. $C_9H_{13}ClSi$ calcd.: Cl, 19.22%.)

Benzyldiethylchlorosilane

Using the same procedure, benzyldiethylchlorosilane was prepared from benzyl chloride (75.95 g, 0.6 mole) and excess magnesium in ether (500 ml) and diethyldichlorosilane (110 g, 0.7 mole) in ether (300 ml). The yield of product was 85.5 g (67% based on benzyl chloride), b.p. 128–130°/15 mm. (Found: Cl, 16.4. $C_{11}H_{17}ClSi$ calcd.: Cl, 16.7%.)

1,1,2,2-*Tetramethyl*-1,2-*diphenyldisilane*

A solution of dimethylphenylchlorosilane (91 g, 0.534 mole) in THF (200 ml) was added to finely-cut lithium wire (3.76 g, 0.54 g-atom) in THF (100 ml). After the initial heat of reaction had dissipated, the mixture was heated at reflux for 30 min and then stirred for 12 h. The mixture was hydrolyzed in dilute hydrochloric acid, the organic layer separated, dried, the solvent removed and the residue distilled to give 1,1,2,2-tetramethyl-1,2-diphenyldisilane (54.6 g, 75%), b.p. 85–87°/0.04 mm, m.p. 34–35°.

1,1,2,2-*Tetraethyl*-1,2-*diphenyldisilane*

Using the procedure described above, 1,1,2,2-tetraethyl-1,2-diphenyldisilane (110.9 g, 80.5%), b.p. 111–113°/0.005 mm, n_D^{20} 1.5655, d_{20}^{20} 0.973, was prepared from diethylphenylchlorosilane (168 g, 0.845 mole) and finely-cut lithium wire (5.95 g, 0.85 g-atom) in THF (700 ml). (Found: Si, 17.15; MR_D, 109.3. $C_{20}H_{30}Si_2$ calcd.: Si, 17.2%; MR_D, 109.47.)

1,2-*Dibenzyl*-1,1,2,2-*tetramethyldisilane*

A solution of benzyldimethylchlorosilane (36.54 g, 0.198 mole) in THF (200 ml) was added dropwise to a suspension of lithium wire (8 g, 1.15 g-atoms) in THF (10 ml). After stirring at room temperature for 3 h, the mixture was heated at reflux for 1 h and then hydrolyzed. The organic layer was separated and dried. Removal of the solvent left an oil which on fractionation gave 1,2-dibenzyl-1,1,2,2-tetramethyldisilane (23.35 g, 79%), b.p. 97–100°/0.05 mm, m.p. 38–40°. Recrystallization from methanol raised the m.p. to 40–41°. (Found: C, 72.64; H, 8.74. $C_{18}H_{26}Si_2$ calcd.: C, 72.4; H, 8.79%.) In two repeat reactions, this product (m.p. 39–40°) was isolated in yields of 66.5 and 77.5%, respectively.

1,2-*Dibenzyl*-1,1,2,2-*tetraethyldisilane* (*attempted*)

Benzyldiethylchlorosilane (85.45 g) was added to a suspension of sodium (11.5 g, 0.5 g-atom) in toluene (500 ml). The mixture was heated at reflux for 36 h. Work-up by hydrolysis, separation of the layers, drying of the organic layer and removal of the solvent left an oil. Fractionation of this product gave benzyldiethylsilanol (49.97 g, 64.3%), b.p. 68–71°/0.13 mm, n_D^{20} 1.4947, d_{20}^{20} 0.9346.

1,1-*Diethyl*-1,2,2,2-*tetraphenyldisilane*

A paste was made from 1,1,2,2-tetraethyl-1,2-diphenyldisilane (5.2 g, 0.015 mole) and lithium wire (0.7 g, 0.1 g-atom) in THF (3 ml). The mixture was vigorously stirred for 30 min whereupon it turned brown. An additional 40 ml of THF was added. After stirring for *ca.* 18 h, titration of an aliquot indicated cleavage to be complete.

The filtered solution was added to chlorotriphenylsilane (12.5 g, 0.042 mole) in THF (20 ml). Work-up by hydrolysis, separation and drying of the organic layer, removal of the solvent followed by the addition of ethanol (70 ml) to the residue gave upon concentration 1,1-diethyl-1,2,2,2-tetraphenyldisilane (5.4 g, 40.4%), m.p. 74–76°. Recrystallization from ethanol raised the m.p. to 76–76.5°. (Found: Si, 13.25. $C_{28}H_{30}Si_2$ calcd.: Si, 13.29%.) Removal of the solvent from the filtrate left an oil which on trituration with petroleum spirit gave triphenylsilanol (4.47 g, 40%), m.p. and mixed m.p. 153–155°.

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REFERENCES

1 D. Wittenberg and H. Gilman, *Quart. Rev.*, (1959) 116; H. Gilman and H. J. S. Winkler in H. Zeiss (Ed.), *Organometallic Chemistry*, Reinhold, New York, 1960.
2 N. S. Vyazankin, G. A. Razuvaev, E. N. Gladyshev and S. P. Korneva, *J. Organometal. Chem.*, 7 (1967) 353.
3 C. Eaborn, *Organosilicon Compounds*, Academic Press, New York, 1960, p. 351.
4 H. Gilman and W. Steudel, *Chem. Ind. (London)*, (1959) 1094.
5 T. G. Selin and R. West, *Tetrahedron*, 5 (1959) 97.
6 (a) W. Schlenk, J. Renning and G. Racky, *Ber.*, 44 (1911) 1178;
  (b) H. Gilman and G. E. Dunn, *J. Amer. Chem. Soc.*, 73 (1951) 5077;
  (c) H. Gilman and T. C. Wu, *J. Amer. Chem. Soc.*, 75 (1953) 3762;
  (d) A. G. Brook and R. G. Mauris, *J. Amer. Chem. Soc.*, 79 (1957) 971.
7 (a) C. A. Kraus and W. K. Nelson, *J. Amer. Chem. Soc.*, 56 (1934) 195;
  (b) H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, 18 (1953) 1743;
  (c) M. G. Voronkov and Yu I. Khudobin, *Zh. Obsch. Khim.*, 26 (1956) 584.
8 (a) L. O. Brockway and N. R. Davidson, *J. Amer. Chem. Soc.*, 63 (1941) 3287;
  (b) H. Bygden, *Ber.*, 45 (1912) 707;
  (c) G. Martin, *Ber.*, 46 (1913) 3289;
  (d) D. N. Andreev and E. V. Kukharskaya, *Zh. Prikl. Khim.*, 36 (1963) 2309.
9 (a) M. P. Brown and G. W. A. Fowles, *J. Chem., Soc.*, (1958) 2811;
  (b) G. R. Wilson and A. G. Smith, *J. Org. Chem.*, 26 (1961) 557;
  (c) W. Sundermeyer, *Z. Anorg. Allg. Chem.*, 310 (1961) 50;
  (d) E. A. Chernyshev, N. G. Tolstikova, S. L. Ioffe and A. D. Petrov, *Zh. Obshch. Khim.*, 32 (1962) 369;
  (e) M. Kumada and M. Ishikawa, *J. Organometal. Chem.*, 1 (1963) 153;
  (f) U. Stolberg, *Ber.*, 96 (1963) 2798.
10 H. Bock, *Z. Naturforsch.*, 17b (1962) 423.
11 M. Kumada, Y. Yamamoto, J. Nakajima, M. Yamaguchi and K. Shiina, *J. Org. Chem.*, 21 (1956) 1264.
12 G. D. Lichtenwalter, unpublished studies.
13 T. C. Wu, unpublished studies.
14 D. Wittenberg, D. Aoki and H. Gilman, *J. Amer. Chem. Soc.*, 80 (1958) 5933.
15 H. Gilman and F. Schulze, *J. Amer. Chem. Soc.*, 47 (1925) 2002.